FOOD GRADE CARBOXYMETHYL CELLULOSE PREPARATION FROM AFRICAN STAR APPLE SEED (*Chrysophyllum albidum*) SHELLS: OPTIMIZATION AND CHARACTERIZATION

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ABSTRACT

α-cellulose isolated from African star apple seed shell (ASASS) was used as the raw material for the production of food-grade carboxymethyl cellulose (CMC). Preparation of CMC from ASASS cellulose was carried out by an etherification process, using sodium hydroxide and monochloroacetic acid (MCA) at various temperature. The cellulose and CMC were characterized by FTIR, XRD and SEM techniques. Degree of substitution (DS) was determined using potentiometric titration. Solubility increased with DS of CMC increased together with varied conditions but decreased at a certain level. The optimum results of varied conditions were 0.8015 DS for 30% NaOH concentrations; 0.6259 DS for 50°C temperature and 0.9254 DS for the amount of MCA. The FTIR spectra revealed the functional group modification of native cellulose to CMC, with absorptions at 1409.49 cm^{-1} and 1640.05 cm^{-1} indicating ether and carboxyl functional group respectively. The results of XRD analysis showed that crystallinity of isolated cellulose decreased in the CMC and SEM showed the elongated long fibres in cellulose while the fibrils in CMC are short and rough. The obtained product is well suited for pharmaceutical and food additives.

Keywords: Food grade, carboxymethyl cellulose, cellulose, optimization, degree of substitution, characterization.

INTRODUCTION

Cellulose is an organic natural polymer. It can be found widely in plants which are used as raw material for producing modified cellulose (Mondal *et al.,* 2015). Due to the abundant supply of the polymer in nature, modified cellulose is now advancing in terms of production and innovation. The sources can range from wood even to the agricultural waste (Yang and Zhu, 2007). African star apple (*Chrysophyllum albidum*) seed shells (ASASS) is an agricultural waste obtained from fleshy and juicy fruits of African star apple and they are very rich source of cellulose. The seeds are usually discarded or threaded as anklets for dancing in southern part of Nigeria or to play outdoor games after which they are thrown away as a waste probably due to lack of information on the potential of the seeds and lack of facilities to process it, thereby causing environment pollution problems (Opadotun *et al.* 2016).

Cellulose is a carbohydrate made up of a linear chain of many hundreds to several thousands of $\beta(1\blacktriangleright 4)$ glycosidic bonds of combined units of glucose (Choi *et al.* 2007). Cellulose is insoluble in either polar or non-polar and also neither melts nor dissolves readily in hot or cold water solvents due to its strong inter- and intra-molecular hydrogen bonds to the nearby oxygen (Hattori *et al.*, 2004). In order to utilize cellulose in the food industry, cellulose must be converted into its derivatives and one of the most common derivatives is carboxymethyl cellulose (CMC), also known as Na-CMC which is presently finding an increasing number of applications in industries. CMC is manmade modified cellulose, water-soluble, biopolymer anionic polysaccharide which is prepared by the reaction of monochloroacetic acid with alkali cellulose in the presence of

isopropyl alcohol (Bono *et al.* 2012).

There are several grades of CMC depending on their applications such as technical, semi-purified and purified. Purified CMC is a white to cream coloured, tasteless, odorless, free-flowing powder (Mario *et al.*, 2005) and it is used in a variety of industries including the food, detergents, personal care products, pharmaceutical etc. ((Mohkami and Talaeipour, 2011; Barba *et al.*, 2002; Stigsson *et al.*, 2001). In the food industry, it can be used as suspending agent, water loss reducer, thickener, emulsifying agent and stabilizer or dispersing agent. It is used as a preservative for coating of fresh fruit and bulk agent, thickener in pharmaceutical industries (Xue and Ngadi, 2009).

Studies have shown that CMC can be prepared from various sources such as pseudo stem of Cavendish banana (Adinugraha *et al.*, 2005), paper sludge (Hattori *et al.*, 2004), waste of Sago (Pushpamalar *et al.*, 2006), Palm Kernel cake (Bono *et al.*, 2009) and Cotton Ginning Industry (Haleem *et al.*, 2014). Every year in Nigeria, large quantities of CMC are being imported to meet domestic demand and the importance of CMC is increasing day-by-day (Alam and Mondal, 2013). Therefore, this study is to investigate the suitability of the ASASS, a locally available cheap raw material as a source of cellulose to produce high purity CMC under optimized reaction conditions.

EXPERIMENTAL
Sample pretreatment
The ASASS obtained from the local market at Ijebu Imusin, Ogun State, Nigeria was thoroughly washed with distilled water to get rid of adhering dirts. It was sun-dried for 10-12 days and later oven-dried at 60°C for two consecutive days. The inner part of the seed was removed and the shell were pulverized using a PYRAMID Electric Blender and Grinder (PM-Y44B2) after which it was sieved with 250 μm analytical sieve to remove larger particles.

Isolation of cellulose from African Star Apple Seed Shells
Cellulose isolation from *Chrysophyllum albidum* seed shells was carried out according to the previous methods described by Adinugraha *et al.* (2005), Pushpamalar *et al.* (2006), with some modifications. The pulverised material was soaked in hot water for 1 h and filtered. The residue was then treated with 20 % (w/v) NaOH solution at a liquid/material ratio of 10:1 (v:w) at 90–100°C for 2 h. The cellulose slurry was then filtered and washed with distilled water several times. The obtained cellulose fibres were bleached with 5 % sodium hypochlorite under alkaline conditions at 60 – 70°C for 15 min. After cooling, the bleached cellulose fibres were washed with distilled water until it attains a neutral pH, dried in an oven at 60°C for 8 h and weighed using an analytical balance. The percentage yield of cellulose isolated was calculated using equation (1).

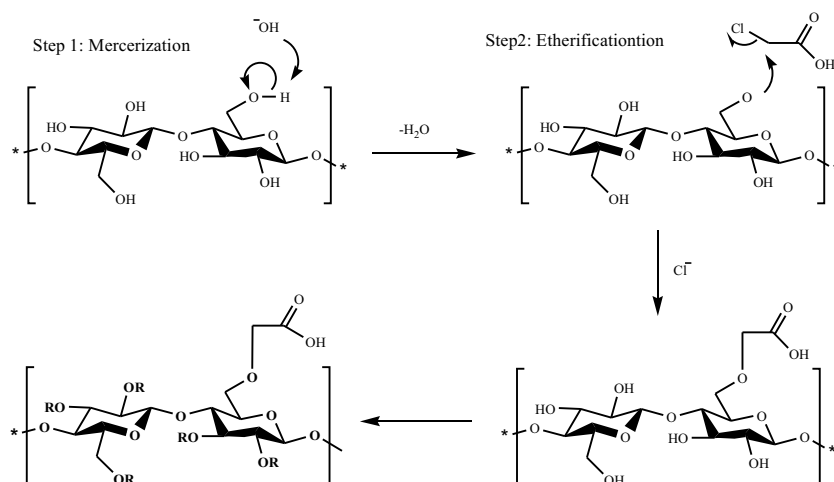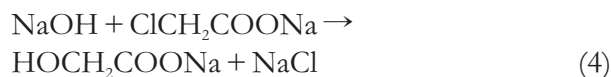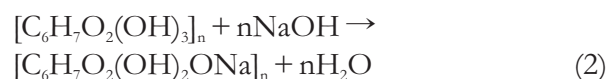$$\% \, Y = \frac{A}{B} \times 100 \qquad (1)$$

Where:

     A = mass of cellulose (g);
     B = mass of pulverised African star apple shell (g).

Preparation of Carboxymethyl Cellulose (CMC) from cellulose isolated
The isolated cellulose from African star apple shells is converted to CMC in two steps, alkalization and etherification of cellulose under heterogeneous conditions. In the alkalization pretreatment, 5 g of cellulose sample was weighed and added to a 600ml beaker followed by 75 ml of isopropanol. The mixture was left to stand for 5 mins. 40 ml of aqueous sodium hydroxide of various concentrations (10, 20, 30, 40 and 50 %) was added drop-wise while it is stirred on a magnetic stirrer for an hour. The reaction between the OH of cellulose and NaOH is known as mercerization process. After alkali treatment, etherification reaction was started by the addition of various amounts of sodium monochloroacetate (MCA) (2, 4, 6, 8 and 10 g) in the reaction mixture at various temperatures (room temp, 40, 50, 60 and 70°C) and stirred for 1 h of reaction time. Longer time of reaction will increase degradation of polymer and will reduce the DS value as well (Bono *et al.*, 2009). The slurry was then soaked in methanol for 4 hours, neutralized with 90 % acetic acid until it reach pH 6 – 8. The slurry was filtered and then purified by

washing with 70 % ethanol to remove undesired byproduct to get pure CMC. Then, the pure CMC was filtered and dried at 60°C in an oven for 24 hours. The total summary of equation of reaction leading to the preparation of CMC and the mechanism of the reaction are given in equations 2-4.

$$[C_6H_7O_2(OH)_3]_n + nNaOH \rightarrow$$
$$[C_6H_7O_2(OH)_2ONa]_n + nH_2O \tag{2}$$
$$[C_6H_7O_2(OH)_2ONa]_n + nClCH_2COONa \rightarrow$$
$$[C_6H_7O_2(OH)_2OCH_2COONa]_n + nNaCl \tag{3}$$
$$NaOH + ClCH_2COONa \rightarrow$$
$$HOCH_2COONa + NaCl \tag{4}$$

Scheme 1. Carboxymethylation reaction mechanism where R may be H or CH₂COOH

Determination of degree of substitution (DS) of CMC

DS is determined by a potentiometric back titration.4 g of the dry powder sodium carboxymethyl cellulose (CMC) was stirred in 75 ml of 95 % ethanol for 5 min. 5 ml of 2 M nitric acid was added to convert CMC to its acid form (H-CMC) under high temperature. The mixture was allowed to cool while stirring for another ten minutes resulting into a solid and liquid phase. The liquid phase was removed, and the solid phase was washed with 20 ml of 80 % ethanol at 60°C for 5 times. The precipitate was washed with a small quantity of anhydrous methanol and filtered. It was dried at 100°C for 3 hours and cool in desiccators for half an hour. About 0.5 g of dry acid CMC was weighed in 250 ml Erlenmeyer flask and 100 ml of distilled water was added and stirred. 25 ml 0.3 M NaOH was added and heated to boil for 15 minutes. After the products dissolved, the mixture was titrated with 0.3 M HCl. Phenolphthalein was added to observe the colour change from dark pink to colourless (Koh, 2013 The DS was calculated according to the equation (5) and equation (6):

$$A = \frac{BC - DE}{F} \tag{5}$$

$$\text{Degree of substitution} = \frac{0.162 \text{ x } A}{1 - (0.058 \text{ x } A)} \tag{6}$$

Where,
A = milli-equivalents of consumed acid per gram of specimen
B = volume of Sodium hydroxide added
C = concentration in normality of sodium hydroxide added
D = volume of consumed chloric acid
E = concentration in normality of chloric acid used
F = specimen grams used
The molecular weight of the anhydrous glucose unit is 162 while 58 is the net increment in the anhydrous glucose unit for every substituted carboxymethyl group (Bono *et al.*, 2009).

Fourier transformed infrared spectroscopy (FTIR)

The functional groups of the cellulose isolated and CMC prepared was determined using SHIMADZU Happ-Genzel Fourier Transform Infrared Spectrophotometer. The samples were dried in an oven at 60 °C to remove the moisture. About 0.2 mg of sample and 2 mg of potassium bromide were mixed and ground finely before the

mixture was compressed to form a transparent pellet. The infrared spectra of these samples were measured in the transmission of a wavelength number range between 4000 and 400 cm^{-1}.

Scanning electron microscope (SEM)
The surface morphologies of cellulose and CMC were examined by SEM (TESCAN JSM- 6490A, Japan Analytical scanning electron microscope). Samples were coated with a thin layer of conducting material (gold) and imaged at ×7000 magnifications with 15 kV accelerating voltage at a pressure of 70 Pa. A focused high energy beam of electron interacted with the surface of sample and generated secondary electron, back scattered electron and characteristic X-rays signals. These signals were perceived by the detector and images were displayed on the cathode ray tube screen.

X-ray diffraction (XRD)
Degree of crystallinity of the isolated cellulose and CMC were determined using X-ray Diffractometer. X-Ray diffractometer (Philip – PW 1011 model) was used to obtain X-Ray diffraction patterns of isolated and modified cellulose. Samples were prepared by pressing the powders between two glass slides into a flattened sheet. The X-Ray patterns were taken by using radiation source CuK by supplying 40 kV and 40 mA to X-ray generator. The patterns were recorded at 2θ from 20° to 80°.

RESULTS AND DISCUSSION
Yields
The yield of cellulose from the sample in the alkalization stage was 47% according to equation (1). Table showed the percentage yield of CMC synthesized at various conditions. In the case of MCA, the percentage yield increased when 2 to 8 g of MCA is used, and then reduced at an amount beyond the 8 g. This might be due to the medium which is now becoming acidic and thus not favouring the production of CMC. Thus, the general increase is due to the reaction of cellulose with monochloroacetic acid (MCA) in an alkaline condition which causes the substitution of the hydroxyl group of cellulose molecules with carboxymethyl group and attributed to a higher mass (Selke et al., 2004)

Table 1: Experimental yield of CMC (without using the model)

	Carboxymethylation conditions					Carboxymethylated cellulose	
1	Sample no	A	B	C	D	E
	NaOH (%)	10	20	30	40	50
	Yield (%)	82.40	84.20	176.60	120.20	80.00
2	Sample no	F	G	H	I	J
	MCA (g)	2	4	6	8	10
	Yield (%)	61.60	69.40	86.80	126.60	95.40
3	Sample no	K	L	M	N	O
	Temperature (℃)	25	40	50	60	70
	Yield (%)	121.00	125.00	126.60	120.00	103.60

The percentage yield of CMC obtained from ASASS was found to increase with increasing NaOH concentration from 10 to 30%. This is because the reaction of cellulose with monochloroacetic acid (MCA) in an alkaline condition resulted in the substitution of the OH group of individual anhydroglucopyronase unit with carboxymethyl group, hence, the characteristics of a higher mass (Selke *et al.*, 2004 & Koh, 2013). The highest CMC yield was observed at 30% NaOH (8.33 g). Above 30% NaOH, the percentage of CMC decreses up to 50% NaOH. This is in conformance with reports showing that high concentration of NaOH tends to result in the degradation of cellulose chains by alkaline hydrolysis and formation of glycolate, resulting in low percentage yield (Ismail *et al.*, 2010; Rachtanapum *et al.*, 2012 & Caroline *et al.*, 2017). Table 1 also reveals that the percentage yield of CMC synthesized from ASASS varies with temperature, with highest yield (%) obtained at 50°C. The increase in percentage yield from room temperature to 40°C and 50°C might be associated with a better reaction environment for

carboxymethylation. The values culminated at 50°C and then declined at 60°C. The chemical elimination of water and inter-molecular elimination of hydroxyl groups, which leads to the degradation of cellulose, is one of the possible explanations attributed to this (Tongdeesoontorn *et al.*, 2011, Yaacob *et al.*, 2011 & Caroline *et al.*, 2017).

Degree of substitution (DS)

The degree of substitution (DS) of the hydroxyl (OH) in cellulose by carboxyl (COOH) group in CMC was determined by titrimetric method. The effect of NaOH concentration on the DS of CMC was studied by varying the concentration of the sodium hydroxide solution from 10 to 50% (Figure 1A). It was observed that the DS of CMC increased with sodium hydroxide concentration until it attained a highest DS of 0.8015 at a 30% NaOH concentration. The DS of CMC obtained from ASASS started declining at higher concentration of NaOH (>30%) which could be due to formation of sodium glycolate and sodium chloride as by-products in the synthesis of CMC. Similar result was also observed in CMC obtained from banana pseudo stem (Adinugraha *et al.*, 2005), sugar beet pulp (Togrul and Arslan 2003) and sugarcane bagasse (Koh, 2013). According to Barai *et al.* (1997), glycolate formation predominates at a high concentration of NaOH, as part of the MCA molecules tends to react with NaOH, resulting in a lower degree of substitution and CMC content. Figure 1B shows the DS of

CMC synthesized at different temperatures. A maximum DS was observed for CMC obtained at 50°C. The increase in DS from 25 to 50°C might be associated with a better reaction environment for carboxymethylation. At higher temperature, degradation of cellulose occurred. Similar results have been reported in literature (Tongdeesoontorn *et al.*, 2011, Yaacob *et al.*, 2011 and Caroline *et al.*, 2017). Varying the amount of MCA (2, 4, 6, 8 and 10 g) for the etherification process revealed that DS increases with increasing amounts of monochloroacetic acid (Figure 1C). The greater availability of acetate ions, active alkoxides and functional groups at higher concentrations of MCA might be responsible for the increase (Nattapulwat *et al.*, 2009). The highest DS value was obtained with 8 g of MCA for ASASS. The reaction efficiency might have culminated at 8 g for African star apple seed shells as a result of the formation of sodium glycolate and sodium chloride from the side reaction between monochloroacetic acid and sodium hydroxide at a higher amount of MCA (> 8 g) (Ismail *et al.*, 2010 and Caroline *et al.*, 2017). Table 2 showed different range values of DS for CMC prepared from cellulose isolated from different agricultural waste products. Commercial CMC has been reported to have a DS in the range of 0.4 to 1.4 (Silva *et al.*, 2004 and Caroline *et al.*, 2017). The DS of the CMC polymer has important implications in its applications i.e. the higher the DS, the more soluble the CMC.
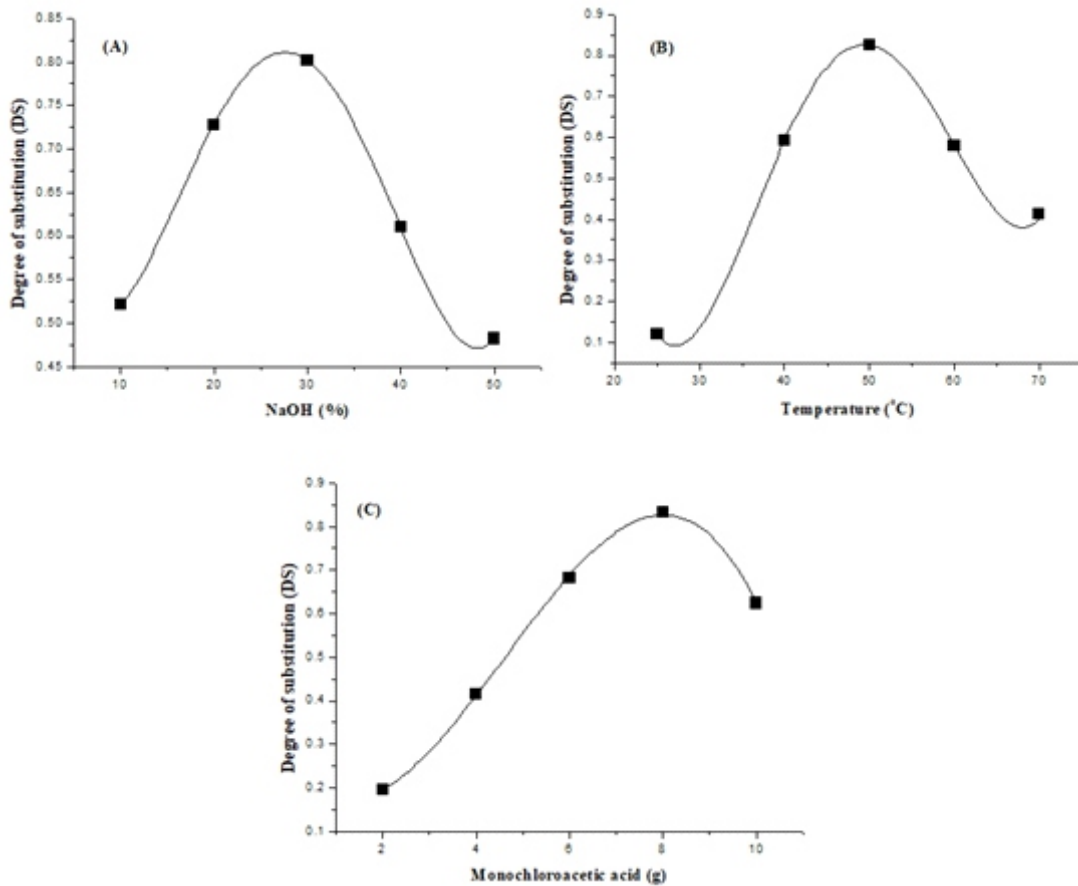
Figure. 1   Determination of optimum conditions in the preparation of CMC from the cellulose isolated from ASASS: (A) 0.8015 DS for 30% NaOH concentrations; (B) 0.6259 DS for 50°C Temperature and (C) 0.9254 DS for the amount of MCA.

Varshney et al., (2006) reported that when DS is less than 0.4, the CMC will be swellable and insoluble but when it is more than 0.4, the CMC will be completely soluble because its affinity for water solubility increases as DS increases. The DS value of CMC prepared from cellulose isolated from ASASS was between 0.15 and 0.93, which indicates that it is completely soluble in water and other solvents (Pushpamalar *et al.*, 2006).

Table 2: DS value of CMC obtained from different sources of cellulose

Sources of cellulose	DS	References
Sugar beet pulp cellulose	0.11 - 0.67	Togrul and Arslan (2003)
Water hyacinth	0.24 - 0.73	Barai *et al.* (1997)
Banana pseudo stems	0.26 - 0.75	Adinugraha, *et al.* (2005)
Sago waste	0.33 - 0.82	Pushpamalar, *et al.* (2006)
Sugarcane bagasse	0.40 - 0.60	Koh (2013)
Sugarcane bagasse	0.45 - 0.78	Asi *et al.* (2017)
African star apple seed shell	0.15 – 0.93	Current Research

Spectroscopic characterization by FTIR

Figure 2 shows the FTIR spectra of cellulose isolated from ASASS and the CMC prepared from it at optimum conditions. The broad band located within the region of 3416-3419 cm^{-1} that appeared in both spectra indicates the free OH stretching vibration as well as inter- and intra- molecular hydrogen bonds in cellulose molecules (Pushpamalar *et al.*, 2006). The band at 2901-2922 cm^{-1} is attributed to C-H stretching vibration (Biswal *et al.*, 2004). The vibration band at 1375 cm^{-1} is attributed to the C-H and C-O bending vibration in the polysaccharide aromatic rings (Nacos *et al.*, 2006). The FTIR spectrum of CMC shows the presence of carboxyl (COO) group at 1600-1604 cm^{-1} and 1417-1327 cm^{-1}. According to Koh (2013), carboxyl groups and its salts show two peaks at wavenumber 1600-1640 cm^{-1} and 1400-1450 cm^{-1} which indicates the presence of carboxymethyl substituent (COO$^-$). The bands at 1417-327 cm^{-1} and 1325 cm^{-1} are attributed to CH$_2$ scissoring and OH bending vibrations respectively. The C-C ring breathing band appeared at 1155-1163 cm^{-1} and C-O-C glycosidic ether band at 1058-1066 cm^{-1} arising from the polysaccharide components (Garside and Wyeth, 2003). In addition, the peak at 1024-1033 cm^{-1} appearing in both spectra indicates the C-O-C pyranose ring stretching vibration. The peak at 896 cm^{-1} is associated with the β-(1,4)-glycosidic linkages between the glucose units in cellulose (Viera *et al.*, 2007). The result of the FTIR obtained was in agreement to that reported previously (Sun *et al.*, 2004; Koh, 2013 & Haleem *et al.*, 2014).
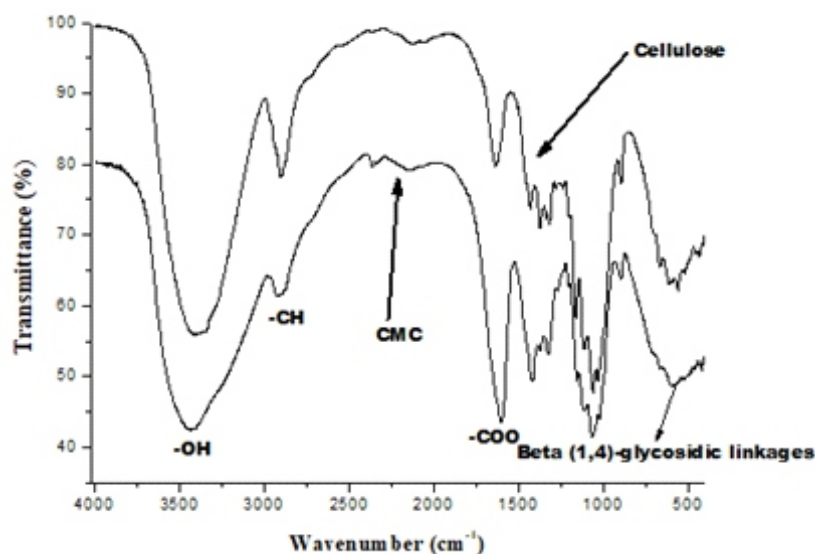

Figure 2: FTIR spectra of isolated cellulose from ASASS and CMC prepared

Morphological characterization by Scanning Electron Microscope (SEM)

The scanning electron micrographs of isolated cellulose and CMC is shown in Figure 3 at different magnifications. At higher magnifications, the cellulose is completely elongated with fibrils of various thicknesses and lengths. Similar observation was also reported in the literature that fiber diameter reduces as the alkali concentration is increased (Aydin *et al.*, 2011). This is because during alkalization of cellulose, the inter and intra molecular hydrogen bond of cellulose are easily broken and the polyhydroxyl group of polysaccharide resulting to swelling of the cellulose and thus the fiber have different reduction in length. Surface analysis of the cellulose by SEM showed the packed structures of the fibrils were separated from each other. Meanwhile, the SEM micrograph of the CMC at higher magnifications shows that CMC had a rough surface with a partial round fibrils and not elongated like cellulose structures, resembling particle of atoms closely packed together to form cluster (Haleema *et al.,* 2014).
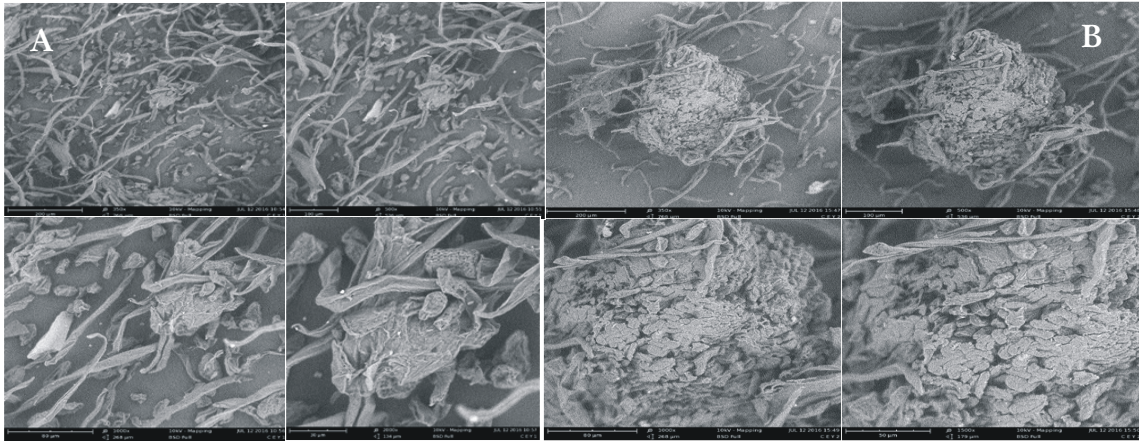
Figure 3: SEM micrographs (×350, ×500, ×1000 and ×5000) of cellulose isolated from ASASS (A) and CMC prepared (B) at optimum conditions.

X-ray diffraction (XRD) analysis

Figure 4 shows the XRD results of pure cellulose obtained from ASASS and CMC prepared afterwards. Diffraction pattern of cellulose illustrates three sharp peaks of cellulose at $2\theta = 18°, 34°$ and $22°$. This pattern is characteristic of cellulose structure of crystal I. However, the absence or weak diffraction in the region $2\theta = 17°$, complete disappearance of $2\theta=34°$ sharp peak and the replacement of wide broad spectrum peak are indications of complete modification of ASASS cellulose to CMC and hence characteristic diffraction pattern of crystalline peaks of CMC (Guozhi *et al.,* 2013). This means that carboxymethyl cellulose crystallinity has been partially transformed into amorphous phase. This is due to the substitution of the OH groups in cellulose with $CH_3COO–$ groups (Haleema *et al.,* 2014).
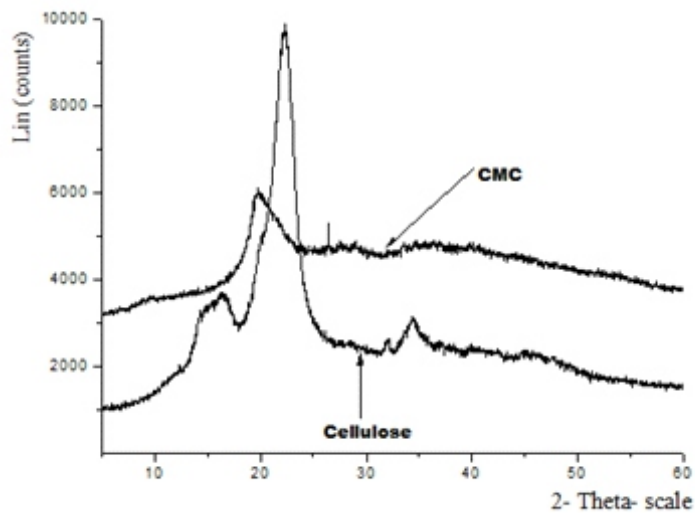

Figure 4: XRD results of cellulose isolated from ASASS (A) and CMC prepared from the cellulose at optimized conditions

CONCLUSION

In this research work, cellulose was successfully isolated from African star apple seed shells (*Chrysophyllum albidum*) through alkali treatment followed by bleaching with sodium hypochlorite. The two-step treatment recovered 47% of cellulose from African star apple seed shells. The isolated cellulose was then converted to carboxymethyl cellulose (CMC) by mercerizing with various sodium hydroxide (NaOH) concentrations and various amounts of MCA at different temperatures in order to determine the optimum conditions for CMC preparation. The optimum conditions for carboxymethyl cellulose production was found to be 30 g/100mL NaOH and 8 g MCA at a temperature of 50°C. The Fourier transform infrared (FTIR) spectrum confirmed the transformation of cellulose to carboxymethyl cellulose in the plant material by the presence of the carboxylic group (COO$^-$) at wavenumber 1600 cm^{-1}-1604 cm^{-1}.

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