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OPTIMIZED CARBOXYMETHYL CELLULOSE PREPARATION FROM COCOA POD HUSKS BY SURFACE RESPONSE METHODOLOGY

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Abstract
This study investigates the synthesis of carboxymethylcellulose (CMC) from cocoa pod husk (CPH) using optimized Williamson etherification process. Response surface methodology (RSM) was used to model the independent variables such as reaction time, concentration of NaOH and amount of monochloroacetic acid (MCA) versus the degree of substitution (DS). The optimum results of independent factors were 20% NaOH, and 3.5 g monochloroacetic acid (MCA) with reaction time of 120 min while DS at that condition was 1.096 at a significant level of $P<0.0001$ and F-value of 15.78. The FTIR spectra revealed the functional group modification of native cellulose to CMC, This is verified from the spectrum transmitting 1409.49 cm^{-1} and 1640.05 cm^{-1} indicating ether and carboxyl functional group consecutively. The results of XRD analysis showed that crystallinity of cellulose had decreased in CMC while SEM/EDS showed the elongated long fibres in cellulose while the fibrils in CMC is short and rough. The optimum percentage yield obtained shows that cocoa pods can be a good alternative for the production of large scale CMC.
Keywords: Cocoa pod husk, carboxymethyl cellulose, cellulose, Response Surface Methodology, degree of substitution, characterization.

1.0 Introduction

It is estimated that about 998 million tonnes of agricultural waste generated around the world yearly are raising huge environmental concern as only negligible amount are being used either as raw materials or as a feedstock for the production of energy [30]. For instance production of *Theobroma cacao*, give about fourty-five percentage of the fruits which are useful commercially while fifty-five percentage are released as a waste products thereby causing environmental pollutions [1]. Hence, the economic sustainability of *T. cacao* production depends on how its wastes can be optimally converted to useful products such as carboxymethyl cellulose (CMC). Plant materials such as agricultural waste are generally a good source of cellulose [6], and this informed the use of Cocoa pod husks for this research work.

Cellulose is a carbohydrate made up of a linear chain of many hundreds to several thousands of $\beta\ (1 \rightarrow 4)$ glycosidic bonds of combined units of glucose [25] [17]. Cellulose is insoluble in either polar or non-polar solvents due to the bonding of hydrogen to the nearby oxygen. However, the morphological significance of these limitations has diminished its applicability and overall relevance [12]. Thus, in order to improve on its applicability and broaden its relevance, the functional group of the cellulose is modified to other derivatives that are more soluble through chemical derivatization reactions [26]. Modification of cellulose to CMC is an example of such derivatizations.

CMC is one of the foremost vital polysaccharide esthers with wide industrial applications in food, textile industries and oil drilling. Apart from industrial applications, CMC is very useful in advanced fields notably in the preparation of membrane for environmental monitoring in

biosensor, tissue engineering and heavy metals removal or adsorptions [16] [31]. The production of CMC globally (approximately ≥360,000 metric tonnes a year) is carried out in a bi-steps based catalysed reaction. It involves reaction between cellulose and etherifying agents using alcohol as a solvent [7] [15]. The cellulose in the starting reaction chain will form carboxymethyl cellulose ethers when introduced to a medium of NaOH-alcohol in excess of alcohol followed by the addition of MCA or its salt. The OH-groups in cellulose is thereafter substituted for carboxymethyl groups on the carbon chain 2, 6 and 3.

Studies have shown that CMC can be prepared from completely different origins like pseudo stem of Cavendish banana [2], waste of Sago [20], Palm Kernel cake [4], Cotton Ginning Industry [11], pulp of Sugar beet [29], Sugarcane straw [5], waste paper [15] and Corn stalk [27]. However, there is no available published work where CMC is produced optimally from CPH using response surface methodology as a model whilst also comparing the results obtained with the studies carried out without the RSM. Therefore, the objectives of this present work were prepare CMC through isolation of cellulose from CPH, optimize the reaction conditions using RSM, compare the results obtained from RSM with studies done without the RSM and then carry out the characterization studies of the CPH cellulose and CMC using FTIR, XRD and SEM . Further objective of this research work is development of effective correlations among the concentration of NaOH, amount of MCA and time of reaction with a DS using RSM in connection with central composite design.

2.0. EXPERIMENTAL PROCEDURE

2.1. Materials

The CPH was obtained from Cocoa plantation in Tekule Oga village, Ijebu-North Local Government of Ogun State, Nigeria. Monochloroacetic acid, Isopropyl alcohol, sodium hydroxide, acetic acid, methanol and ethanol were obtained from Sigma- Aldrich, UK

2.2. Sample pretreatment

The CPH was thoroughly washed with distilled water to get rid of adhering dirt. It was sun-dried for 10-12 days and later oven-dried at 60°C for two consecutive days. The dried husks 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.

2.3. Isolation of cellulose from the Agricultural waste (CPH)

300 g of pulverized CPH was weighed, dissolved in deionized water for 24 h to remove water-soluble organic compounds. It was thereafter, cooked with 1000 mL of 15% sodium hydroxide (NaOH) for 2 h with continuous stirring at a constant temperature of 90-100 ºC until a dark slur was obtained. The slur was filtered, washed using a large quantity of deionized water until the sample was free from NaOH. The cellulose obtained was further de-lignified to remove the remaining unremoved lignin from the extract by refluxing the cellulose with 20% HNO_3 in C_2H_5OH, then filtered and later washed using deionized water. The cellulose obtained was bleached using sodium chlorate (3% $NaClO_3$) in alkaline medium (pH 11) at room temperature to increase the brightness and additionally to provide pulp with lower attainable lignin whilst maintaning the yield and strength of the pulp. Thereafter, the pH of the cellulose was modified to 4.5 with acetic acid. The bleached sample was later washed with distilled water, filtered and oven-dried at 60 ºC for 24 h [8].

2.4. Percentage yield (a)

The percentage yield (%Y) of cellulose was determined using the equation (1):

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

Where:

A = mass of cellulose (g);
B = mass of CPH (g).

2.5. Preparation of CMC from cocoa pod husk (CPH) cellulose

The CMC was prepared from CPH cellulose via three stages namely; alkalization, etherification and neutralization of cellulose. In the alkalization stage, 5 g of CPH cellulose was weighed into a beaker containing 75mL of isopropanol and the solution was constantly agitated at room temperature. Thereafter, 40 mL of (5 - 30% w/v) sodium hydroxide was added in

drops and stirred with magnetic stirrer for 2 hours at 25^{o}C [8].

In the second stage which is the etherification stage, the alkali cellulose reacted with monochloroacetic acid (MCA) to produce carboxymethyl cellulose using Williamson etherification process [28]. The carboxymethylation began when the various amount of (1 - 6) g of MCA was added to the alkali cellulose and thereafter agitated for another 2 h. The procedure was repeated at different time scale measured in the range of 60-180 minutes and thereafter filtered and the residue obtained was soaked in methanol for 24 hour, filtered and neutralized with dilute acetic acid, then filtered again, and the residue was oven-dried at 60^{o}C for 24 hours to arrive finally at the CMC. The summary of the equations for the reaction that resulted in CMC are as follows:

$$CEL{-}OH + NaOH \longrightarrow CEL{-}ONa + H_2O \quad (2)$$

$$CEL{-}ONa + ClCH_2COOH \longrightarrow CEL{-}OCH_2COOH + NaCl \quad (3)$$

$$NaOH + ClCH_2COOH \longrightarrow HOCH_2COOH + NaCl \quad (4)$$

Where; CEL-OH is cellulose, $ClCH_2COOH$ is MCA and $HOCH_2COOH$ is glycolic acid

Equation (2) stands for the cellulose activation reaction occurring in aqueous NaOH in presence of isopropanol whilst equation (3) represents the reaction of alkali cellulose with MCA to give CMC and equation (4) indicates the formation of glycolic acid and NaCl as a side reaction where MCA hydrolysis occurred.

2.7. Characterization of CPH cellulose and CMC

2.7.1. Determination of degree of substitution (DS)

The DS of a polymer is the mean number of substituent or attachment that may have taken part in a reaction. 2 g of CMC and 50 mL of 95% absolute ethanol was stirred in beaker for 7 minutes and 5 mL 2 M HNO_3 was added and the mixture was boiled for 5 minutes and stirred for another 10 minutes. The resulting mixture was filtered using Whatmann no1 filter paper whilst the residue was washed severally with absolute ethanol until the nitric acid was completely removed. Thereafter, the precipitate obtained was rinsed using methanol, and slowly heated until all the ethanol was completely removed. The precipitate was later allowed to cool in a desiccator. 1 g of dry CMC was dispersed in 100 mL deionized water and, 25 mL 0.5 M sodium hydroxide was added and stirred. The mixture was heated for 16-20 minutes and was allowed to cool and later titrated against 0.5 M hydrochloric acid using phenolphthalein indicator until the colour changed from dark pink to colourless which signifies the end point of the titration [14].

The CMC yield (%Y) was obtained using the equation (5):

$$\%\,Y = \frac{C}{D} \times 100 \quad (5)$$

Where:

C = mass of CMC obtained (g);

D = mass of CPH cellulose (g).

The DS was then calculated using equation Eq. (6) and (7) respectively

$$Z = \frac{GH - TI}{P} \quad (6)$$

$$DS = \frac{0.162\ X\ Z}{1-(0.058\ X\ Z)} \quad (7)$$

where; Z is milli equivalents of acid absorbed for each mass of the sample, G is the volume of NaOH, H is concentration of NaOH added measured in molar concentration, T is volume of consumed HCl measured in mL, I is concentration of HCl used measured in molar concentration, P is sample in grams used, 162 is the molecular mass of anhydrous glucose unit while 58 is the anhydrous glucose unit per each carboxymethyl group substituted [14].

2.7.2. FT-IR Spectroscopy

The Spectra of native cellulose and CMC were determined to know the functional group present using Automated Bruka Alpha Fourier Transform Infrared Spectrophotometer in the transmission range of 4000-400 cm^{-1}

wavelength. Samples were dried (50^{o}C) in the oven for 1 hour for moisture removal and thereafter small quantities (0.2 mg) was taken for analysis.

2.7.3. Scanning electron microscope (SEM)/Energy Dispersive X-ray Spectrometry (EDS)

Morphological features and elemental compositions of isolated cellulose and CMC were determined using TESCAN S8000 combined with EDS. The dry powdered samples were coated using Au and images taken at 10 kV mapping. The dimension of the samples were taken between the range of 200 μm and 30 μm at different magnifications.

2.7.4. X-ray diffraction (XRD)

Degree of crystallinity of the isolated cellulose and CMC were determined using X-ray Diffractometer, Philip – PW 1011 model. The X-Ray patterns were evaluated by using CuKα as a radiation source and at a λ lambda of 1.54050, 40 kV and 40 mA. The output was reported at 2θ in the range of 10 to 60^{o}.

2.8. Experimental design/statistical analysis

Experimental design, product optimization, adequacy of model and correlation of variables were carried out using Design-Expert (version 11, State-Ease Minneapolis, MN, USA). A 3-level and 3-factor central composite design was carried out comprising of one independent (DS) and three independent variables (NaOH, MCA and time of reaction). while Origin version 18 was used for FTIR and XRD plotting of spectra.

3.0. Results and discussion

3.1. Isolation of Cellulose from CPH and modification to CMC

The cellulose was successfully isolated from the sample using concentrated sodium hydroxide. The cellulose was further converted to CMC through etherifying chemical agent. The summary of the equations for the reaction that resulted in CMC are as follows:

3.2. Yields

The yield of CPH cellulose from the CPH sample in the alkalization stage was 48.5% according to equation (1). **Table 1**.showed the percentage yield of CMC synthesized at various conditions. In the case of MCA, the percentage yield increased when 1 to 4 g of MCA is used, and then reduced at an amount beyond the 4g. 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 [23].

The effect of sodium hydroxide concentration was studied by varying the concentration of the sodium hydroxide solution from 5 % to 30 % (**Fig. 3**). It was observed that the DS of CMC increased with sodium hydroxide concentration and attained a maximum DS of 0.6047 at an alkali concentration of 100 mL of 25 % (w/v). The increase in the DS of CMC improved the ability of CMC to immobilize water in a system. At particular alkali concentration, the DS was maximum after which it started declining. Beyond 25 % of NaOH concentration, the DS decreased, probably due to the degradation of cellulose structure and glycolate formation leading to inactivation of monochloroacetate and its utilization by this side reaction. Similar observation has reported in literature [20]. Besides, a similar result was also observed in CMC from the sugar beet pulp [29] and sago waste [20].

3.4. Adequacy of the model

The adequacy of the model was confirmed to know if the model would give incorrect or deceptive results. **Fig. 1a** shows the normal percentage (%) probability plots where the respone of residuals was closely distributed to each other on a straight line without any deviation in variance. Also, **Fig. 1b** shows the residuals plotted against predicted responses and hence, a residual analysis where the good fit of the model was determined by plotting the internally studentized residuals versus

experimental runs (**Fig. 1c**). The results revealed that data points were within the limits. Similarly, **Fig. 1d** shows the predicted values versus the actual values, this implies that predicted and actual values obtained were in close agreements due to the presences of all the points on a straight line and hence the model used for this study successfully captured the correlations between the response of the variables
.

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

Carboxymethylation conditions		Carboxymethylated cellulose					
1	Sample no	A	B	C	D	E	F
	NaOH (%)	10	15	20	25	30	-
	Yield (%)	117	119	127	151	137	-
2	Sample no	G	H	I	J	K	L
	MCA (g)	1	2	3	4	5	6
	Yield (%)	99	107	120	139	137	117
3	Sample no	M	N	O	P	Q	R
	Time (min)	60	80	100	120	140	160
	Yield (%)	99	101	109	117	120	132

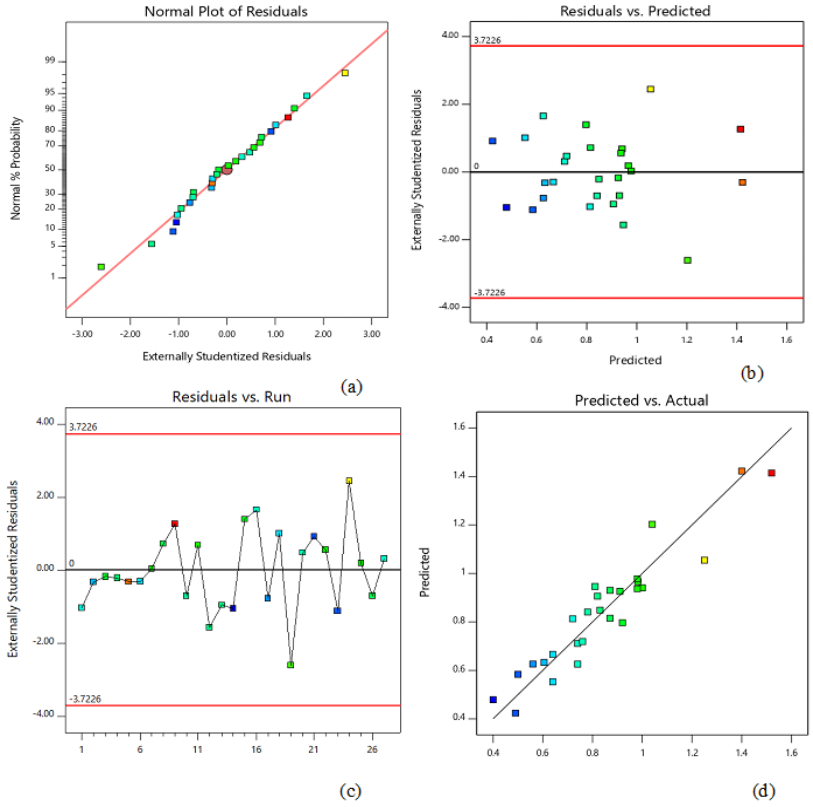

Fig. 1. Model adequacy for residual diagnostic plots for DS: (a) normal probability (b) residuals versus predicted (c) residuals versus run order (d) predicted versus actual.

3.3. Statistical analysis of the model

In the present study. The equation for the correlation of DS is given as:

$$DS = \dot{\omega}_o + \dot{\omega}_1 A + \dot{\omega}_2 B + \dot{\omega}_3 C + \dot{\omega}_{12} AB + \dot{\omega}_{13} AC + \dot{\omega}_{14} BC + \dot{\omega}_{11} A^2 + \dot{\omega}_{22} B^2 + \dot{\omega}_{33} C^2 \quad (8)$$

Where:

$\dot{\omega}_o$ = formula constant;

$\dot{\omega}_1$ to $\dot{\omega}_3$ = linear coefficients;

$\dot{\omega}_{12}$ to $\dot{\omega}_{14}$ = cross product coefficients and

$\dot{\omega}_{11}$ to $\dot{\omega}_{33}$ = quadratic coefficients.

The variables of A–C in equation (8) were concentration of NaOH, quantity of MCA and the rate of carboxymethylation respectively whilst the overall number of analysis was 27 runs at 6 center points.

Table 2. The total experiments with their result.

	Factor A	Factor B	Factor C	Response D
Run	A: NaOH %	B: MCA G	C: Time Min	The degree of Substitution (DS)
1	10	3	120	0.72
2	20	1	60	0.6047
3	20	6	120	0.91
4	10	3	180	0.83
5	10	6	60	1.4
6	30	1	120	0.64
7	20	1	180	0.98
8	10	1	180	0.87
9	20	6	60	1.52
10	30	3	180	0.78
11	30	3	60	1
12	20	3	180	0.81
13	20	3	120	0.82
14	10	1	60	0.4
15	30	3	120	0.92
16	10	6	180	0.74
17	20	6	180	0.56
18	10	1	120	0.64
19	30	6	60	1.04
20	30	6	120	0.76
21	30	6	180	0.49
22	30	1	180	0.98
23	30	1	60	0.5
24	20	3	60	1.25
25	10	3	60	0.982
26	10	6	120	0.87
27	20	1	120	0.74

The results of the experiments for DS are given in **Table 2** indicating the relationship between the DS and the alphabet independent coded variables in equation (8) as shown below:

$DS = +0.9322 + 0.0244A + 0.1075B + 0.1109C + 0.0811AB + 0.0043AC + 0.2832BC - 0.1015A^2 - 0.1138B^2 + 0.0943C^2$. (9)

Table 3 shows the ANOVA results of the experiment. The results revealed that the model applied in this present work is significant since P-value is less than 0.0001 ($P<0.0001$). Thus this is an indication that the formula for DS in equation (9) and the model terms are significant. The variables B, C, AB, BC, A^2, B^2, and C^2 are significant while A and AC are not significant because their P-values greater than 0.1000. The predicted R^2 is in reasonable agreement with the adjusted R^2 as a result of the distinction between the two r-squares (0.1305) which was below 0.2. "Adequate Precision" in Table 3 connotes the signal to noise ratio where a ratio greater than 4 is considered as good. In this present study, the ratio of 15.5503 obtained implies an adequate signal and thus, the model can be used to navigate the experiment.

Table 3. The responses of analysis of variance (ANOVA) for quadratic model.

s/n	Source	Sum of squares	df	Mean square	F-value	p-value	
1	Model	1.58	9	0.176	15.78	< 0.0001	significant
2	A-NaOH	0.0107	1	0.0107	0.9556	0.342	
3	B-MCA	0.2081	1	0.2081	18.66	0.0005	
4	C-Time	0.22	1	0.22	19.73	0.0004	
5	AB	0.08	1	0.08	7.18	0.0159	
6	AC	0.0002	1	0.0002	0.0202	0.8886	
7	BC	0.9751	1	0.9751	87.46	< 0.0001	
8	A^2	0.0618	1	0.0618	5.55	0.0308	
9	B^2	0.0707	1	0.0707	6.34	0.0221	
10	C^2	0.0533	1	0.0533	4.78	0.043	
11	Residual	0.1895	17	0.0111			
12	Cor Total	1.77	26				
13	R^2	0.8931					
14	Adjacent R^2	0.8365					
15	Predicted R^2	0.7060					
16	Adequate precision	15.5503					

3.2. Sensitivity

Since the correctness and reliability of equation (9) in predicting the variables have been significantly proven, therefore, equation (9) can be employed to investigate the effects NaOH concentration, MCA and rate of carboxymethylation on DS.

3.2.1. Effect of sodium hydroxide concentration and quantity of MCA against the DS

The effect of concentration of NaOH and quantity of MCA against the DS are shown in **Fig. 2(a)**. At a constant reaction time of 60 min, the DS of CMC increased when the NaOH concentration was gradually increased from low values of 10% to 20% and also when the quantity of MCA was increased. Furthermore, the DS started to decline when the time of carboxylation was increased. The net effect is that reduced time of carboxymethylation favours high DS in the presence of optimum sodium hydroxide concentration and high MCA whilst increased time of carboxymethylation will lead

to degradation of polymer and hence, lower DS. This is probably due to the reacting medium becoming more acidic (equation 4) and thus not favouring the production of CMC but that of glycolic and NaCl. Similar observations have also been reported by Pushpamalar [20].

3.2.2. Effect of reaction time and sodium hydroxide concentration against DS

Fig. 2b shows the effect of NaOH concentration and the period of carboxymethylation cellulose to CMC. When the amount of MCA is increased (≥6g), the DS is rapidly high as the concentration of NaOH is increased gradually from 10 to 25% at a very low reaction time of 60 to 70 min. However, the DS starts to decline at a reaction time above 80 min. Thus, as the time was raised coupled with a high amount of MCA, polymer degradation occurred at 120 min.

Design Expert software was used to evaluate the optimum values of independent variables to aid DS optimization. Optimum results for all the experimental conditions according to RSM are as follows: DS of 1.095 for DS at sodium hydroxide concentration of 20%, quantity of MCA of 3.5 g and time of carboxymethylation reaction of 120 min. The software results generated were confirmed by performing the experiments at the optimum conditions. There was no significant difference at 95% confidence interval between the experimental and software results. Furthermore, determination of optimum results for all the varied conditions was also done without the use of software (design experts) and the results (**Fig. 3**) obtained are in agreement with the software. However, since the solubility of CMC is a function of DS, hence most DS obtained in this present work were high and therefore the CMC prepared was soluble.

3.2. Determination of optimum conditions

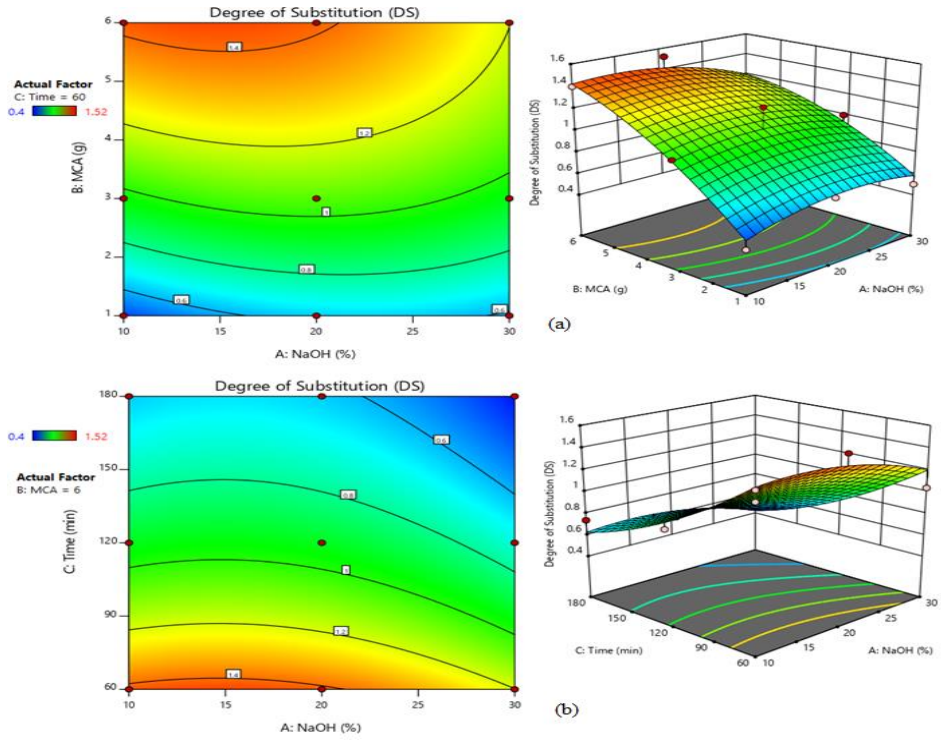

Fig. 2. Contour and 3D surface plot showing the effects of concentration of sodium hydroxide and the quantity of MCA against the DS (modelled variables): (a) effect of sodium hydroxide concentration and time of carboxymethylation against the DS (b)

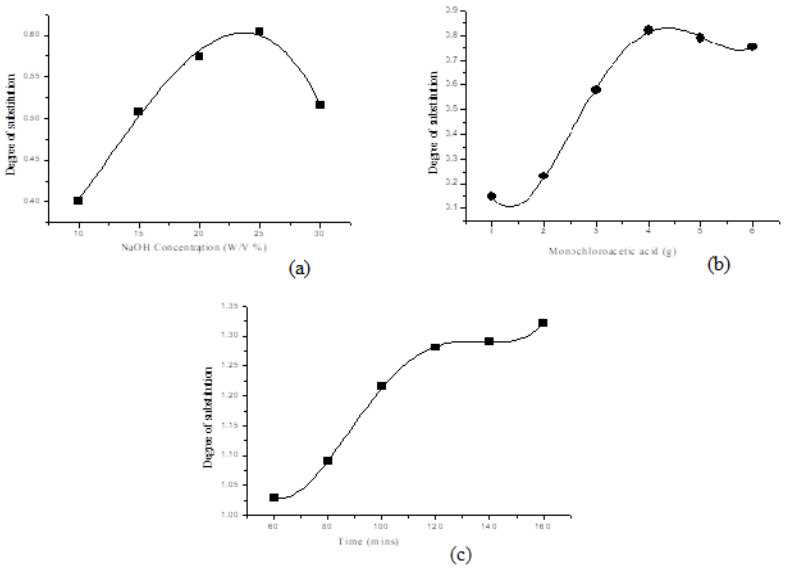

Fig. 3. Determination of optimum DS without using design experts for modeling;(a) 0.60 DS for 25% NaOH concentrations; 0.80 DS for 4.00 g MCA and 1.30 DS for 120 min time of reactions

3.3. Characterization of isolated cellulose and CMC

3.3.1. Functional group analysis

Functional group analysis of CPH sample, cellulose isolated from CPH and CMC was determined to verify the modification and conversion of cellulose CPH into CMC. **Fig. 4** shows the absorption peak of cellulose isolated with the appearance of a broad absorption band at 3333.56 cm^{-1} reflecting -OH group while the band at 2896.29 cm^{-1} is due to alkane (-C-H) stretching vibration. The spectrum of CMC shows the presence of a broad absorption band at 3353.56cm^{-1} which indicates the presence of –OH group. The absorption peak at 2904.95cm^{-1} reflects alkane-stretching while the strong sharp absorption peak at 1640.05cm^{-1} verifies the presence of ether (-COO) group which confirmed the modifications of functional group of cellulose to CMC. Other importants peaks are 1409.49 and 1324.35 cm^{-1} which are due to CH_2 scissoring and hydroxyl group bending vibrations respectively [13]. The wavelength 894 cm^{-1} was due to 1, 4 – β glycosidic bond in cellulose structure.

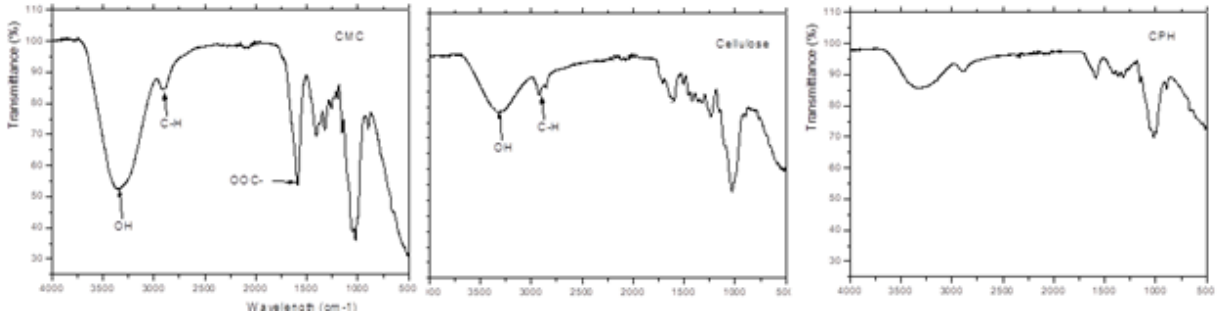

Fig. 4. FTIR of CPH, the isolated cellulose, and the optimized CMC.

3.3.2. SEM

Morphological analysis of cellulose and CMC was carried out to know the sample's surface characteristics such as size, shape, and roughness. The SEM micrographs of isolated cellulose and CMC are shown in **Fig. 5**. In the micrograph plate of the cellulose, the fiber is fluffy, elongated, with lustrous and curly fibers. These elongated fibers possess a very smooth

surface without any defects at the surface of the cellulose [3]. It also shows that the arrangement of the fibres at the surface is not affected by treating the sample with high concentration of sodium hydroxide. However, a notable decrease in the cotton fibers size is observed upon the addition of NaOH during carboxyl methylation stage, the period during which the –OH group of CPH cellulose is being modified to CMC [3]. This is because during alkalization of cellulose, the inter- and intra-molecular hydrogen bond of CPH cellulose destroys the hydroxyl group of cellubiose units resulting to cellulose swelling similar to the appearance of cotton. Another method used for the confirmation of prepared CMC from CPH cellulose is Energy dispersive spectrometry (EDS) which was used to detect the percentage elemental composition in the sample. EDS results showed the elements present in CPH cellulose and the prepared CMC. Carbon and oxygen were found to be almost similar in values. Succinctly put, CMC was successfully prepared from CPH cellulose using NaOH, MCA, and isopropanol as a solvent.

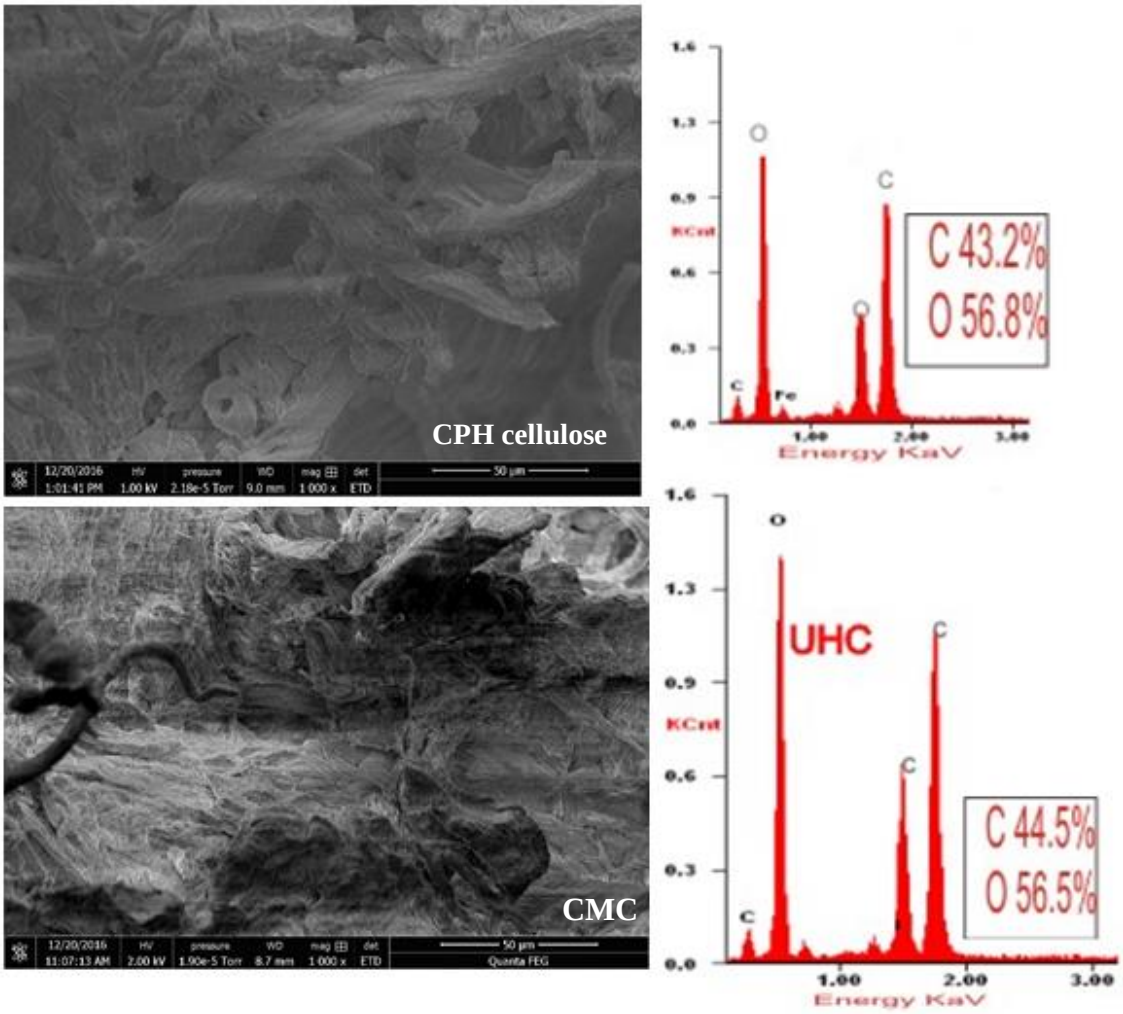

Fig. 5: SEM micrographs (magnification of 1000) and EDS of CPH cellulose and CMC

3.3.3. Analysis by XRD technique

The diffractogram of XRD reveals the degree of crystallinity between the CPH cellulose and carboxymethylated cellulose which is a measure or confirmation of CPH cellulose modification to CMC. The diffraction patterns of X-ray in cellulose obtained from CPH and CMC are shown in **Fig. 6.** The picture (Fig. 6) shows four diffraction peaks at 17º, 24º and 34.8º respectively which is a characteristic cellulose structure of crystal I. Furthermore, the CPH cellulose crystals exhibit characteristic assignments of 101, 002, and 040 diffraction planes which are also characteristic nature of cellulose I [19]. A shoulder peak in the region 2θ=17 º and a weak peak in the region 2θ=34.8º are indications of complete removal of lignin, pectin and hemicelluloses from CPH raw sample [9].

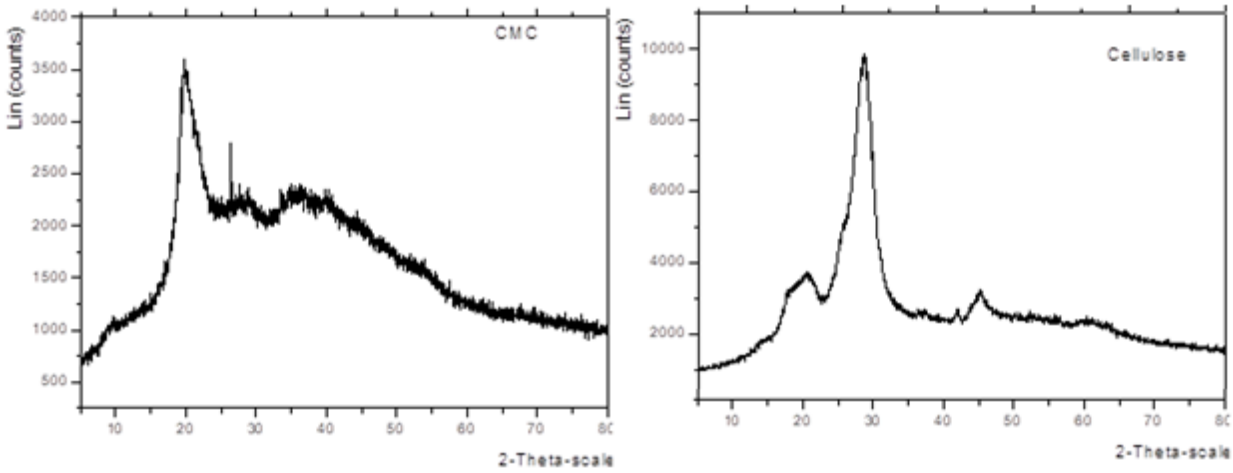

Fig. 6: XRD spectra of optimized CMC and the isolated CPG cellulose

However**,** the absence or weak diffraction in the region 2θ=17°, complete disappearance of 2θ=34.8º sharp peak and the replacement of wide broad spectrum peak are indications of complete modification of CPH cellulose to CMC and hence characteristic diffraction pattern of crystalline peaks of CMC II. The XRD peak height method developed by Segal and coworkers [22] was used to determine the crystallinity index (C.I.) which was calculated according to Eq. 10 as 67.9% for CPH cellulose while CMC was 28. 6% respectively. According to C.I, The CMC displayed a low degree of crystallinity when compared to CPH cellulose due to the cleavage of weak hydrogen bonds in the crystalline part of cellulose when treated with NaOH. Hence, this is an evidence that there was a conversion of cellulose I to cellulose II in CMC produced. Furthermore, the cellulose XRD pattern had high intensity than CMC in the present work and thus similar to those reported in the literature (Golbaghi et al., 2017

$$(\mathrm{C.I.}) = \frac{(I_{002} - I_{am})}{I_{002}} \times 100 \qquad (10)$$

C.L = Crystallinity Index

Where, I_{002} is the height of maximum (I_{002}) peak (2θ=24º) and I_{am} is the minimum peak height between the plane 002 and the 101 peaks (2θ=17º).

4. Conclusion

This present work showed the investigation of the preparation of carboxymethylated cellulose from cellulose isolated from CPH. Furthermore, design expert software (version 11, 2018) was used to evaluate the optimum conditions. It was possible to isolate cellulose from CPH by using alkaline and acid treatments to remove soluble non-cellulosic materials e.g. lignin, pectin, and hemicelluloses respectively. Carboxymethylated cellulose could be successfully prepared from isolated cellulose from CPH in the presence of NaOH, MCA and time of reaction using

Isopropanol as a solvent. The results revealed that the concentration of sodium hydroxide, amount of MCA and time of reaction had profound influence on DS. Considering the DS results plotted against the varied conditions, it was deduced that the highest DS of 1.092 could be achieved at 20% NaOH concentration, 3.5 g of MCA and 120 min reaction time of carboxymethylation and that there was no significance difference between the results obtained without the model and design expert. The apperance of a strong absorption in the region of 1427.28 cm^{-1} in cellulose to 1641.05 cm^{-1} in CMC confirmed the presence of –COO group which is evidence of carboxymethylation. XRD analysis results revealed cellulose isolated to belong to cellulose I and the CMC prepared to II. Apart from this, C.I index revealed high crystallinity of the cellulose and that there was reduction of C.I in CMC. Both SEM and EDS confirmed the change in chemical and surface configuration of cellulose to CMC. Lastly, the results showed that CPH can be a potential source of cellulose and CMC due to its percentage yield.

References

[1]. E. O Adeleke, B. O. Omafuvbe, I. O Adewale, and M. K. Bakare (2012). Purification and characterization of a cellulase obtained from cocoa (*Theobroma cacao*) pod-degrading *Bacillus coagulans Co4. Turkish Journal of Biochemistry* **37** (2), 222–230.

[2]. M. P Adinugraha, D. W Marseno, and G. Haryadi, (2005). Synthesis and characterization ofsodium carboxymethyl cellulose from Cavendish banana pseudo stem (*Musa cavendishii LAMBERT*). *Carbohydrate Polymers.* **62**(1), 164-169.

[3]. M. Aydin, H. Tozlu, S. Kemaloglu, A. Aytac and G. Ozloc (2011). Effects of alkali treatment on the properties of short flax fiber-poly (lactic acid) eco-composites. *Journal of Polymers and the Environment.* **19**(1), 11-17.

[4]. A. Bono, P. H. Ying, F. Y. Yan, C. L. Muei, R. Sarbatly, and D. Krishnaiah (2009). Synthesis and characterization of carboxymethyl cellulose from palm kernel cake. *Advances in Natural and Applied Sciences*, **3** (1), 5-11.

[5]. R.G. Candido, and A. R. Gonçalves (2016). Synthesis of cellulose acetate and carboxymethylcellulose from sugarcane straw. *Carbohydrate Polymers* **152**(5) 679-686.

[6]. K. Chandra, and M. P Adinugraha (2002). Synthesis of Cellulose Pulp from Banana Pseudo Stem with Soda and Neutral Sulfite Processes. Unpublished Research. Faculty of Engineering, *Department of Chemical Engineering, Widya Mandala Surabaya Catholic University, Indonesia (Indonesian).*

[7]. S. Dapía, V. Santos, and J. C. Parajó (2003). Carboxymethylcellulose from totally chlorine free-bleached milox pulps. *Bioresouresource Technology*, **89**, 289–296

[8]. G. R. Filho, M. N. D. A. Rosana, J. G. Vieira, C. D. S. Meireles, A. C. Daniel, D. S. B. Hernane, S. J. L. Ribeiro, and Y. Messaddeq (2007). Characterization of methylcellulose produced from sugarcane bagasse cellulose. Crystallinity and thermal properties. *Polymer Degradation Stability*, **92**, 205-210.

[9]. F. Guozhi, W. Min, L. Chongjing, F. Tao, L. Jianfen, and Z. Ronghui, (2013). Isolation of cellulose from rice straw and its conversion into cellulose acetate catalyzed by phosphotungstic acid. *Carbohydrate Polymers*, **94**, 71–76.

[10]. L. Golbaghi, M. Khamforoush, and T. Hatami (2017). Carboxymethyl cellulose production from sugarcane bagasse with steam explosion pulping: Experimental, modeling, and optimization. *Carbohydrate Polymers*, **174**,780-788.

[11]. N. Haleema, M. Arshada, M. Shahidb, and M. A. Tahir (2014). Synthesis of carboxymethyl cellulose from the waste of cotton ginning industry. *Carbohydrate Polymers*, **113**, 249–255.

[12]. K. Hattori, E. Abe, T. Yoshida, and J. A. Cuculo (2004). New solvents for cellulose II ethylenediamine/thiocyanate salt system. *Polymer Journal*, **36**(2), 123-130.

[13]. I. Hossain, S. Mostofa, U. Muslima, F. Akter, S. A. Tania, A. Saha, S. Debnath, T. Muslim and M. A. Rahman (2015). Isolation of

Cellulosic Material from Agro-wastes and their Derivatization. *Dhaka University Journal of Science*, **63**(1), 43-46.
[14]. M. Jiang, M. M. Zhao, Z. W. Zhou, T. Huang, X. L. Chen, and Y. Wang (2011). Isolation of cellulose with ionic liquid from steam exploded rice straw. *Industrial Crops and Products 3***3**(3), 734–738.
[15]. G. Joshi, S. Naithani, V. Varshney, S. S. Bisht, V. Rana, and P. Gupta, (2015). Synthesis and characterization of carboxymethyl cellulose from office waste paper: A greener approach towards waste management. *Waste Management*, **38**, 33–40.
[16]. F. Khan, and S. R. Ahmad (2013). Polysaccharides and their derivatives for versatile tissue engineering application. Macromolecular Bioscience, **13**, 395–421.
[17]. D. Klemm, B. Heublein, H. P. Fink and A. Bohn (2005). Cellulose: Fascinating biopolyme**r** and sustainable raw material, *Angewandte Chemie International Edition*, **44**(22), 3358–3393.
[19]. H. Matsumura, J. Sugiyama, and W. G. Glasser (2000). Cellulosic nanocomposites. I. Thermally deformable cellulose hexanoates from the heterogeneous reaction. *Journal of Applied Polymer Science*, **78**, 2242–2253.
[20]. V. Pushpamalar, S. J. Langford, M. Ahmad, and Y. Y. Lim (2006). Optimization of reaction conditions for preparing carboxymethyl cellulose from sago waste. *Carbohydrate Polymers*, **64**, 312-318.
[21]. J. L. Ren, R. C. Sun and F. Peng (2008). Carboxymethylation of hemicelluloses isolated fromsugarcane bagasse, *Polymer Degradation Stability*, **93**(4), 786–793.

[30]. I. S. A. Zailani, Aviceena, D. N. Jimat, and M. S. Jami (2016). Extraction of microcrystallinecellulose (MCC) from cocoa pod husk via alkaline pretreatment combined with ultasonication, *International Journal of Applied Engineering Res*earch, **11**(9):9876 9879.

[22]. L. Segal, J. J., Creely, A. E.Martin and C. M. Conrad (1962). An empirical method for estimating the degree of crystallinity of native cellulose using the x-ray diffractometer**.** *Tex Res J.*, **29**, 786-794.
[23]. Selke, S.E.M., Culter, J.D. and Hernandez, R.J. (2004). Plastics Packaging. 2nd edition.Cincinnati: Hanser Publishers. Pp. 57-65.

[24]. D. A. Silva, R. C. M. Paula, J. P. A. Feitosa, A. C. F. Brito, J. S. Miciel, and H. C. B Paula, (2004). Carboxymethylation of cashew treeexudates polysaccharide. *Carbohydrate Polymers*, **58**, 136-171.
[25] R. K. Singh, & O. P. Khatri (2012). A scanning electron microscope based new method for determining the degree of substitution of sodium carboxymethylcellulose. *Journal of Microscopy*, **246**, 43-52.
[26] R. K. Singh and A. K. Singh (2012). Optimization of reaction conditions for preparing carboxymethyl cellulose from corn cobs agricultural waste. *Waste Biomass Valorixation*, **74**, 102-109.
[27]. T. Shui, S. Feng, G. Chen, A. Li, Z. Yuan, H. Shui, T. Kuboki and C. Xu (2017). Synthesis of sodium carboxymethyl cellulose using bleached crude cellulose fractionated from cornstalk. *Biomass Bioenergy*, **105**, 51-58
[28]. V. Stigsson, G. Kloow, and U. Germgard (2001). A historical overview of carboxymethylcellulose (CMC) production on an industrial scale. *Paper Asia*, **10** (17), 16-21.
[29]. H. Togrul, ans N. Arslan (2003). Production of carboxymethyl cellulose from sugar beet pulp cellulose and rheological behavior of carboxymethylcellulose. *Carbohydrate Polymers*, **54**, 73-82.
[31]. P. Zhang, S.J. Dong, H.H. Ma, B.X. Zhang, Y.F. Wang andX.M. Hu (2015). Fractionation of corn stover into cellulose: Hemicellulose and lignin using a series of ionic liquids. *Industrial Crops and Products*, **76**, 688–696.