

Microwave synthesis of Carboxymethylcellulose (CMC) from Rice Husk

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Abstract: Carboxymethylcellulose is an important non-toxic cellulose derivative which plays vital roles in paper coating, pharmaceuticals, food, detergents, and others. Research work involving the extraction of cellulose from agricultural biomass and its modification cellulose using a microwave has been reported, but not much work has been done on the rice husk, thus helping in managing associated waste. In this study, cellulose extracted from rice husks was used as the raw material for the synthesis of food-grade carboxymethylcellulose (CMC). In the process of the synthesis of carboxymethylcellulose from rice husk, cellulose was carried out by alkalization, an etherification process, using sodium hydroxide (NaOH) and monochloroacetic acid (MCA). Characterizations of CMC products was carried out by Fourier Transform Infrared (FTIR) spectroscopy and X-ray Diffraction (XRD). The reaction conditions optimized include power (microwave), sodium hydroxide concentration, amount of monochloroacetic acid and reaction time. The degree of substitution (DS) was determined using a potentiometric titration method and the maximum DS of 0.79 was obtained when 30% NaOH was used.

Keywords: Cellulose, Carboxymethylcellulose, Degree of substitution (DS), Microwave.

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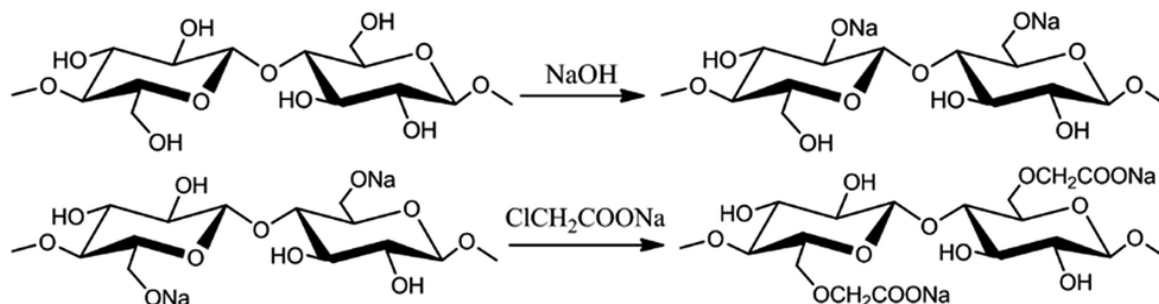
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I. Introduction

Cellulose is the most abundant natural polymer on earth. They are linear, long-chain, water-insoluble, inexhaustible, biocompatible, degradable and environmentally friendly. It is broadly circulated in the plants such as grass (Sutiya *et al.*, 2012), straw (Xue *et al.*, 2013), wood (Sunardi *et al.*, 2016) and cotton (Li *et al.*, 2014). Cellulose has been isolated from several agricultural wastes such as, orange peels (Arslan, 2007) palm oil (Palamae *et al.*, 2017), banana (Adinugraha *et al.*, 2005), cotton waste (Haleem *et al.*, 2014), durian (Rachtanapunt *et al.*, 2012), and sago squander (Pushpamalar *et al.*, 2006). Cellulose can hardly exist in pure form but can be found in the plant cell wall with hemicellulose and lignin (Pushpamalar *et al.*, 2006). Its isolation can be possible, utilizing accessible less expensive chemicals that produce physical and chemical properties better than cellulose obtained commercially. The cellulose obtained from palm oil is higher (44%) (Fatah *et al.*, 2014) compared to other agricultural waste materials: 33% from durian (Penjumras *et al.*, 2015), and 41% from bamboo cane (Scurlock *et al.*, 2000). It serves as a starting material for the synthesis of carboxymethylcellulose and its derivatives, cellulose acetate, methylcellulose, cellulose nitrate, and ethylcellulose. Being a polysaccharide, it is formed as a result of the repeating unit of D-glucose, linked by glycosidic linkage β (1-4). The presence of three reactive hydroxyl groups (C2, C3, and C6) on each glucan unit of cellulose makes it relatively easy to modify (Singh and Singh, 2013).

Carboxymethylcellulose (CMC) happens to be among the cellulose derivative which is non-toxic to human health. Due to its availability as raw material (used in a diet pill, toothpaste, food additive) (Hussain *et al.*, 2010) more attention has been given to its properties as anionic polymer (Chai and mohamad, 2011), and aqueous solubility (Zhou and Zhang, 2000).

Sodium carboxymethylcellulose can be obtained when cellulose is reacted with monochloroacetic acid (MCA) or its sodium salt under the alkaline condition in the presence of an organic solvent. The OH groups of cellulose C2, C3 and C6 are substituted by sodium carboxymethyl group, depending on the degree of substitution, which is the average number of OH in the cellulose structure which was replaced by carboxymethyl group (CH₂COO) at C2, C3, and C6 (Haleem *et al.*, 2014).



Several studies have been done on the synthesis of carboxymethylcellulose from cellulose obtained from agricultural waste materials such as sugarcane bagasse (Alizadehet *et al.*, 2017), palm carnal cake (Bono *et al.*, 2009) and cotton ginning (Haleem *et al.*, 2014), sago waste (Pushpamalar *et al.*, 2006), mulberry paper waste (Rachtanapunet *et al.*, 2015), papaya peel (Rachtanapunet *et al.*, 2010), sugar beet pulp (Togrul and Arslan, 2003). So far there is limited information on the synthesis of carboxymethylcellulose from rice husk using a microwave.

Rice (*Oryza sativa*) is a major source of food in the majority of the developing nations, Rice husks (RH) serve as the defensive cover of individual rice grains, which are expelled during the production of consumable rice. Rice husk has to a great extent been considered as a waste material that is regularly burnt or dumped in landfills. Rice husks are essentially left as agricultural waste or smoldered, which causes genuine capacity and transfer issues in addition to environmental contamination (Giddel and Jivani, 2007). The increasing environmental concerns have constrained the scientists to acquire valuable materials from plant material. Literature has shown that the organic part rice husk contains cellulose, hemicellulose, and lignin, therefore, this serves as the basis for isolation of cellulose from rice husk.

Microwave chemistry is the science of applying microwave radiation to chemical reactions (Arunkumar *et al.*, 2010). Nowadays, scientists employed the use of microwaves as the new system of heating polymers and organic compounds (Zhang *et al.*, 2011). In comparison with other methods of heating, microwave irradiation speeds up the reaction rate within a few minutes. There is little information on the utilization of microwave heating, though some were performed under dissolvable free condition (Vladimira *et al.*, 2008).

Therefore, this work aimed at optimizing the synthesis of carboxymethylcellulose (CMC) from Rice husk using a microwave and study the effect of NaOH concentrations, amounts of monochloroacetic acid (MCA), power outputs, time and Degree of substitution.

II. Materials And Method

2.1 Materials

The rice husk was sampled from Euro rice mills in Mwea, Kirinyaga County – Kenya. Glacial acetic acid and sodium hydroxide were prepared from Merck Chemical Co. (Darmstadt, Germany). Nitric acid, Ethanol and methanol were provided from the local market. Monochloroacetic acid was purchased from Daejung Co. (South Korea), Ramtons microwave (RM 240).

2.2 Methods

2.2.1 Cellulose extraction

About 5.00g of rice husk was weight in 250mL Erlenmeyer flask and 100mL of 80% glacial acetic acid, 10mL of 70% nitric acid was added. The flask was covered using aluminium foil and heated in an oven at 120°C for 20min. The sample mixture was allowed to cool and 60mL of distilled water was added, the mixture was filtered and washed with distilled water and 95% ethanol. The residue was dried in an oven at 60°C for 19hrs.

The extract yield of cellulose was calculated using the formula below

$$\text{The yield of cellulose (\%)} = \frac{\text{Dryweig hextractofRH}}{\text{Weigh tofRH}} \times 100\%$$



Extracted cellulose from rice husk, cellulose after alkalization and etherification

2.2.2 Synthesis of carboxymethylcellulose (CMC)

The synthesis of carboxymethylcellulose (CMC) involves two stages: alkalization and carboxymethylation (etherification). About 5.00g of the extracted cellulose was added to 100mL of distilled water in a 250mL Erlenmeyer flask. Then 10mL of 5, 10, 15, 20 and 25% of sodium hydroxide solution was added dropwise. The alkalization process was carried out for 1hr at 25°C on a fitted shaker. Then 2, 3, 4, 5, 6 and 7g of monochloroacetic acid was added to the mixture and heated in a microwave at various power outputs of 2, 4, 6, 8 10 that corresponds to 140, 280, 420, 560 and 700 watt respectively for 1, 2, 3, 4, 5 minutes, and the resultant contents were filtered. Neutralization obtained residue by soaking with 100mL of methanol for 24hrs, then the mixture was neutralized using glacial acetic acid. The mixture was filtered and the residue was dried in an oven at 60°C.

The yield of carboxymethylcellulose was calculated using the formula,

$$\text{The yield of CMC (\%)} = \frac{\text{Weight of CMC (g)}}{\text{Weight of Cellulose (g)}} \times 100$$

2.2.3 Degree of substitution

The degree of substitution was investigated using potentiometric titration. About 1g of carboxymethylcellulose was added to 250mL of Erlenmeyer flask, followed by 50mL of 95% ethanol. At room temperature, 5mL of 2M of nitric acid was added, it was heated for 5 minutes using a hot plate and allowed to settle. The solution was filtered and the residue was washed with 100ml of 95% ethanol to remove the salt. About 0.5g of Carboxymethylcellulose was added to 250ml of Erlenmeyer's flask, 100ml of distilled water was added, then 25 milliliters of 0.5M NaOH was added and heated for about 20 minutes, then the mixture was allowed to cool, it was titred with 0.3ml HCl with phenolphthalein as an indicator to monitor colour. The degree of substitution of carboxymethylcellulose was calculated using the equations below (Jiang *et al.*, 2011).

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

$$DS = \frac{0.162 \times A}{1 - (0.58 \times A)}$$

Where, A= Milli equivalent of consumed acid per gram of specimen

B= Volume of NaOH added

C= Concentration of NaOH

D= Volume of consumed HCl

E= Concentration of HCl used

F= Specimen gram used

2.3 Characterisation

2.3.1 Fourier Transform Infrared (FTIR)

The Functional groups of cellulose and carboxymethylcellulose were investigated using the infrared spectroscopy spectrum (Shimadzu IR Tracer -100). Pellets were made by CMC with potassium bromide (KBr). Absorbance levels were measured for wavenumbers of 3800-400 cm^{-1} .

2.3.2 X-ray Diffraction (XRD)

The diffraction patterns of the cellulose and carboxymethylcellulose were recorded on a D2 PHASER Bruker AXS X-ray diffractometer. A hot air oven was used to dry the powder samples at 105°C for 3 hours before testing. The scattering angle (2θ) ranged from 10 to 60° at a scan rate of 5°/min.

III. Results And Discussions

The percentage yield of Cellulose

The percentage of cellulose extract obtained from rice husk was found to be 81.67%.

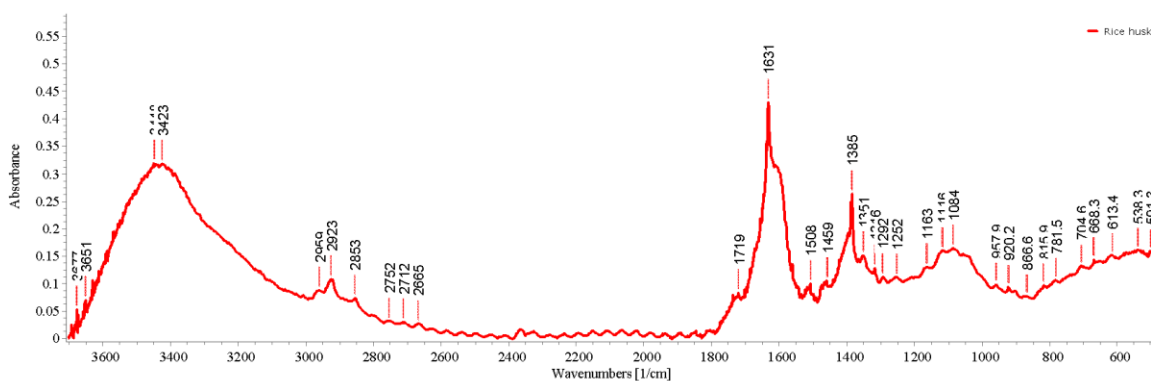


Figure 1: FTIR of rice husk

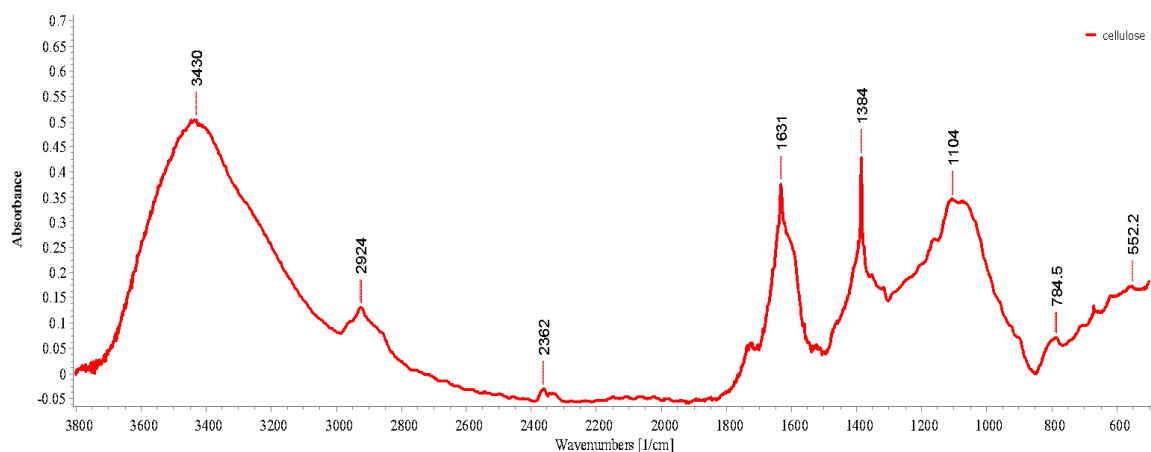


Figure 2: FTIR spectra of extracted cellulose from rice husk

Cellulose FTIR

The figure above represents the FTIR of cellulose. The broad absorption band at 3432.39 cm^{-1} is a feature of the present of OH stretching vibrations and revealed the formation of hydrogen bond and intramolecular and intermolecular hydrogen bond (Wingerson and Richard, 2002). The peak at 2924.13 cm^{-1} is due to C-H stretching vibration. The absorption band at 1631.81 cm^{-1} is the absorbed water, the band at 1383.95 cm^{-1} is characteristic for symmetric CH_2 bending vibrations. The hemicellulose and lignin peaks at 1508 and 1459 fully disappeared after extraction as shown in figure 1. The band at 1104.55 cm^{-1} appears due to C-O-C stretching (Kondo, 1997). Therefore the product obtained confirms that cellulose was successfully extracted from rice husk.

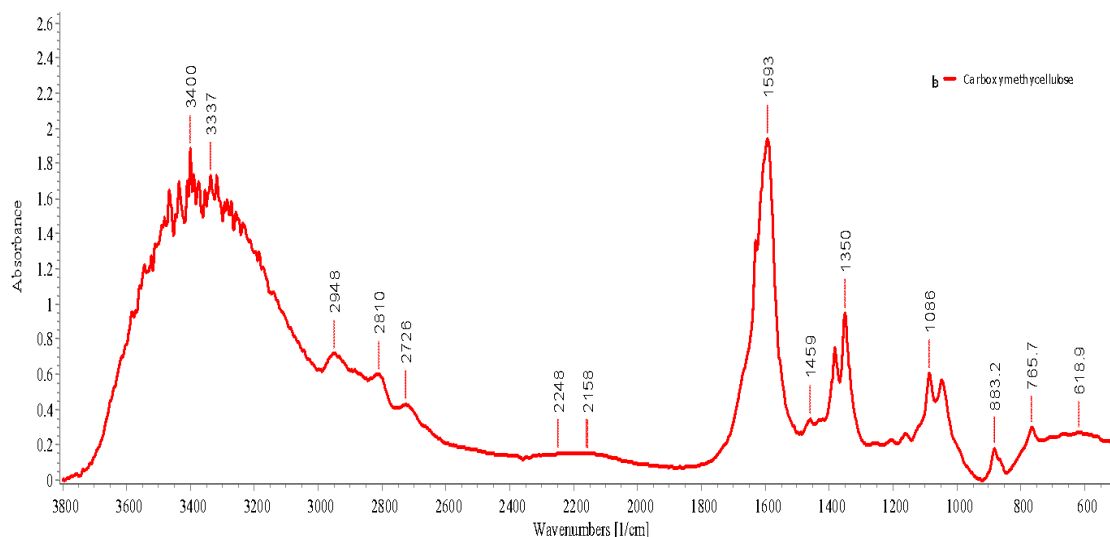


Figure 2: FTIR spectra of carboxymethylcellulose (CMC).

The infrared of carboxymethylcellulose is similar to that of cellulose, the broad absorption band at 3337 cm^{-1} result in stretching frequency of OH group and formation of the intramolecular and intermolecular hydrogen bond. The peak at 2948 cm^{-1} is due to C-H stretching vibration (Vieraet *al.*, 2007). The new band at 1593 cm^{-1} is assigned to COO^- group while the band at 1459 cm^{-1} and 1086 are attributed to CH_2 scissoring C-O-C stretching (Yeasmin and Mondal, 2015). This confirms that the cellulose has been modified to Carboxymethylcellulose.

X-ray Diffraction.

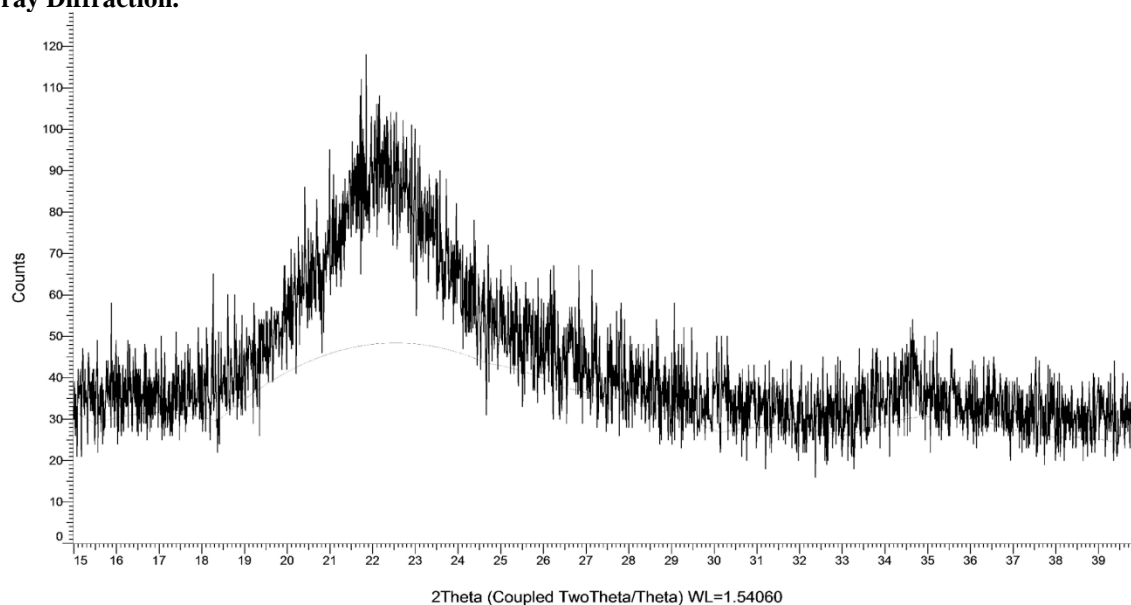


Figure 3: XRD of extracted cellulose from rice husk

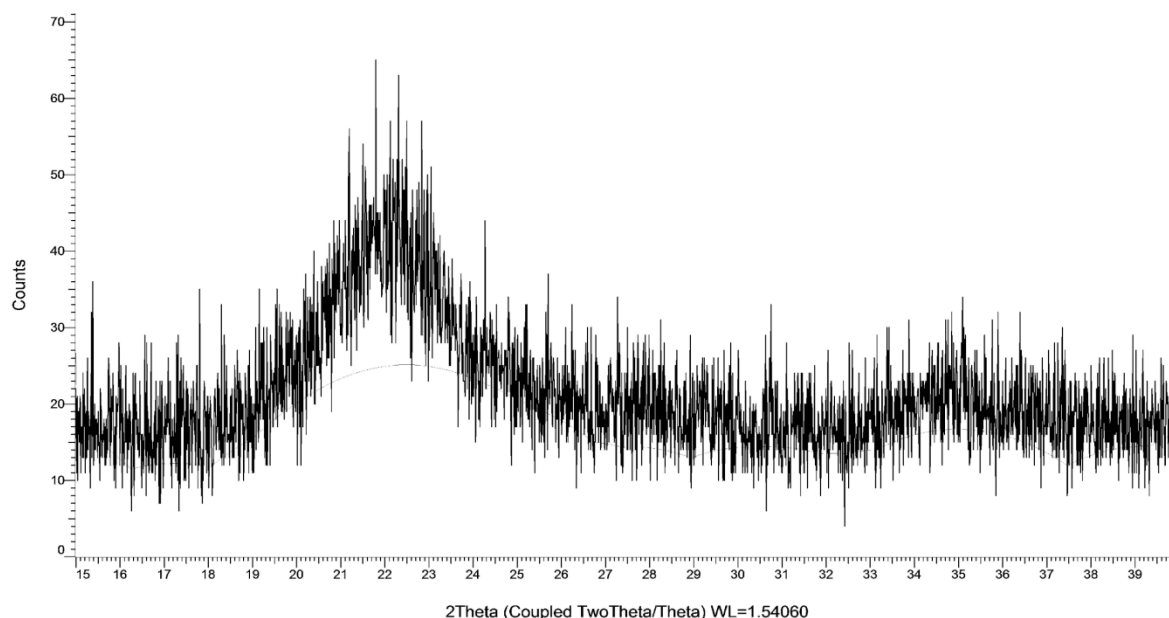


Figure 4: XRD of carboxymethylcellulose

The x-ray diffraction of CMC shows less crystallinity because it has lower peak intensity than cellulose, this is as a result of cleavage of the hydrogen bond. The decrease in crystallinity was as a result of NaOH (alkalization) added to the cellulose structure by adding monochloroacetic acid. A similar result was reported by Adinugraha *et al.*, 2005, the addition of 15g/100mL of NaOH to Cavendish cellulose leads to a decrease in the crystallinity of the obtained CMC. The increase in the degree of substitution, lead to a decrease in crystallinity (Lin *et al.*, 1990).

Optimization condition for synthesis

Effect of NaOH concentration

The percentage yield (%) of carboxymethylcellulose was determined at various NaOH concentration, as shown in the figure below. It was observed that, as the concentration of NaOH increases from 10-30%, the percentage yield also increases from 67-81%. The percentage yield is a function of the weight of material lost during filtration (Silva *et al.*, 2004).

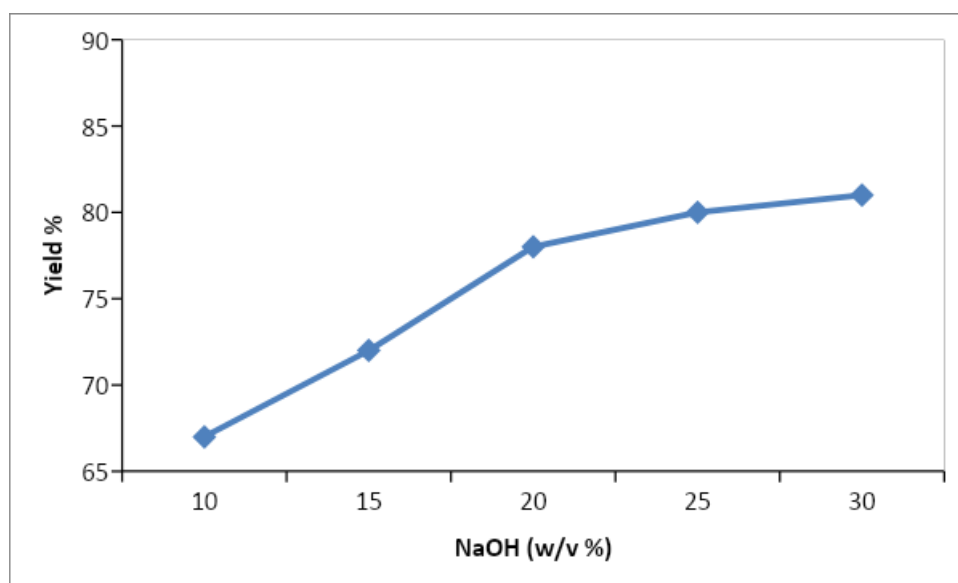


Figure 5: Percentage yield of sodium carboxymethylcellulose synthesized with various alkali concentration.

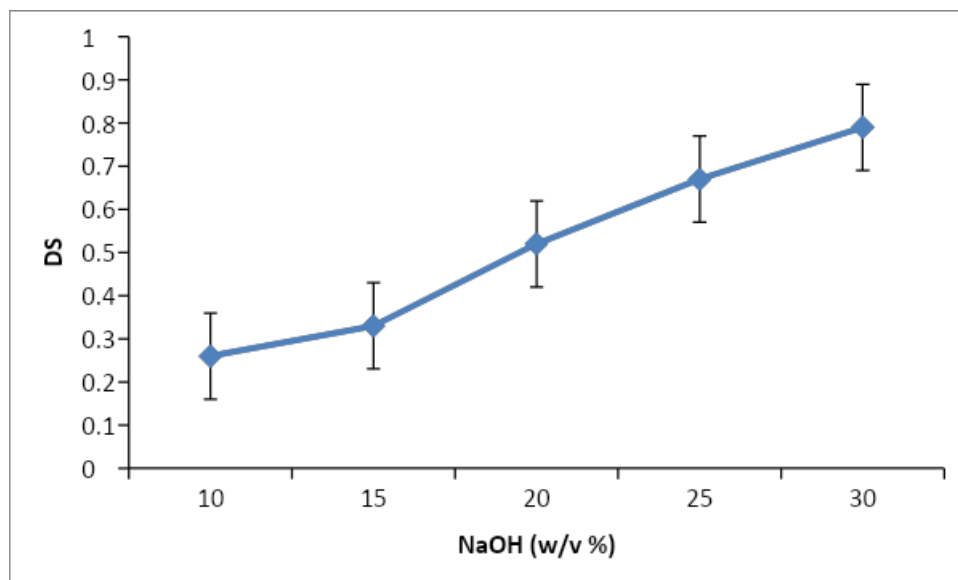


Figure 6: The effect of NaOH concentration on the degree of substitution (DS).

The impact of the degree of substitution was investigated at different NaOH concentrations. The degree of substitution gradually increased from 0.26 to 0.79 respectively, at NaOH concentration of 10 to 30% (w/v).

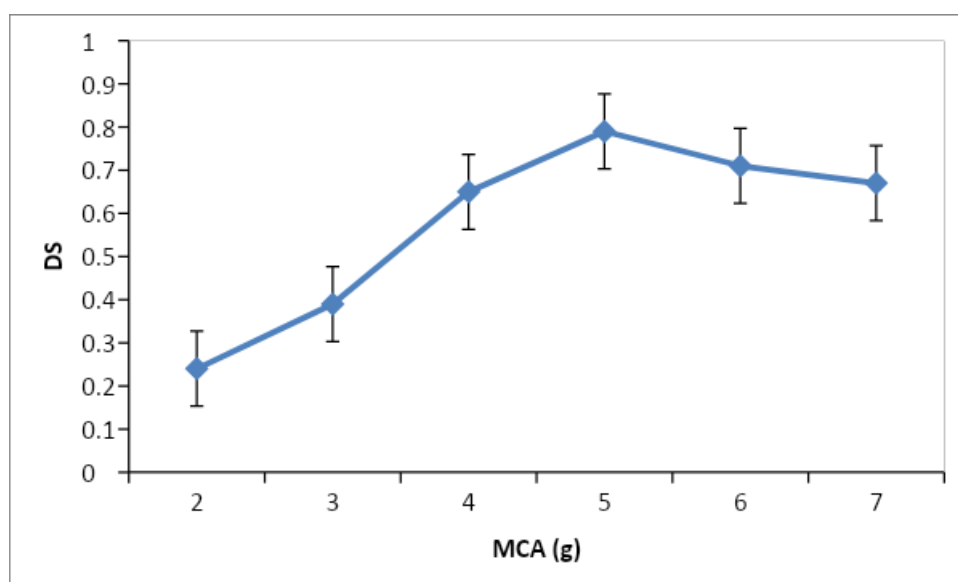


Figure 7: The effect of monochloroacetic acid (MCA) on degree of substitution (DS).

The effect of monochloroacetic acid at different doses was investigated on the degree of substitution. The degree of substitution increased with an increase in the amount of monochloroacetic acid, the highest degree of substitution was attained at 5g of monochloroacetic acid, further decrease of DS was observed as the amount of monochloroacetic acid increased. This is a result of higher accessibility of surface at a high amount of monochloroacetic acid in contact with cellulose. The increase in monochloroacetic acid can lead to the utilization of NaOH, and will favour the formation glycoate. A similar trend was reported by (Zhao *et al.*, 2013).

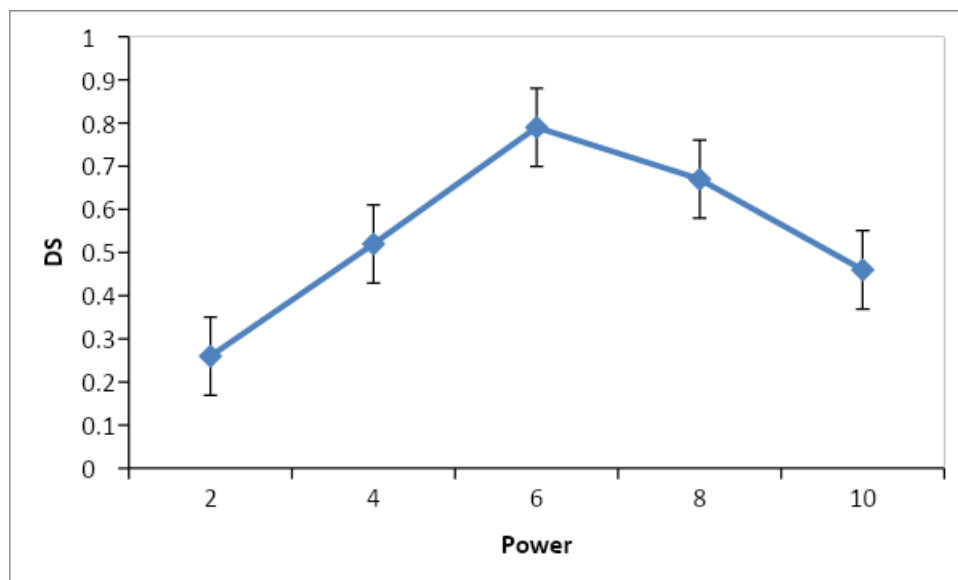


Figure 8: The effect of power outputs on degree of substitution(DS)

The figure above shows the effect of power outputs (microwave heating) on the degree of substitution. It was observed that the degree of substitution increased (0.26 to 0.79) with an increase in power outputs from 2 to 6 that corresponds to 140 to 420 watts respectively, further decrease of degree of substitution was observed (from 0.79 to 0.46) as the power increased (6 to 10, that corresponds to 420 to 700 watts). The increase is on the ground that the diffusion of the monochloroacetic acetic can be enhanced by the high power of microwave up to the power of 6, and provide a better condition for carboxymethylation. The decrease may be due to intermolecular and intramolecular elimination between the OH groups, thereby crosslinking with ethers, therefore the hydroxyl group for carboxymethylation decreases. Lin *et al.*, 1990 reported that cellulose loses its water between the temperatures of 24- 400°C.

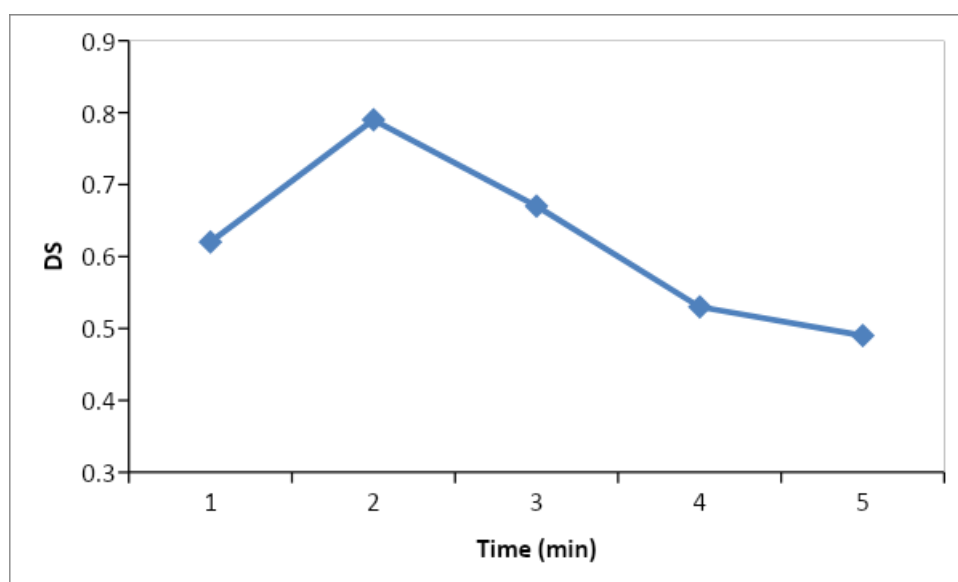


Figure 9: The effect of time on degree of substitution (DS)

The duration was varied from 1 to 5minute on the degree of substitution. It was observed that the degree of substitution increased (0.46 to 0.79) with an increase in time from 1 to 2 minutes, further decrease of degree of substitution was observed (from 0.79 to 0.49) as the time increased (2 to 5 minutes).The increase in degree of substitution can be attributed to adequate time and accessibility for carboxymethylation, Drawing out the span of the response prompts the great impact of time on dissemination and retention of the reactants with a definitive impact of initiating better contacts between the etherifying agent and cellulose (Pushpamalar *et al.*, 2006).

IV. Conclusion

Cellulose was successfully isolated cellulose from rice husk, followed by a modification to carboxymethylation as shown by Fourier transform infrared (FTIR) and x-ray diffraction (XRD). There was less in crystallinity in CMC because of low peak intensity, which exhibits amorphous nature at high concentration. The product attained the highest degree of substitution of 0.79, the optimum condition for the synthesis of Carboxymethylcellulose from cellulose isolated from rice were reaction time 2minutes, 5g of monochloroacetic acid (MCA), power of 6 and NaOH concentration 30%(w/v). The carboxymethylcelluloseobtained from rice husk shows a better degree of substitution than CMC from other different sources of cellulose.

References

- [1]. Adinugraha M. P., Marseno D. W., Hayadi A. (2005). Synthesis and characterization of sodium carboxymethylcellulose from cavendish banana pseudo stem (Musa cavendishii LAMBERT). *Carbohydrate Polymers*, **62**: 164-169.
- [2]. AlizadehAsl S., Mousavi M., Labbafi M. (2017). Synthesis and characterization of carboxymethyl cellulose from sugarcane bagasse. *Journal of Food Process Technology*, **8**: 687-694.
- [3]. Arslan N. (2007) Flow properties of cellulose and carboxymethylcellulose from orange peel. *Journal Food Engineering*, **81**: 187–199.
- [4]. Arunkumar R., Subramani K., Ravichandran S. (2010). International Journal Chemistry Technology. *Resources*, **2**: 278-281.
- [5]. Bono A., Ying P. H., Yan F.Y. (2009). Synthesis and characterization of carboxymethyl cellulose from palm kernel cake. *Advanced Natural Applied Science*, **3**: 5–11.
- [6]. Chai M., Mohamad Isa M. I. N. (2011). Carboxyl methylcellulose solid polymer electrolytes: ionic conductivity and dielectric study. *Journal Current Engineering Research*, **1**:23–27.
- [7]. Fatah I. Y. A., Khalil H. P. S. A., Aziz A. A. (2014). Exploration of a chemo-mechanical technique for the isolation of nanofibrillated cellulosic fiber from oil palm empty fruit bunch as a reinforcing agent in composites materials. *Polymers (Basel)*, **6**: 2611–2624.
- [8]. Giddel M. R., and Jivani A. P. (2007).Waste to Wealth - Potential of Rice Husk in India a Literature Review. Proceedings of the International Conference on Cleaner Technologies and Environmental Management PEC, Pondicherry, India. January 4-6, 586-590.
- [9]. Haleem N., Arshad M., Shahid M., Tahir M. A. (2014). Synthesis of carboxymethylcellulose from waste of cotton ginning industry. *Carbohydrate Polymer*, **113**: 249–255.
- [10]. Hussain P. R., Meena R. S., Dar M. A., Wani A. M. (2010). Carboxymethyl cellulose coating and low-dose gamma irradiation improves storage quality and shelf life of pear (*Pyruscommunis L.*, cv. Bartlett/ William). *Journal of Food Science*, **75**: 586–596.
- [11]. Jiang M., Zhao M. M., Zhou Z. W., Huang T., Chen X. L., Wang Y. (2011). Isolation of cellulose with ionic liquid from steam exploded rice straw. *Industrial Crops and Products*, **33**(3): 734–738.
- [12]. Kondo T. (1997). The assignment of IR absorption bands due to free hydroxyl groups in cellulose. *Cellulose*, **4**(4), 281–292.
- [13]. Li Y., Li G., Zou Y., Zhou Q., Lian X. (2014). Preparation and characterization of cellulose nanofibers from partly mercerized cotton by mixed acid hydrolysis. *Cellulose*, **21**: 301-309.
- [14]. Lin X., Qu T., Qi S. (1990). Kinetics of the carboxymethylation of cellulose in the isopropyl alcohol system. *ActaPolymerica*, **41**: 220-222.
- [15]. Palamae S., Dechatiwongse P., Choorit W., Chisti Y., Prasertsan P. (2017). Cellulose and hemicellulose recovery from oil palm empty fruit bunch (EFB) fibers and production of sugars from the fibers. *Carbohydrate Polymer*, **155**: 491–497.
- [16]. Penjumras P., Rahman R. A., Talib R. A., Abdan K. (2015). Response surface methodology for the optimization of preparation of biocomposites based on poly (lactic acid) and durian peel cellulose. *Science World Journal*, **1**: 293609.
- [17]. Pushpamalar V., Langford S. J., Ahmad M., Lim Y. Y. (2006). Optimization of reaction conditions for preparing carboxymethylcellulose from sago waste. *Carbohydrate Polymers*, **64**(2): 312–318.
- [18]. Rachtanapun P., Eitssayeam S., Pengpat K. (2010). Study of carboxymethyl cellulose from papaya peels binder in ceramics. *Advanced Materials Research*, **93**(94): 17-21
- [19]. Rachtanapun P., Luangkamin S., Tanprasert K., Suriyatem R. (2012). Carboxymethylcellulose film from durian rind, *LWT - Food Science and Technology*. **48**: 52-58.
- [20]. Rachtanapun P., Kumthai S., Mulkarat N., Pintajam N., Suriyatem R. (2015). Value added of mulberry paper waste by carboxymethylation for preparation a packaging film. *Materials Science and Engineering*, **87**: 1-7.
- [21]. Scurlock J. M. O., Dayton D. C., Hames B. (2000). Bamboo: an overlooked biomass resource? *Biomass Bioenergy*, **19**: 229–244.
- [22]. Silva D. A., Paula de R. C. M.,Feitosa J. P. A., Brito de A.C. F., Meciel J. S., Paula H. C. B. (2004). Carboxymethylation of cashew tree exudate polysaccharide. *Carbohydrate Polymer*, **58**: 163-171.
- [23]. Singh R. K., Singh A. K. (2013). Optimization of Reaction Conditions for Preparing Carboxymethyl Cellulose from Corn Cob Agricultural Waste, *Waste Biomass Valorization*, **4**: 129-137.
- [24]. Sunardi J., Tanabe F., Ishiguri J., Ohshima K., K Iizuka., Yokota S. (2016). Changes in lignocellulolytic enzyme activity during the degradation of Piceajezoensis wood by the white-rot fungus *Porodaedaleapini*. *International Biodeterioration and Biodegradation*, **110**: 108-112.
- [25]. Sutiya B., Istikowati W. T., Rahmadi A., Sunardi J. (2012). Kandungkimiadansifatalang-alang (*ImperatacyIndrica*) sebagaigambaranbahanbaku pulp dankertas. *Bioscientiae*, **9**(1): 8-19.
- [26]. Togrul H., Arslan N. (2003). Production of carboxymethyl cellulose from sugar beet pulp cellulose and rheological behavior of carboxymethyl cellulose. *Carbohydrate Polymers*, **54**: 73-82.
- [27]. Viera R. G., Filho G. R., Assuncao R. M. N., Meireles C. S., Vieira J. G., Oliveira G. S. (2007). Synthesis and characterization methylcellulose from sugar cane bagasse cellulose. *Carbohydrate Polymers*, **67**: 182-189.
- [28]. Vladimira T., Krysztof P., Iva S., Alena Ž., Vlasta S., Anna E. (2008). Microwave-assisted synthesis of carboxymethylcellulose-based polymeric surfactants, *Polymer Bulletin*. **60**: 15–25.
- [29]. Wingerson A., Richard C. (2002). Method of treating lignocellulosic biomass to produce cellulose, <http://www.patentstorm.us/patents/6419788-description.html>, US. Patent Issued on July 16.
- [30]. Xu Y., Salmi J., Kloser E., Perrin F., Grosse S., Denault J. (2013). Feasibility of nanocrystalline cellulose production by endoglucanase treatment of natural bast fibers. *Industrial Crops Production*, **51**: 381-384.
- [31]. Yeasmin M. S., Mondal M. I. H. (2015). Synthesis of highly substituted carboxymethyl cellulose depending on cellulose particlesize. *International Journal of Biological Macromolecules*, **80**: 725-731.

- [32]. Zhang G., Zhang L., Deng H., Ping Sun. (2011). Preparation and characterization of sodium carboxymethylcellulose from cotton stalk using microwave heating. *Journal of Chemical Technology Biotechnology*, **86**: 584–589.
- [33]. Zhou J., Zhang L. (2000) Solubility of cellulose in NaOH/urea aqueous solution. *Polymer Journal*, **32**: 866–870.
- [34]. Zhao X., Li Q., Mi Y. (2013). Optimization of reaction conditions for preparing carboxymethylcelluloseguaze. *Advanced Materials Research*, **709**: 40-44.