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Comparative Study of Carboxymethyl Cellulose Synthesis from Selected Kenyan Biomass

P. K. Kimani[1*], P. G. Kareru[1], S. E. Madivoli[1], P. K. Kairigo[1], E. G. Maina[1] and O. S. Rechab[1,2]

[1]Department of Chemistry, Jomo Kenyatta University of Agriculture and Technology, P.O.Box 62,000-00200, Nairobi, Kenya.
[2]Department of Physical Sciences, University of Kabianga, P.O.Box 2030-20200, Kericho, Kenya.

Authors' contributions

This work was carried out in collaboration between all authors. Authors PKK and PGK designed the study, wrote the protocol and wrote the first draft of the manuscript. Author SEM reviewed the experimental design and all drafts of the manuscript. Authors PKK and EGM managed the analyses of the study. Authors PGK and OSR performed the statistical analysis. All authors read and approved the final manuscript.

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ABSTRACT

Materials that are of low cost, bio-based and biodegradable are the basis within which today's industrial technology is trying to accommodate. Cellulose being a low cost polymer is naturally occurring, bio-based, renewable and biodegradable thus its derivatives are incorporated in today's industrial technology either as transient intermediates or as permanent products. The Isolation of cellulose from *Miscanthus sinensis*, *Eichhornia crassipes* and *Cyperus papyrus* biomasses was done by soda process followed by treatment with acetic acid: hydrogen peroxide mixture. The percentage yield of isolated cellulose from *M. sinensis, E. crassipes* and *C. papyrus* was found to be 30.25± 0.25%, 31.64 ± 1.46% and 29.55 ± 0.64% respectively. Characterization of the obtained microcrystalline cellulose revealed presence of functional groups typical of cellulose whereby a

**Corresponding author: E-mail: paulkimani90.pk@gmail.com;*

peak at 3359.8 cm^{-1} represented –OH stretching vibration. The peak at wave number 1051.1 cm^{-1} characteristic of C-O-C group was also observed. Functionalization of Isolated cellulose to obtain carboxymethyl cellulose was done by alkalization followed by Esterification with sodium monochloroacetic acid (SMCA). This was confirmed by presence of CH_2COO stretching vibration peak between 1598 – 1605 cm^{-1}. The degree of crystallinity for *Miscanthus sinensis* was calculated to be 73.93% while the crystal size was calculated to be 1.31 nM. The degree of crystallinity and crystal sizes were calculated to be 71.42% and 0.059 nm for *E. crassipes* and 46.15% and 0.068 nm for *C. papyrus* respectively. The yield, degree of substitution and swelling capacity of CMC from *M. sinensis*, *E. crassipes* and *C. papyrus* were found to be dependent on the source of cellulose. This demonstrated that *M. sinensis, E. crassipes* and *C. papyrus* are reliable non-conventional sources of cellulose which can be used to synthesize commercial grade CMC products.

Keywords: Cellulose; carboxymethyl cellulose; FT-IR; WXRD.

1. INTRODUCTION

There has been a dramatic increase in cellulose research in the past 10 years, due to significant advances in cellulosic modifications to subsequent products with unique chemical, physical and physiological properties. Cellulose availability from sources other than wood for example agricultural waste products, grasses and also invasive species like the water hyacinth is what has shifted the focus on cellulose and its derivatives [1].

Natural polymers such as cellulose are of renewable nature, hence environmentally friendly and cost effective technologies can be developed by functionalization of these polymers [1]. In this regard, cellulose rich biomass acquires enormous significance as chemical feedstock since it consists of cellulose, hemicelluloses and lignin which contain functional groups suitable for functionalization [2]. Annual plants are considered as potential resources because of their higher yield of cellulose than wood [3,4], Lower lignin contents, lower fibril structures than wood, consumption of less pulping chemicals and energy [5,6] have same main chemical components as woody plants, i.e., cellulose, hemicelluloses, lignin, and extractives, ease of cultivation, harvesting and transportation [3]. Under the consideration of the economical objective, environmental influence, the sufficient supply, and the higher yield of cellulose, annual plants are now substituting wood as alternative sources of cellulosic products [7].

In this investigation *M. sinensis, E. crassipes* and *C. papyrus* were used as alternative sources of production of cellulose and CMC. Microcrystalline cellulose was isolated from *M. sinensis, E. crassipes* and *C. papyrus* and modified to carboxyl methyl cellulose. The effectiveness of bonding carboxymethyl group onto cellulose was estimated by comparing the FT-IR spectra of modified and unmodified cellulose and the recovered weights of the treated samples and control.

2. MATERIALS AND METHODS

2.1 Sample Collection

M. sinensis, E. crassipes and *C. papyrus* were collected from Juja, Kiambu County. After drying the collected samples were milled using a milling machine (locally assembled, no model number) at the mechanical department, J.K.U.A.T, washed several times and dried in an oven at 105℃ to constant mass.

2.2 Isolation of Cellulose

The isolation of cellulose in this research was done according to the method described elsewhere [8]. Dried and ground biomass was mixed with 10% aqueous NaOH solution in a ratio of 1:10. The mixture was stirred for 3 hours at 100℃, followed by filtration of the pre-treated biomass and then washed with 10% ethanol. Hemi cellulose free biomass was then mixed with peracetic acid and the mixture was stirred for 2 hour at 80℃ repeatedly, the residue filtered and washed with distilled water repeatedly and oven dried at 100℃ to constant weight. The resulting alpha cellulose was further treated with 1L, 30% (v/v) hydrogen peroxide at 40℃ repeatedly until the material became milky white. The material obtained was then rinsed with distilled water, filtered and dried in an oven set at 60℃. Cellulose was then converted to microcrystalline cellulose according to a method described elsewhere [8].

2.3 Synthesis of Carboxymethyl Cellulose

CMC was synthesized according to a method described elsewhere [9,10]. The extracted cellulose was converted to CMC in two steps, alkalization and Esterification of cellulose under heterogeneous conditions. In alkalization pre-treatment, 5 g of prepared cellulose were weighed and added to 100 ml of isopropanol. Aqueous Sodium hydroxide (20%) was then added drop wise while stirring for an hour at 30℃. Esterification reaction was accomplished by adding 7.5 g of sodium mono chloroacetic acid (SMCA) and the reaction mixture heated for 2 hours at 50℃. After the first Esterification process, the sample was washed in 90% ethanol, filtered and dried. The Esterification process was carried out again using the same process [10].

2.4 Determination of Bulk and Tapped Density

One grams of the cellulose powder was accurately weighed into a 10 ml graduated cylinder [11]. The cylinder was stoppered and the bulky density recorded. For tapped density, the cylinder was tapped on a hard surface to a constant volume. The final (constant) volume was recorded and the tapped density was calculated. The bulk density, D_{bulk}, and tapped density, D_{tap} were determined using below.

$$D_{tap} = \frac{Mass}{Volume_0}$$

$$D_{bulk} = \frac{Mass}{Volume_1}$$

2.5 Determination of Carr's Index Hausner Ratio

Carr's index and Hausner ratio for cellulose were calculated from the bulk and tapped densities using Equations 5 and 6, respectively [11].

$$\text{Carr}'\text{s index} = \left[\frac{\mathrm{D_{tap}} - \mathrm{D_{Bulk}}}{\mathrm{D_{Tap}}}\right] \mathrm{x}\ 100$$

$$\text{Hausner}'\text{s ratio} = \frac{D_{Tap}}{\mathrm{D_{Bulk}}}$$

2.6 Determination of Degree of Substitution

The degree of substitution (DS) of the synthesized CMC sample were determined by the standard method (ASTM. 2005). The degree of substitution were calculated as follows:

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

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

DS = Degree of substitution
A = Milli-equivalents of consumed acid per gram of specimen
B = Volume of Sodium hydroxide added
C = Concentration in normality of sodium hydroxide used
D = Volume of consumed hydrochloric acid
E = Concentration in normality of hydrochloric acid used
F = Grams of CMC used

2.7 Fourier Transform Infrared Spectroscopic Analysis

The properties of the cellulose extracted and synthesized CMC were characterized by FT-IR using a shimadzu Fourier Transform Infrared Spectrometer, Model FTS-8000. The 13 mm KBr pellets were prepared in a standard device under a pressure of 75 kN-2 for 3 minutes. The spectral resolution was set at 4cm^{-1} and the scanning range was from 400-4000 cm^{-1}.

2.8 Determination of Degree of Crystallinity and Crystal Size

To determine the degree of crystallinity, wide angle XRD measurements were carried out with a Rigaku miniflex II desktop diffractometer. The X-ray generator was equipped with a copper tube operating at 30 kV and 15 mA and irradiating the sample with a monochromatic Cu Kα radiation with a wavelength of 0.1545 nm. XRD spectra were acquired at room temperature over the 2θ range of 3°– 60° at 0.05° intervals with a measurement time of 10° second per minute. The XRD crystallinity index (CI_{XRD}) for native cellulose were calculated using the peak height method from the following height ratio:

$$\mathrm{CI}(\%) = \left[\frac{\mathrm{I_{002}} - \mathrm{I_{am}}}{\mathrm{I_{002}}}\right] \mathrm{x}\ 100$$

Where I_{002} is the intensity of the 002 crystalline peak at 22° and I_{am} the height of the minimum (I_{am}) between the 002 and the 001 peaks, as shown in Fig. 1. The crystalline size D_{002} were determined using the diffraction pattern obtained from the 002 lattice planes of cellulose:

$$D_{002} = \frac{K\lambda}{B_{002}\text{Cos}\theta}$$

where k is the Scherrer constant (0.94), λ is the X-ray wavelength (1.5405 nm), B (0.16) in radians is the full-width at half of the peak of 002 reflection and Cos 23.05 the corresponding Bragg's angle [12].

3. RESULTS AND DISCUSSION

3.1 Percentage Yield of Cellulose

The recovered cellulose was a white powder with a milky color. The % yield of cellulose in *M. sinensis* grass was calculated to be 30.25 ± 0. 25% while that from *E. crassipes* and *C. papyrus* were calculated to be 31.67± 1.46% and 28.91 ± 1.46% respectively. Generally, lignocellulosic biomass consists of 35–50% cellulose, 10–25% lignin, and 20–35% hemicellulose. Proteins, oils, and ash make up the remaining fraction [1,13]. Bulk density and Tap density provide an estimate of the ability of a material to flow and be packed into a confined space. In general, the higher the bulk and tapped densities, the better the potential for a material to flow and to rearrange under compression [11]. This suggests that *C. papyrus* microcrystalline cellulose (CPMC) and *M. sinensis* microcrystalline (MSMC) powders might have better flow properties than the *E. crassipes* microcrystalline cellulose (ECMC) (Table 1).

For Carr's index, values in the ranges of 5-10, 12-16, 18-21, and 23-28 indicate excellent, good, fair, and poor flow properties of the material. A Hausner ratio value of less than 1.20 indicates good flowability, whereas a value of 1.50 or higher suggests that the material will have poor flow properties [11]. In this study the Carr's index and Hausner ratio (Table 1) for the *M. sinensis*, *C. papyrus* MCC and *E. crassipes* indicated that MCC from these sources have poor flow properties.

3.2 Percent Yield of CMC

The CMC yield is a function of the material lost during dialysis step [14]. More degradation and larger amount of low molecular weight material are obtained when more drastic reaction condition (high temperature, NaOH and SMCA concentration) are applied. The degree of substitution, DS, is one of the most important properties of CMC. It not only influences the solubility of the CMC molecule but also affects the solution characteristics [15]. By definition, the DS is the average number of carboxymethyl groups per anhydroglucose unit. Theoretically, the maximum DS is 3. The normal DS range for commercially available CMC is approx. 0.5 - 1.5 [16]. When the DS is below 0.4, the CMC is swellable but insoluble, while above this value, CMC is fully soluble with its hydro affinity increasing with increasing DS value [17]. Since DS value for CMC from *M. sinensis* is 0.35, it is insoluble in water but swellable thus a good material for superabsorbent biopolymers. From the results obtained (Table 2), Esterification of cellulose increased the water uptake of the material hence CMC [14,15] could be used as a superabsorbent polymer.

Table 1. Physical parameters of cellulose isolated from *M. sinensis, E. crassipes* and *C. papyrus*

Property	Cellulose powder samples		
	MSMC	**ECMC**	**CPMC**
Percent recovery (%)	30.25 ± 0. 25	31.67 ± 1.46	28.91 ± 1.27
Bulk density (g/cm^3)	0.26 ± 0.03	0.28 ± 0.05	0.12 ± 0.02
Tapped density (g/cm^3)	0.38 ± 0.02	0.37 ± 0.01	0.28 ± 0.05
Carr's index	31.58	24.32	57.14
Hausner's ratio	1.46	1.32	2.33
Wettability (%)	504.22 ± 61.19	156.6 ± 1.95	141.6 ±1.40

Table 2. Characteristics of CMCs after two consecutive esterification

Parameter	Carboxymethyl cellulose source		
	M. sinensis	***E. crassipes***	***C. papyrus***
Percent Recovery	87.12 ± 0. 25	79.80 ± 1.74	59.98 ± 1.56
Swelling Capacity	488.59 ± 32.36	205.55 ± 29.76	419.66 ± 35.70
Degree of substitution	0.35 ± 0.00	0.80 ± 0.01	0.76 ± 0.01

3.3 Interpretation of the FT-IR Spectrum of Cellulose

Despite minor differences in the FT-IR spectra of microcrystalline cellulose from *M. sinensis*, *E. crassipes* and *C. papyrus* biomass, the spectrum are characteristic of cellulose. The absorption band at 3359.8cm^{-1} were due to the stretching frequency of the –OH group. Peaks at wavenumber 1051.1 cm^{-1} are due to C-O-C group, a C-H stretching vibration at 2904.6 cm$^{-1,}$ [18]. Peaks between 1420.00 cm-1 and 1320.00cm-1 assigned to C-H scissoring and –OH bending vibrations. The bands in the region between 1431.10cm^{-1} can be assigned to C-H in plane deformation of CH_2 groups, while the peak at 1053.10 cm^{-1} can be assigned to the linkage present in cellulose [8,10]. The absorbance at 1377.4, 1326.9, 1261.4, 1053.1 and 916.1 cm^{-1} are typical of pure cellulose [16]. Fig. 2 shows a FT-IR spectrum of carboxymethyl cellulose. A broad absorption band at 3425.3 cm^{-1}, is due to the stretching frequency of the –OH group and a band at 2920 cm^{-1} was attributed to C–H stretching vibration. The presence of an intense absorption band between 1598-1620.1 cm^{-1} and 1420 cm^{-1} (Fig. 2) confirms the presence of CH_2COO group [10,17,18,19]. The CI values obtained from FITR, indicates that the partial hydrolysis of MSMC, ECMC, and CPMC led to the increase in the value (MSMC 74%, ECMC 72% and CPMC 46%). Thus, this observation agrees fairly well with the results from the X-ray diffraction measurements mentioned in the next section.

Table 3. Common FT-IR peaks of microcrystalline cellulose obtained from three Kenyan biomass

Wave number	Functional group
3359.8 cm^{-1}	OH stretch
2904.6 cm^{-1}	C-H scissoring
1420.00	CH plane deformation
1320.00 cm	OH bending vibrations
1051.1 cm^{-1}	C – O - C

3.4 Degree of Crystallinity and Crystal Size

From WXRD diffractogram of microcrystalline cellulose obtained from *M. sinensis*, the diffraction pattern is similar to that of cellulose, which is characterized by two main peaks and a broad amorphous background band. The lower angle peak is the result of merging the diffraction peaks at 2θ = 15° and 16.5° into a broader one, as also reported in other literature [20], where it is assigned to the [1] crystalline plane. The peak observed at 2θ = 22.4° is assigned to the [2] crystalline plane and is used for the calculation of the crystallinity index CI_{XRD} [21,22]. Compared to all X-ray diffraction approaches, peak height method gives the highest X-ray crystallinity values [12]. From the WXRD diffractogram obtained Fig. 3, the inter-planar distance (d) for [2] indices was found to be 3.9078 for microcrystalline cellulose derived from *M. sinensis* respectively. The degree of crystallinity of MCC synthesized from *M. sinens is*

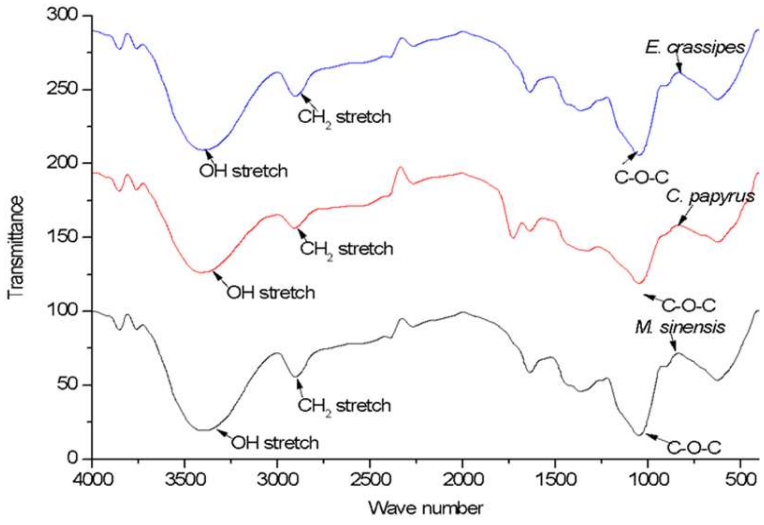

Fig. 1. FT-IR spectrum of microcrystalline cellulose obtained from *M. sinensis*, *C. papyrus* and *E. crassipes* biomass

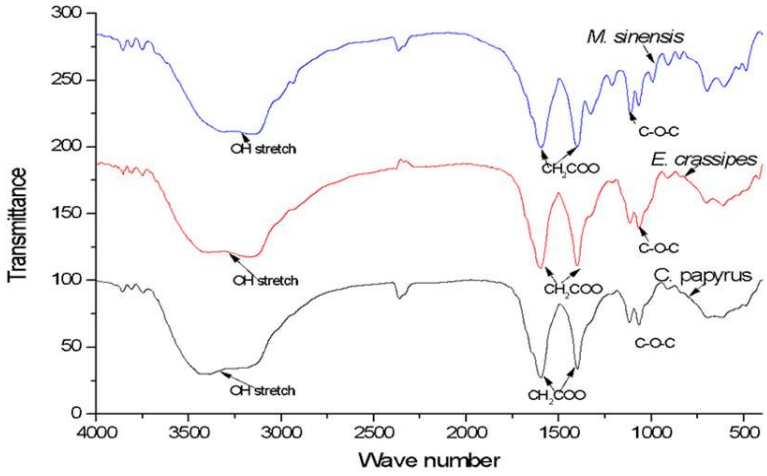

Fig. 2. FT-IR spectrum of carboxymethyl cellulose synthesized from *M. sinensis*, *E. crassipes* and *C. papyrus* biomass

was found to be 73.93%. Using the Scherrer equation, Scherrer constant (0.94), X-ray radiation wavelength of 1.5405 nm, the full-width at half of the peak of 002 B = 1.2, the crystal size was calculated to be 1.3114 nm [21]. The degree of crystallinity and crystal sizes were calculated to be 71.42% and 0.059 nm for *E. crassipes* and 46.15% and 0.068 nm for *C. papyrus* respectively and are reported elsewhere [22,23,24].

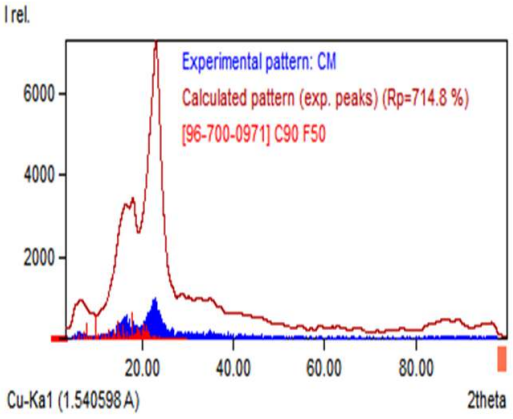

Fig. 3. WXRD diffractogram of microcrystalline cellulose obtained from *M. sinensis* biomass after sulfuric acid treatment

4. CONCLUSIONS

Microcrystalline cellulose and carboxyl methyl cellulose with different degrees of substitution and degree of crystallinity can be synthesised from *M. sinensis*, *E. crassipes* and *C. papyrus* biomass by varying reaction parameters. Furthermore, powder flowability was dependent on the biomass used. Overall, the better flow properties of the microcrystalline celluloses are dependent on source, variations in particle shape, size, and surface area of the powders which are directly related to the process of partial hydrolysis of the original cellulose. The conditions for carboxymethylation cellulose from *M. sinensis* were: pure isopropyl alcohol as the solvent medium, reaction period of 120 min, 6.0 g of sodium mono chloroacetic acid, NaOH concentration of 10 mL of 17.5% and reaction temperature of 50℃.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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