

## EFFECT OF TIME PARAMETER ON THE PHYSICOCHEMICAL PROPERTIES OF CARBOXYMETHYL CELLULOSE FROM DELONIX REGIA PODS

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### ABSTRACT

The need to make cellulose (natural polymer-insoluble in water) a water soluble material is essential to enhance its use in the pharmaceutical and food processing industries. This paper investigates the effect of time parameter on the physicochemical properties of carboxymethyl cellulose from Flamboyant plant seed pods. Cellulose isolated from Flamboyant plant (Delonix regia) seed pods (FSP) was modified to carboxymethyl cellulose (CMC) via mercerization and etherification using sodium hydroxide (NaOH) and monochloroacetic acid (ClCH<sub>2</sub>COOH) respectively. The concentration of sodium hydroxide at 20g/100mL and 60 minutes solubility of the CMC produced a high quality product. Moisture contents of the native and carboxymethyl cellulose were calculated to be 33.6% and 30.8% at 110°C respectively, with a slight decrease in the crystallinity of the CMC compared to the native cellulose. Swelling capacities of the CMC were determined and reported to increase with increasing temperature. The degree of substitution on the cellulose backbone was calculated to be 0.77 which clearly show that the CMC produced is highly substituted and therefore soluble in water. FTIR analysis produced peak at 1589.07cm<sup>-1</sup> and a broad band at 3353.56cm<sup>-1</sup> for the carboxyl and hydroxyl functional groups respectively. Solubility of the CMC obtained after etherification process increased with increase in reaction time. This solubility of the CMC in aqueous system explains the potential for its use and application in the production/manufacturing industries, and can be used extensively for various applications in paper, food, detergents, cosmetics, and textiles.

**Keywords:** Natural polymer; *Delonix regia*; Etherification; Carboxymethyl Cellulose; Swelling Capacity.

### INTRODUCTION

On the surface of the earth, cellulose is the most abundant renewable organic material. It constitutes about 33% of all plants matter and the major component of cotton (over 94%) and wood (over 50%) [7]. Cellulose is the major structure components of plants. It is a glucose polymer bounded in the β (1→4) linkage configuration. The β (1→4) linkage allows the cellulose polymer to crystallize in a linear configuration, with a high degree of intermolecular hydrogen bonding, which gives it substantial shear and tensile strength.

Chemically, this can be seen by the presence of three hydroxyl groups (OH) with different acidity/reactivity, where the secondary hydroxyl group (OH) is located at C-2, and C-3 position, and the primary hydroxyl group (OH) located at C-6 position [10, 16]. Because of its chemical makeup, cellulose can be purified for use as a food ingredient. Cellulose is probably the least soluble of all fibre compounds, being insoluble not only in cold or hot water, but also in hot dilute acids and alkalis as well. Depending on the type of plant, most of the plant materials consist of approximately 40-50% of cellulose, 15-35% lignin and 25-40% hemicelluloses. In the natural plant cell wall, crystalline cellulose is embedded with these substances, which makes it difficult to obtain pure cellulose [15]. Cellulose can be extracted from various materials such as soybean hull, pea hull, corn bran, sugarcane bagasse, maize cob, banana peel, saw dust, dried beet pulp and oat hull [17].

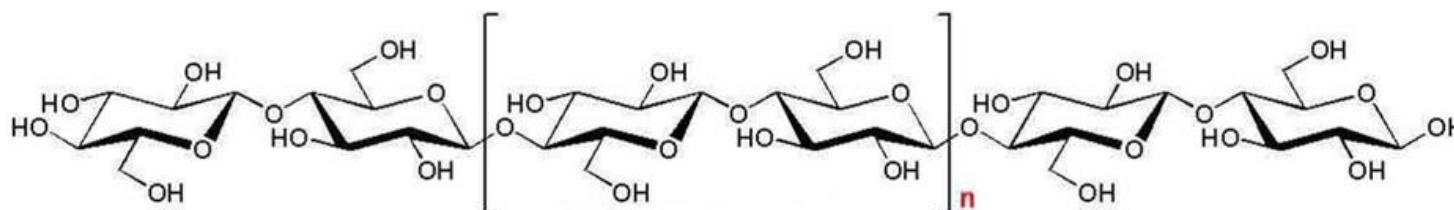


Fig. 1: Structure of repeating units of cellulose [7]

In recent years, the interest in cellulose based materials has been increasing due to the demand for renewable resources and growing on environmental awareness [12]. Because of the high cellulose content of woody materials, agro-wastes materials such as coconut husk fibres, banana rachis, maize cob, sugarcane bagasse, mulberry bark, soybean, wheat straw, and soy hulls have been studied as a resource in the production of cellulose fibre. Although a variety of natural fibres were investigated in detail, the use of Flamboyant (*Delonix regia*) seed pods as a natural source for the production of cellulose is yet to be explored.

The flowers of flamboyant (*Delonix regia*) are large, with four spreading scarlet or orange red petals up to 8 cm long, and a fifth upright petal, which is slightly larger and spotted with yellow and white. *Delonix regia* pods are green and flaccid when young and turn dark-brown and woody when matured [5]. The pods can be up to 60 cm long and 5 cm wide. The seeds are small weighing around 0.4 g on average. The compound leaves have a feathery appearance and are a characteristic light, bright green and are doubly pinnate. Each leaf is 30-50 cm long with 20-40 pairs of primary leaflets [5]. In addition to its ornamental value, it is also a useful shade tree in tropical conditions because it usually grows to a modest height (mostly 5 metres, but it can reach a maximum of 12 metres) but spreads widely, and its dense foliage produces full shade [5]. *Delonix regia* is of the Plantae kingdom and Fabaceae family with genus-*Delonix* and species-*regia* and thus having the binomial name; *Delonix regia*.

Cellulose in its natural state is insoluble in water distinct from carboxymethyl cellulose which is water soluble. Carboxymethyl cellulose unlike native cellulose is a cellulose derivative similar to cellulose nitrate, hydroxypropyl cellulose and oxidized cellulose but differs in the functional group attached to the cellulose backbone. It is a water soluble derivative with a wide range of applications in the manufacturing/production industries. The need to investigate the effect of time parameter on the physicochemical properties of carboxymethyl cellulose (water soluble) produced from native cellulose (water insoluble) isolated from *Delonix regia* seed pods is essential to enhance its applications in industries.

## EXPERIMENTAL

### Sample Preparation

Flamboyant seed pods (FSP) were collected in a local farm in Ago Iwoye, Ogun State, Nigeria. The pods were thoroughly washed and sun dried for several days, pounded and reduced to smaller sizes. The pods were further milled, the resulting pulverized material were sieved into fine powders using a 1 mm mesh size sieve.



Fig. 2 Flamboyant (*Delonix regia*) seed pods

### Cellulose Isolation

Delignification of the cellulosic material was done using 3.5% nitric acid and 0.01% sodium sulphite at 90°C for 2 hours in a reaction vessel. The residue was washed severally with distilled water until the filtrate became neutral to litmus paper. The washed cellulosic material was hydrolysed with 2% sodium hydroxide and 2% sodium sulphite for 1.5 hr at 80°C after which it was then washed until the filtrate became neutral to litmus paper. The resulting cellulosic material was further delignified with 17.5% sodium hydroxide for 1 hr at 70°C [19].

### Cellulose Bleaching

120 g of sodium chlorite was dissolved in 4000 mL of distilled water. To reduce the pH, acetic acid was added in drops till the pH became 4.5. The resulting acidic solution was introduced gradually into the sample and heated for 2 hours. The process was repeated. The bleaching process is to ensure that colours not chemically bind to the cellulose were washed-off.



Fig. 3 Bleached cellulose

### Percentage Yield of Cellulose

The yield percentage of cellulose was determined by comparing the weight of the starting powdered flamboyant seed pods mass with the dry weight of isolated cellulose and calculated thus:

$$\text{Yield percentage (\%)} = \frac{W_2}{W_1} \times 100$$

$W_1$  = Initial weight of powdered flamboyant seed pods

$W_2$  = Final weight of dried cellulose

### Preparation of Carboxymethyl Cellulose

5.0 g of cellulose powder from Flamboyant seed pods (FSP) was weighed and added to 100 mL of isopropanol with continuous stirring. Then, 25 mL of 20% sodium hydroxide was added in drops into the mixture and further stirred on a magnetic stirrer for 1 hour at room temperature. The carboxymethylation started when 6.0 g of monochloroacetic acid (MCAA) was added with continuous stirring for

another 1.5 hours. The mixture was then filtered and the residue washed with methanol, and filtered again. The obtained carboxymethyl cellulose (CMC) samples were covered with aluminum foil and placed into the hot air oven at 60°C for 3.5 hours [2]. The process was repeated and the time varied from 20-60 minutes respectively.

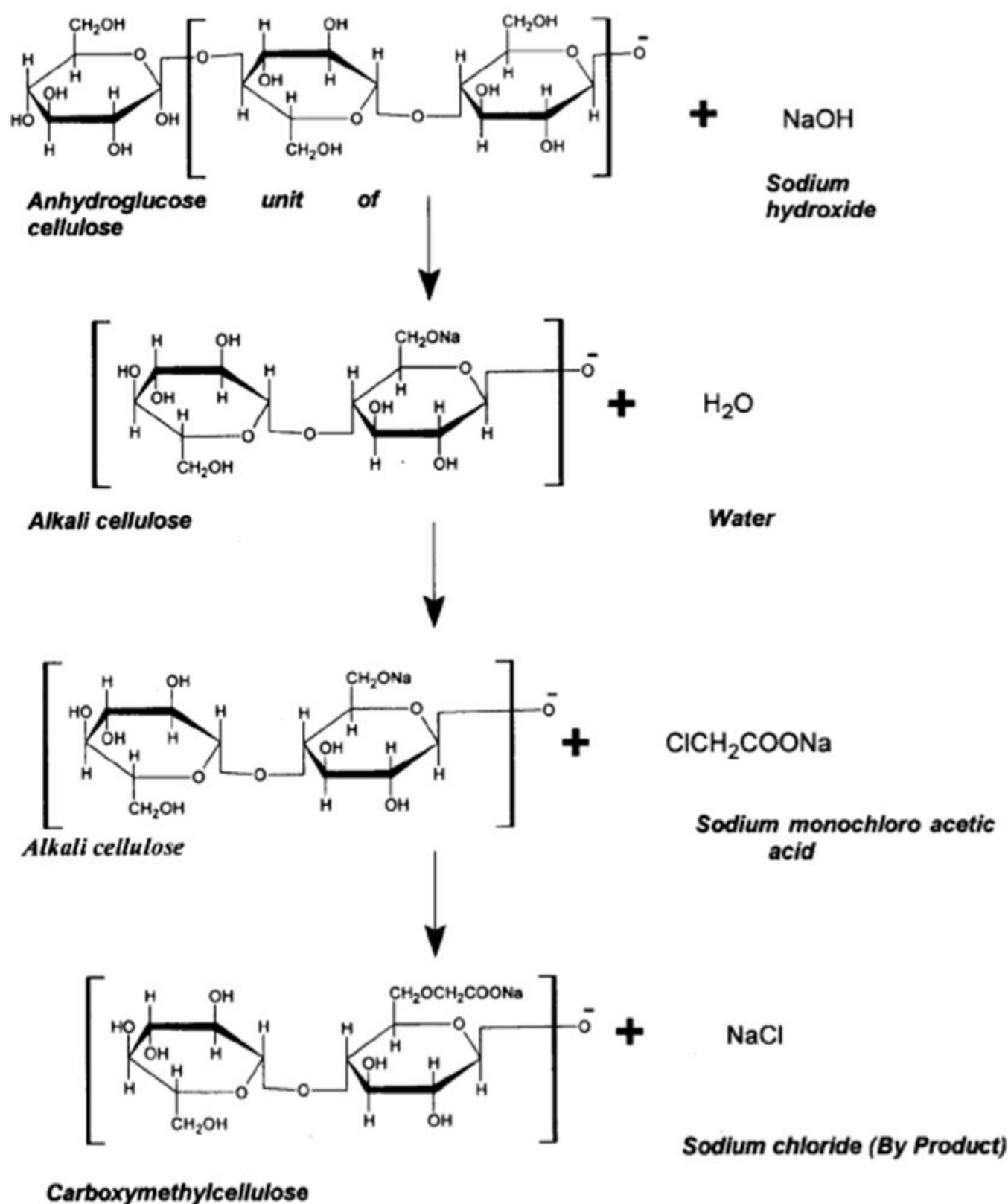


Fig. 4 Carboxymethyl cellulose reaction [2]

#### Moisture Content

CMC (5.0 g) and native cellulose (5.0 g) were placed in a crucible and heated in an oven. The temperature was maintained at 110 °C for 1 hour. The heated CMC and native cellulose were weighed on an analytical balance [9]. The following calculation was then performed to determine the moisture content;

$$M_n = \frac{W_w - W_d}{W_w} \times 100$$

$M_n$  = moisture content of the material.

$W_w$  = wet weight of the sample.

$W_d$  = weight of the sample after drying.

#### Free Swelling Capacity

The free swelling capacities of the carboxymethyl cellulose and native cellulose were determined using the teabag method. Carboxymethyl cellulose and pure cellulose (0.4 g) were packed inside teabag. It was soaked inside distilled water (500 mL) for 4 hours. After the time interval, the sample was removed from water and allowed to drain for 5 minutes to ensure uniformity [8]. The weight of empty teabag and amount of water absorbed by the empty teabag were predetermined.

#### Degree of Substitution

Degree of substitution of carboxylic group in carboxymethyl cellulose is the average number of hydroxyl group in the cellulose structure which was substituted by carboxymethyl groups at C2, C3 and C6. The value of degree of substitution was determined by potentiometric titration described by Jiang *et al.* [6].

10.0 g of CMC was weighed and added to 250 mL beaker followed by 50 mL of 95 % ethanol and stirred. Then, 5 mL of 2M nitric acid was added and the mixture stirred for 10 minutes at room temperature. The mixture was then heated to boiling using magnetic hot plate for 5 minutes and stirred further for 20 minutes and left to settle. After the solution had settled, the solution was filtered and the residue was washed with 100 mL of 95 % ethanol until the acid and salts were removed. The precipitate was washed with methanol and transferred to beaker and heated until the alcohol was removed. The beaker with the precipitate was dried in the oven at 90°C for 3 hours. CMC (3.0 g) was weighed in 250 mL Erlenmeyer flask and 100 mL distilled water added and stirred. 25 mL of 0.5M sodium hydroxide (NaOH) was added and boiled for 20 minutes. Then the heated solution was titrated with 0.3M hydrochloric acid (HCl) by

using phenolphthalein as an indicator to observe color change from dark pink to colorless [6]. The degree of substitution of CMC can be calculated using the equations below.

$$A = \frac{BC - DE}{F}$$

$$DS = \frac{0.162 \times A}{1 - (0.058 \times A)}$$

A = Milli-equivalents of consumed acid per gram of specimen

B = Volume of sodium hydroxide added

C = Concentration of sodium hydroxide

D = Volume of hydrochloric acid consumed

E = Concentration of hydrochloric acid used

F = Mass of specimen used.

Molecular weight of anhydrous glucose unit (AGU) = 162g/mol

Net increment in the AGU for every substituted carboxymethyl group = 58g/mol

### FTIR Spectroscopy

Native cellulose (5.0 g) and CMC (5.0 g) were sent to University of Lagos, Akoka, Lagos state, Nigeria for FTIR analysis. These spectra were recorded with a Perkin-Elmer 1600 spectrophotometer.

## RESULTS AND DISCUSSION

### Percentage yield of cellulose

**Table 1** Yield percentage of cellulose at different reactant concentrations

Weight of Flamboyant seed pods(g)	Dry weight of cellulose(g)	Yield percentage (%)
100 g	59 g	59 %

It can be deduced from the table above that the highest yield of cellulose obtained from flamboyant seed pods was 59%. This result can be compared to the yield obtained from other agricultural wastes reported in previous works. Wheat straw (30%), hardwood stem (45%), softwood stem (45%), sugar cane bagasse (40%) [4, 10]. The observed differences can be attributed to the variations in the cellulose content of plants. This difference can also be attributed to the variation in the colour and texture of the powdered forms of these agricultural wastes.

The difference can also be attributed to the woody nature of the materials. Cellulose has been reported to constitute about 33% of all plant matter and the major component of cotton (Over 94%) and wood (Over 50%) [7].

### Effect of time parameter on percentage yield

As the reaction for the isolation of cellulose from flamboyant seed pod proceeded, an observation was noted. It was observed that as the time for heating in the reaction vessel increases from 2 hrs to 4 hrs, the delignified cellulose obtained was easily bleached with the application of small amount of sodium hypochlorite. This observation can be attributed to increased chance for homogenization of the solute and solvent, increased surface area for the reaction i.e delignification occur giving room for more extraction of cellulose from the flamboyant seed pod powders.

### Effect of time parameter on carboxymethyl cellulose solutions

**Table 2** The effects of time parameter on the solubility of carboxymethyl cellulose

Samples	Stir time (min)	MCAA(g)	CMC formed in H <sub>2</sub> O
CMC-20	20	6	Insoluble
CMC-30	30	6	Insoluble
CMC-40	40	6	Partially soluble
CMC-50	50	6	Partially soluble
CMC-60	60	6	Very soluble

By varying the time and keeping the concentration of monochloroacetic acid (MCAA) and NaOH constant, it was observed that the degree of carboxymethylation increases from 20 minutes to 60 minutes stirring time respectively. Also, the solubility in water of the carboxymethyl cellulose (CMC) formed increases with increase in time. It is believed that there is an increase in the surface area of the cellulose for reaction as the reaction time increases. This translates to mean that the degree of carboxymethylation of cellulose changes with time, and the etherification process is observed to be complete at 60 minutes (1 hr). Canary yellow coloration was observed in the CMC formed at 60 minutes of carboxymethylation after subjecting 5 g of the CMC formed to 10 mL of 5% potassium hydroxide solution and heated [13]. The color change confirms that 60 minutes stir time of carboxymethylation produced high quality carboxymethyl cellulose soluble in water.

### Moisture Content

The moisture content for CMC and native cellulose from flamboyant seed pod are 33.6% and 30.8% respectively. Comparing the moisture content of native cellulose and CMC at temperature 110°C, the difference observed is attributed to the slight decrease in crystallinity of carboxymethyl cellulose compared to native cellulose which can be explained by X-ray diffraction.

### Free Swelling Capacity (FSC)

The results of the free swelling capacity of carboxymethyl cellulose carried out in distilled water at different temperatures are given in Table 3.

**Table 3** Free swelling capacities of CMC at different temperatures

CMC Samples(°C)	Weight after swelling(g)	Free Swelling Capacity(g)
CMC 30°C	3.88 g	1.30 g

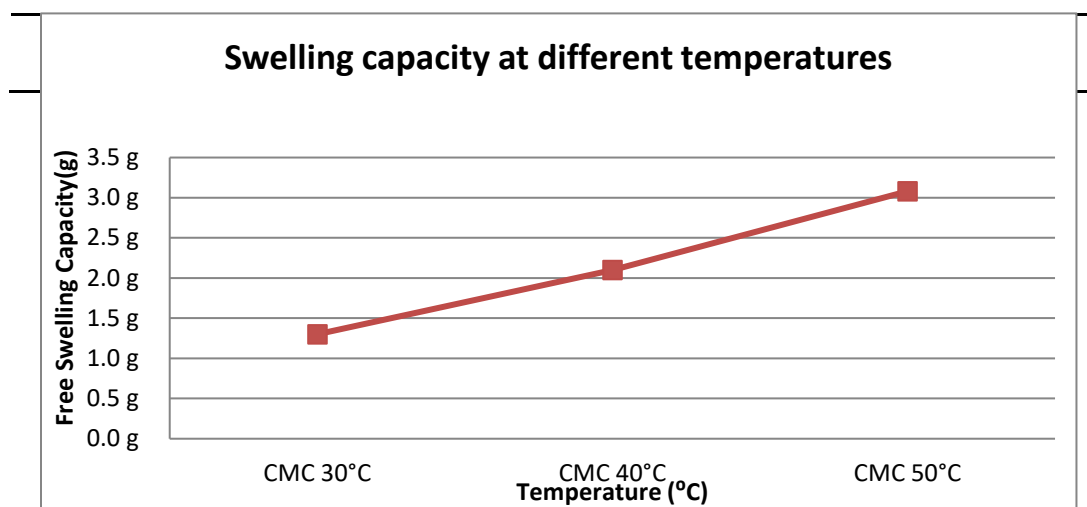


Fig. 5 Graphical representation of swelling capacities of carboxymethyl cellulose at different temperatures.

The swelling capacity of the carboxymethyl cellulose was observed to increase with increase in temperature (Fig. 5) in distilled water. This can be attributed to the fact that increase in temperature weakens the intra-granular binding of the carboxymethyl cellulose.

### Degree of Substitution

The degree of substitution value of CMC which was obtained by alkalization of cellulose followed by carboxymethylation process using monochloroacetic acid (MCAA) is 0.77. This fulfils the normal DS requirement range 0.5-1.2. The DS range for carboxymethyl cellulose is 0.5-1.2 [1]. When DS is below 0.3, the CMC is swellable but insoluble, while above this value, CMC is fully soluble with its hydro affinity increasing with increasing DS in agreement with Wagberg *et al.*, [18]. Since the DS value obtained for CMC is between 0.5-1.2, obviously, it is fully soluble in water and its solubility will increase with increasing temperature.

### FTIR Analysis

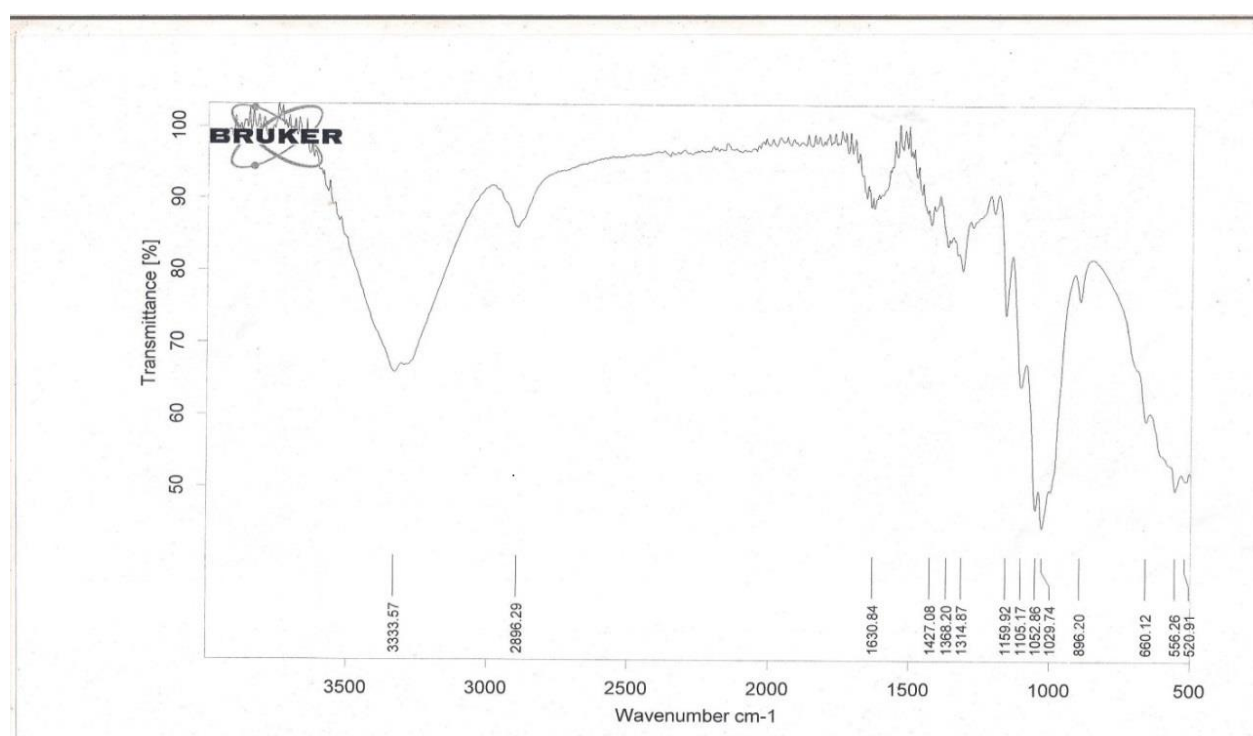


Fig. 6 FTIR spectrum of native cellulose

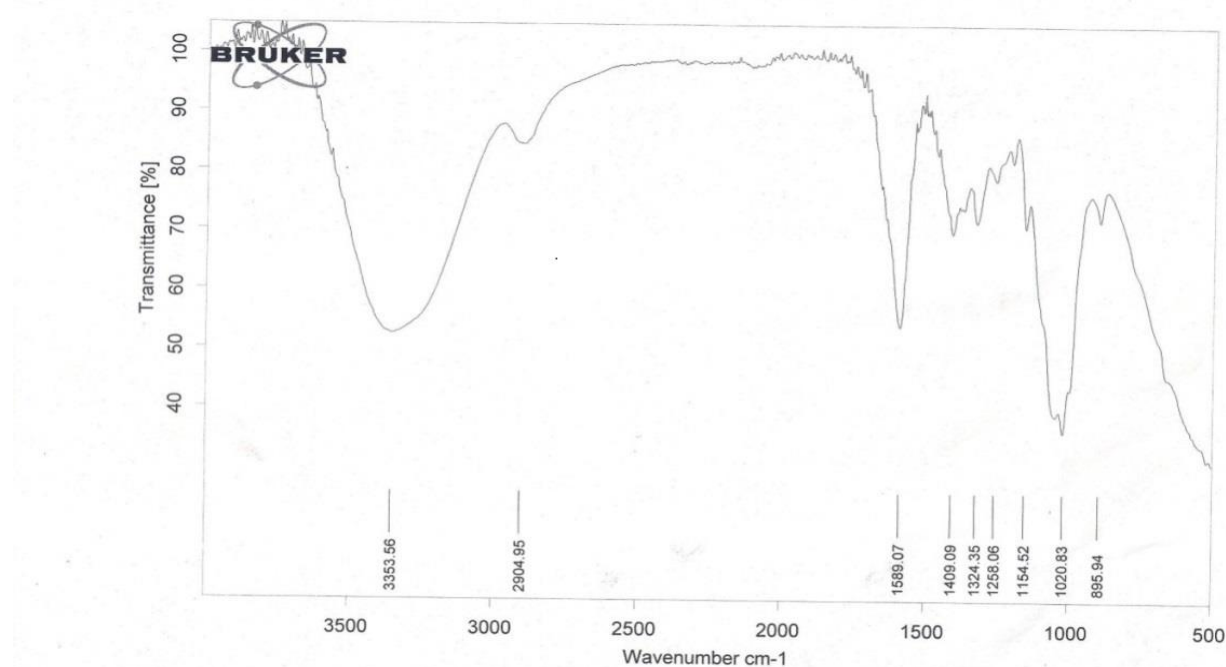


Fig. 7 FTIR spectrum of carboxymethyl cellulose

FTIR analysis was carried out on native cellulose and carboxymethyl cellulose. Fig. 6 represents the infrared spectrum of native cellulose obtained from flamboyant seed pods. The absorption band at  $3333.57\text{cm}^{-1}$  is attributed to the O-H stretch. The band at  $2896.29\text{cm}^{-1}$  is attributed to the C-H alkane stretch of the flamboyant seed pod cellulose. Also, the peak at  $1029.74\text{cm}^{-1}$  is due to C-O (ether linkages) stretch of the cellulose respectively. Other absorption bands are evidenced by literatures.

Fig. 7 represents the infrared spectrum of carboxymethyl cellulose obtained from the flamboyant seed pod. The FTIR spectrum of the CMC showed that the carboxyl and hydroxyl functional groups are found at  $1589.07\text{cm}^{-1}$  and  $3353.56\text{cm}^{-1}$  respectively. It is obvious that the broad band  $3353.56\text{cm}^{-1}$  is due to the stretching frequency of the hydroxyl group (-OH). The broad band observed is attributed

to the intramolecular and intermolecular hydrogen bonds of cellulose [14]. The band at  $2904.95\text{cm}^{-1}$  is due to carbon-hydrogen (C-H) stretching vibration of an alkane.

The presence of strong absorption band at  $1589.07\text{cm}^{-1}$  confirmed the presence of  $\text{COO}^-$  which is in conformation with literature. Mario *et al.*, [11] have also found carboxyl groups and its salt in this region. This peak is absent in the spectra of native cellulose. This is the evidence that the hydroxyl group of cellulose was replaced with carboxyl group when carboxymethylation reaction occurs. The band  $1409.09\text{cm}^{-1}$  is attributed to the  $-\text{CH}_2$  scissoring stretching.

### CONCLUSION

This study revealed that the carboxymethyl cellulose formed at 6 g of MCAA at 60 minutes produced a desirable, reproducible, and high quality product which dissolves easily in water-showing its high hydrophilic capacity. Prompting further applications, its feasibility as a reliable source of cellulose is proven by its high percentage yield. It was also observed that the carboxymethylation increases with increase in time and the carboxymethylation improves the swelling capacity in aqua system. FTIR spectrum of the CMC shows bands at  $3353.56\text{cm}^{-1}$  and  $1589.07\text{cm}^{-1}$  which reveal the presence of the hydroxyl functional group and the carboxyl functional group respectively; absent peaks which implies complete delignification confirms the high purity and strength of the product. Considering the physicochemical properties, and solubility of the carboxymethyl cellulose obtained in water, it can be used in pharmaceutical applications and as food additives. It can be further used in different industrial processes to manufacture food products, detergents, adhesives, cosmetics and ceramics. Based on the remarkable physicochemical properties of the products in this study, the authors therefore conclude that preparation and production of large scale industrial raw materials from agricultural wastes is feasible, renewable and economical, and it is highly recommended in manufacturing industries.

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