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Research Article

Synthesis of Industrial Raw Material from Cellulosic Agricultural Wastes: Focus on Carboxymethyl Cellulose

Moses Onigbinde, Adeago Vivian
Chemical Sciences Department, Samuel Adegboyega University, P.M. B. 001, Ogwa, Edo State, Nigeria.

**Corresponding author: monigbinde@sau.edu.ng*

Abstract

Agricultural wastes such as sugarcane bagasses, maize cob, palm kernel cake, palm oil empty fruit bunches, banana pseudo stem and orange mesocarp have been known to be potential sources of cellulose. From these cellulose sources sodium carboxymethylcellulose (NaCMC), a water soluble cellulose derivative and an essential raw material in the food, cosmetic, pharmaceutical and detergent industries could be synthesized. Importantly, orange mesocarp generated from orange peel is an abundant agricultural by-product which consists of about 62.5% cellulose. It is significantly considered as one of the alternative secondary resources for cellulose. In this work, cellulose was extracted from orange mesocarp and then converted to NaCMC. The orange mesocarp was dried and ground to pass 20 mesh screen. Cellulose was extracted using 8% NaOH at 100^{o}C for 3.5 hrs and bleached using 3.85% NaOCl at 30^{o}C for 3 hrs. Carboxymethylcellulose (CMC) was consequently synthesized from the extracted cellulose by alkalization followed by etherification. The physicochemical properties of the NaCMC were determined in terms of the degree of substitution, viscosity and with the use of FTIR spectroscopy. The NaCMC resulted from this work has a viscosity of 14.0cP at 29.8^{o}C and DS 1.02 and therefore was categorized as technical grade with medium viscosity. After optimization and scaling up of the production process the NaCMC synthesized will be a useful and cheap raw material for the industries.
Keywords: Agricultural wastes, industrial raw material, orange mesocarp, sodium carboxymethylcellulose.

Introduction

Agricultural activities and agro-based processing yearly generate enormous volumes of agricultural wastes that contain cellulose fibers which are allowed to rot away and eventually polluting the environment. Orange mesocarp, maize stem and cobs, banana and plantain pseudostem, raffia from Raphia hooker; coconut shell, groundnut husk, sugar cane bagasses, soybean, oath, wheat and rice hull are common examples [1]. Interestingly, semi-processing of various agricultural crops in Africa generates close to 300 million tons of agricultural wastes annually [2]. Perhaps, up to half of these wastes are potential low-cost sources of cellulose but no known attempt has been made at commercial level about them. Woody plants and cotton were the major sources of cellulose but cost and competing uses have made it imperative that other materials be investigated as potential sources.

Cellulose is a linear and high molecular weight polymer as well as natural, renewable and biodegradable material. It is a polysaccharide of anhydroglucose units linked at C-1 and C-4 by β-glycosidic bonds. This is confirmed by the presence of three hydroxyl groups, secondary OH at the C-2, secondary OH at the C-4 and primary OH at the C-6. They have different reactivity and form strong inter-and intra-molecular bonds. To utilize cellulose in the industry it must be converted to its derivatives. Common derivatives like cellulose nitrate, cellulose acetate, cellulose phosphate, sodiumcarboxylmethyl cellulose, hydroxyl ethyl cellulose, methyl cellulose have been reported to be useful in the paper, textile, pharmaceutical, ceramic and cement, cosmetic, detergent, paint, oil, pesticide and plant growth regulator industries. They are used as thickener, emulsion stabilizer, good bonding agent, explosives, packaging materials, adhesive, moisture proof coatings, separation membranes and fire extinguishers [3].

Of all the various cellulose derivatives known, sodiumcarboxymethyl cellulose (NaCMC) is an important cellulose ether, a water-soluble, anionic, man-modified polysaccharide utilized in food and chemical industries. Purified NaCMC is a white to cream coloured, tasteless, odourless, free-flowing powder [4]. Various works have been done on the synthesis of NaCMC but none of them utilize orange mesocarp as cellulose source [5, 6, 7, 8].

The objective of this work is to examine the possibility of synthesizing NaCMC from cellulosic agricultural waste like orange mesocarp. This is a preliminary study into the industrial applications of this locally sourced carboxymethyl cellulose in comparism with the imported commercial grade NaCMC known to be used in the industries as anti-caking agent, emulsifier, stabilizer, dispersing agent, thickener, and gelling agent.

Materials and Method

Extraction of cellulose

Orange mesocarp was generated from sweet oranges which were bought at Fagba station market in Lagos state Nigeria, after removing the endocarp and epicarp by peeling. It was sun dried and latter put into the oven at 60^oC for about 6 hours. Thereafter, it was fed into a laboratory grinding mill. The grounded samples were sieved with a standard sieve of 20 meshes. The dried, grounded and sieved agricultural wastes was boiled in 8% NaOH at ratio of cellulose to solvent 1:20 (w/v) for 3.5h at 100^0C, the obtained black slurry was filtered and washed using distilled water and bleached with 3.85% NaOCl for 3hrs at 30^0C.The bleached cellulose was washed again using distilled water until the odour of hypochlorite could no longer be detected, then dried at 60^0C in an oven.

Synthesis of sodium carboxymethylcellulose

The synthesis of sodium carboxymethylcellulose was done according to the work of Adinugraha etal [8].Two gram of the cellulose powder was alkalized at 25^0C for 1hr in a waterbath under continous shaking with 20ml of 15% concentration of NaOH in 100ml of isopropanol as a solvent. After the alkalization process is over, 3g of Monochloroacetic acid was added and the temperature raised to 55^0C and the reaction continued for 3hr. The slurry was neutralized with 90% of acetic acid and then filtered. The solid obtained as CMC was washed by 70% ethanol for four times to remove undesirable by-products. The obtained cellulose derivative (CMC) was dried at 60^0C in an oven.

Characterization of sodium carboxymethylcellulose

Degree of substitution (DS), viscosity and other physico-chemical properties of the synthesized CMC were determined by standard methods reported in the literatures. [6, 7]

FT-IR spectroscopy of sodium carboxymethylcellulose

The extracted cellulose and carboxymethyl cellulose product were characterized by using Fourier Transform IR (FTIR) instrument. To get the spectra, a pellet made from sample was grounded with KBr. Transmission was measured at the wave number range of 4000-4400cm^{-1}.

Result and Discussion

Percentage cellulose

It is quite important and fundamental to know the percentage cellulose composition of any potential agricultural waste intended to be used for the synthesis of cellulose. From the literature among some common agricultural wastes considered orange mesocarp is seen to have the highest percentage of cellulose i.e. 62.5% as shown in Table 1. This made it suitable for this study.

Table 1 - The % cellulose in some agricultural wastes.

S/N	Crop	Species	Component	Cellulose (%)	References
1	Orange	Citrus sp	Pulp-shredded	62.5	[9]
2	Sugarcane	Saccharum officinarum	Bagasse	62	[10]
3	Maize	Zea mays	Stover/cob	43	[10]
4	Soybean	Glycine, max	Hulls	52	[11]

5	Plantain	Musa paradisiaca	Pseudo stem	52.44	[1]
6	Oil Palm	Elaeis guineensis	Palm kernel cake	20 – 30	[7]
7	Coconut	Cocos nucifera	Shell	35.70	[1]
8	Wheat	Triticum aestivum	Straw	45	[12]

Cellulose Extraction and Percentage Yield

There are various methods discovered from the literatures for the extraction of cellulose from wood and other ligno-cellulosic materials. The general principle involves the subjection of the raw material (the untreated raw cellulose) to reagents which either dissolve or destroy all non-cellulosic impurities (lignin, hemicellulose, colouring matter etc.) while having little or no effect on cellulose. Sulphite process which involve the use of calcium or sodium bisulphite with sulphur dioxide, kraft process using a mixture of sodium hydroxide and sodium sulphide, soda process using sodium hydroxide alone, acidified sodium chlorite process using glacial acetic acid with sodium chlorite and modified process using sodium hydroxide with sodium hypochlorite have been successfully used [13,7]. In this work the latter process was used and it gave a percentage cellulose yield of 32.6%. This result was comparable to the result of other researchers. Khullar etal [14] got 35% yield from *Dendrocalamus striticus*, a widely distributed bamboo in India using standard Tappi method (TAPPIT2003OM-88). Bono etal[7] using acidified sodium chlorite process recovered 13-20% cellulose yield from palm kernel cake. Ekebafe etal [15]using Tappi method of extraction with acetic acid and nitric acid got 55. 52% yield from rubber sheed shell. Azubuike etal [16] using sodium hypochlorite for bleaching after delignification got 30% of α-cellulose from maize cob. Bakre and Odumala [17] using a similar extraction method with this work got 15.5% and 34.45 cellulose from sugarcane scrapping and bagasse respectively. For extraction of cellulose the method use depends on the source of the material and the cellulose intended use which significantly determine the yield. The average yield gotten from this work is due to the experimental conditions and the fact that some of the cellulose may be lost in the course of removing the supernatant.

Degree of Substitution (DS)

The DS is a major factor in the water solubility of CMC. Below approximately 0.4 the polymer is swellable but insoluble, above this the polymer is fully soluble with its hydroaffinity increasing with increasing DS [5]. Reuben and Conner [18] in their work showed that CMC gotten through alkalization of cellulose then followed by carboxymethylation process using NaMCA was in the range of 0.4 – 1.3. The DS value for CMC from orange mesocarp in this work is 1.02 and it falls within the expected range. Because of the DS value the CMC is soluble in water and its solubility increases with temperature. The use of isopropanol (a high polar solvent) as solvent in carboxymethylation reaction is to provide miscibility and accessibility of the etherifying reagent to the reaction center of the cellulose chain which prevent the side reaction formation of sodium glycolate [8]. The DS of CMC gotten from different sources including this work is shown in Table 2.

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

Sources of Cellulose	Degree of Substitution(DS)	References
Water hyacinth	0.24-0.73	[5]
Sago waste	0.33-0.82	[19]
Sugar beet pulp cellulose	0.11-0.67	[7]
Lantana camara	0.20-1.22	[7]
Palm kernel cake	0.67	[7]
Banana pseudostem	0.26 – 0.75	[8]
Orange mesocarp	1.02	[This work]

Yield of CMC

The CMC produced in this work is of fair appearance and a powdery form. The yield is 46.5%. The yield is determined by the amount of material lost in the preparation process. Degradation becomes more pronounced and large quantity of low molecular weight material were released due to more drastic reaction conditions like higher temperature and concentration of reagents used.

Viscosity of CMC

The viscosity of CMC for this work at 29.8^0C is 14.0cp. Indeed, is a medium viscosity. The commercial range for low viscosity CMC is 20-50cP in 2% concentration of solution. Bono et al [7] got a viscosity of 66.6cP for palm kernel cake CMC when the percentage of carboxymethyl palm kernel dissolved in distilled water was 3% dry weight. The viscosity of CMC is very essential because it suggest the type of application it can be subjected to in the industry. More importantly, it provides information for flow characteristics of the fluid flow involved in the processing operations and products. This can be manipulated by changing CMC concentration. The reduction in viscosity of CMC synthesized in this work may be due to the degradation of the polysaccharide or the presence of remnant of NaOH in the product which was not removed during the washing process with ethanol after the hemicellulose removal step. Table 3 gives the parameters of the CMC product.

Table 3: CMC product parameters

Parameters	**Orange mesocarp CMC**
Formula	$[C_6H_7O_2(OH)_2COONa]n$
Degree of substitution	1.02
Colour	Cream
Form	Powder
Yield (%)	46.5
Viscosity at 29.8^0C	14.0cP
pH	7.64
Solubility in water	Soluble in water

FTIR Characterization

Cellulose prepared from orange mesocarp represents a milky white powder. Fig. 1 shows the FTIR spectra. The cellulose spectra are of the cellulose gotten using acidified sodium chlorite extraction method. Absorption band at 3448.84 is due to the stretching frequency of the –OH groups as well as the intramolecular and inter molecular hydrogen bonds in cellulose [8]. Peak at wave number of 1066.67 cm^{-1} is due to >CH_2-O- CH_2. C-H stretching vibration shown at peak 2918.40cm^{-1}. Other proof of cellulose are that of –CH_2 scissoring and –OH bending vibration at 1417.73 and 1338.64 cm^{-1}respectively.

Infrared spectroscopy (FTIR) spectra of CMC were shown in fig.2. The peaks at wave number 1417.73 $cm^{-1}$and 1597.11 cm^{-1} for orange mesocarp indicated the presence of Carboxymethyl substituent. According to report from the literature, carboxy groups and its salts have wave number about 1600-1640 cm^{-1} and 1400-1450 cm^{-1}[8].These spectra compared to the commercial CMC reported by Adinugraha et al [8] was similar except for the peaks at 2125.63 and 2360.95 cm^{-1}. These peaks were supposed to be contamination from impurities or combination band from water. The similarity of the CMC in this work with those reported in the literature from other agricultural wastes and commercial CMC showed that CMC could be synthesized from orange mesocarp[1,7].

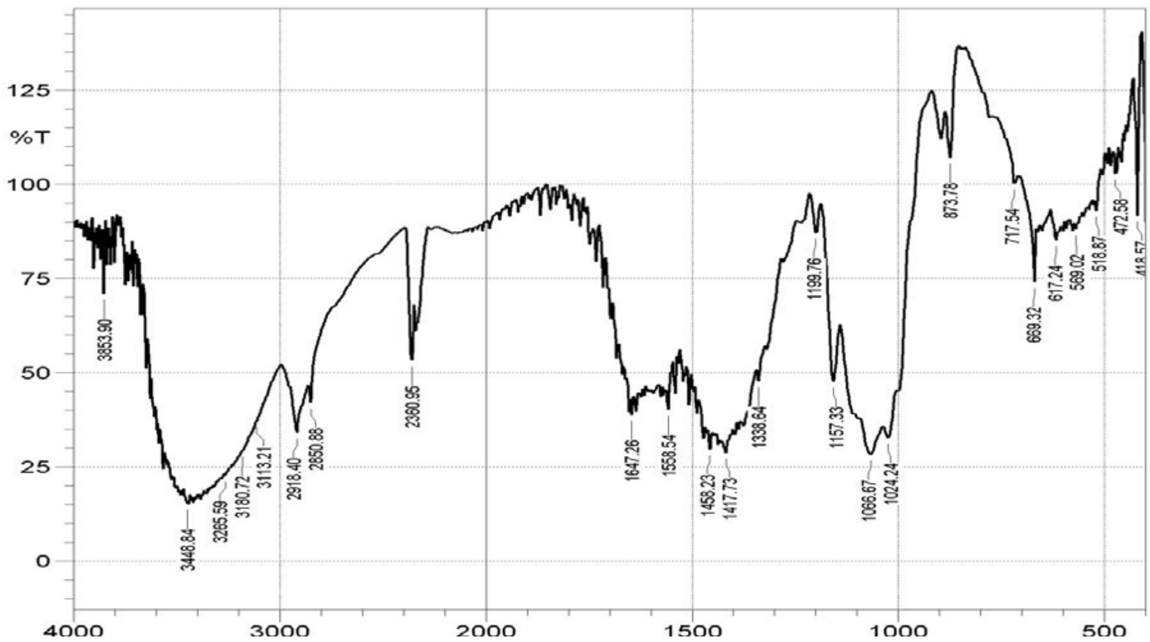

Fig. 1: FTIR spectrum for Orange mesocarp Cellulose

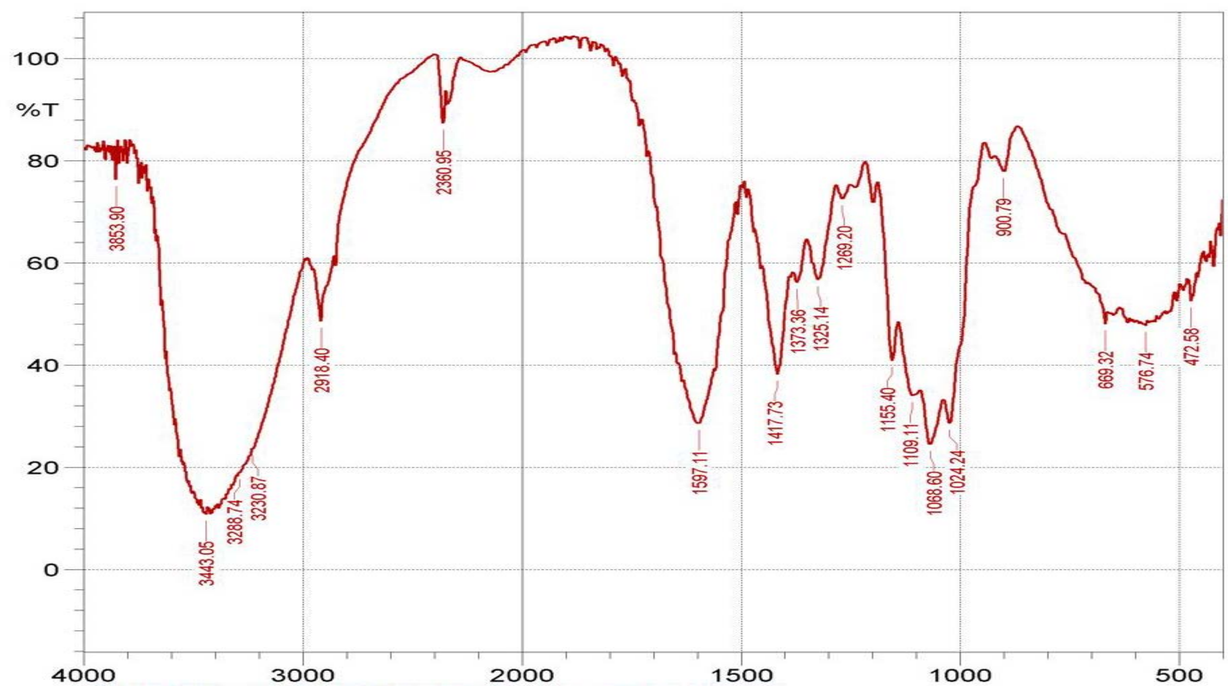

Fig.2: FTIR Spectrum for Orange mesocarp carboxymethyl cellulose (CMC)

Conclusion

This work has confirmed the possibility of extracting cellulose from orange mesocarp for the synthesis of sodiumcarboxymethyl cellulose a versatile raw material in the food and chemical industries. The NaCMC obtained from this work was soluble in water with DS 1.02, fair in appearances and of medium viscosity. The NaCMC resulted from this work could be categorized as technical grade. Optimization of the reaction conditions for the synthesis of NaCMC can be carried out to ascertain the optimum conditions which will give the highest yield, DS value and improved viscosity such that the synthesized CMC can compete with commercial grade CMC for industrial application.

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