

Adsorbent Material from Grafting Polymethylacrylate unto Methylcellulose from Elephant (*Napier*) Grass Cellulose

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Abstract:- The study examined the potential of elephant (*Napier*) grass cellulose in producing useful adsorbents that are biodegradable. Cellulose fibers were extracted from elephant grass fibers by chemical process. This was methylated into methylcellulose. Methylacrylate (MA) was also polymerized to polymethylacrylate (PMA). This was copolymerized with methylcellulose to form a PMA-graft methyl cellulose copolymer. The polymerization was carried out using acidified KMnO_4 as initiator. All polymerization reactions were done in a batch reactor at 90°C under inert condition. Fourier transform infrared spectroscopy (FTIR) and proton Nuclear Magnetic Resonance ($^1\text{H-NMR}$) were used to characterize the methylcellulose, PMA and the copolymer.

The percentage of the PMA formed is 27.8%. The copolymer grafted percentage was 43.3% while the grafting efficiency was 72.2%. The prominent bands in the FTIR spectrum of the cellulose are 1080.02cm^{-1} confirming the presence of C-O-C bond and 3347.00cm^{-1} confirming sharp and strong O-H peak. The methylcellulose showed a broad O-H peak at 3431.98cm^{-1} and a C-O peak at 1081.10cm^{-1} to confirm methylation. The MA showed an important IR band at 1737.14cm^{-1} to confirm C=O bond. Its PMA showed similar peak at 1747.37cm^{-1} . The copolymer showed an important IR peak at 3446.24cm^{-1} confirming O-H stretch in the copolymer. $^1\text{H-NMR}$ studies confirms $\text{H}_2\text{C-O}$ at 3.62ppm in the methylcellulose, allylic proton at 1.98ppm and alpha carbonyl proton at 3.42ppm in the PMA. The peak at 12.42ppm is due to CO_2H group and it's the novel peak found in the copolymer. It is an evidence that grafting occurred between PMA and the methylcellulose backbone. The result showed that *Napier* grass has potential for industrial production of cellulose fibers that can be modified into useful adsorbents.

Keywords: Adsorbent, Biodegradability, Cellulose, Copolymer, Methylcellulose.

I. INTRODUCTION

The increased environmental consciousness and rising society concerns on environmental pollutions has forced scientists to amalgamate new green materials and processes that enhance the environmental quality of products (Gupta *et al.*, 2001). In this perspective, biodegradability, eco-friendliness, easy availability and light weight have become important considerations in the development of new materials (Thakur *et al.*, 2010; Singha and Thakur, 2009; Yoichi and Yutaka, 2010). Due to the abundance, biodegradability and

remarkable properties of cellulose, Cellulose fibers have constantly been exploited as a source of materials for different potential applications (Ghoshal *et al.*, 2010). Currently, cellulose represents the most abundant biodegradable polymer available in the biosphere and is cost-effective when compared to other biopolymers and as well as conventional non-biodegradable polymers (Klemm *et al.*, 2005; Omotoso and Akinsanoye, 2018).

Furthermore, cellulose attracted much attention because of its outstanding properties, such as biocompatibility, thermal and chemical stability and selective chemical conversion to obtain derivatives (Klemm *et al.*, 2005; Lejeune and Deprez, 2010). Thus, cellulose has been extensively used in industries, such as pulp and paper, textile, food, composites, coating and pharmaceuticals (Lejeune and Deprez, 2010; Ounaies, 2006; Siqueira *et al.*, 2010; Kamel *et al.*, 2008). They could be incorporated as reinforcing elements in thermoplastic biopolymers, improving mechanical properties of compounds and recovering losses from mechanical recycling of plastics (Carballo *et al.*, 2009; Gupta and Khandekar, 2003; Bergo *et al.*, 2008). Although cellulose has good properties, it has some undesirable ones such as low tensile strength, high moisture re-gain, and low strength against microbial attack (Chundawat *et al.*, 2011). Researchers have widely reported that grafting of synthetic polymers onto cellulose could contribute greatly to the elimination of these drawbacks and allows the acquisition of additional properties of the grafted polymers without destroying its own properties (Gupta *et al.*, 2002; Singha and Rana, 2012; Priya *et al.*, 2014). This research therefore involve the preparation of a copolymer of methyl cellulose (MC) from elephant (*Napier*) grass and polymethylacrylate (PMA) and its characterization to verify its efficiency as a green adsorbent biopolymer.

II. METHODOLOGY

Materials

Elephant (*Napier*) grass were obtained from University of Ibadan environs. All chemicals used for the preparation of methylcellulose and copolymerization process were Analar grade. The reagents used are sodium hydroxide (NaOH), hydrogen peroxide (H_2O_2), dimethyl sulphate ($(\text{CH}_3)_2\text{S}$,

acetone (C₃H₅OH), methyl acrylate (C₄H₆O₂), acetic acid (CH₃COOH), ethanol (C₂H₅OH), hydroquinone (C₆H₆O₂), potassium permanganate (KMnO₄), sulphuric acid (H₂SO₄) and Sodium sulphate (Na₂SO₄). The apparatus used were ANALAB steel ultrasonic bath (sonicator) autoclave and a three necked batch reactor. The analytical instruments are Perkin-Elmer (Waltham, USA) FT-IR Spectrum Two Spectrometer and N analysis NM Ready PRO 60 60MHz nuclear magnetic resonance spectrometer.

Cellulose Extraction

500g of washed and dried Napier grass (Elephant grass) sample were soaked for 48hours in 2% w/v NaOH solution. This resulted in the swelling of the grass. The soaked grass were then treated with 10% w/v NaOH solution in an autoclave (121°C, 15psi for 2hours) with solid elephant grass to liquor ratio 1:10. The washed pulp was then bleached overnight with 8% v/v solution of hydrogen peroxide followed by several washings. 10% v/v hydrochloric acid was added to the bleached pulp to acidify it. The acidic treatment assisted in the breakdown of amorphous moieties of cellulose. The acidic suspension of fibers was sonicated using a ANALAB steel ultrasonic bath (sonicator) in order to loosen the cellulose fibers and breakdown agglomerates of cellulose fibers, followed by repeated washings.

Synthesis of Methyl cellulose (MC)

The methodology described by Viera *et al.* (2007) was used to methylate the cellulose fibers from elephant grass. 500g of the cellulose fiber was initially mercerized using 100ml of 50% w/v solution of sodium hydroxide (NaOH) for 2hours at ambient temperature. After this time, the mixture was filtered to remove excess NaOH. 75ml of acetone and 3ml of dimethyl sulfide (DMS) solution were added to the mixture. It was left to react for 5hours at 50°C by shaking in a closed system. The reaction mixture was changed hourly by filtering off the mixture (DMS + acetone). Finally, the mixture was neutralized with 100ml acetic acid at 10% v/v solution. It was then filtered in a plate funnel and washed with three successive portions of acetone. The final product obtained was dried in an oven at 50°C for 6hours. This was taken as the methylcellulose.

Polymerization of methylacrylate

300ml of methylacrylate monomer was charged inside a 1.5litres 3-necked batch reactor equipped with a mechanical stirrer, an inlet for nitrogen gas and a temperature regulator. 10ml of acidified potassium permanganate (KMnO₄) was added to the monomer in the reactor as catalyst and homogenization occurred for 30mins. The reaction was allowed to proceed for 3hours at 90°C. 5ml of 0.1M of hydroquinone was added to bring the reaction to a halt. The reaction mixture was allowed to cool to room temperature. The final product was washed with methanol so as to remove the unreacted methylacrylate, catalyst and other impurities.

Grafting of polymethylacrylate unto methyl cellulose backbone

120g of methyl cellulose, 28ml acidified KMnO₄ were added in a 1.5litres, 3-necked batch reactor. These were thoroughly stirred for 20mins with a mechanical stirrer. Then, 20g of the prepared poly-methyl acrylate was added and the mixture was homogenized again for 5minutes in an inert environment under nitrogen gas. The reaction was allowed to continue for 8hours. It was terminated by adding 6ml of 0.1M of hydroquinone with continuous stirring for 10minutes. The product obtained was allowed to cool to room temperature for 3minutes and was washed with 200ml of methanol to remove the unreacted Polymethylacrylate (PMA), methyl cellulose(MC) and catalyst from the grafted fraction. The final product was dried over sodium sulphate (Na₂SO₄).

Grafting Parameters

Grafting Percentage: The grafting percentage (GP) indicates the increase in weight of original cellulose subjected to grafting with a monomer and is calculated generally by the following equation:

Grafting percentage =

$$\frac{\text{Weight of polymer grafted}}{\text{Initial weight of backbone}} \times 100$$

$$= \frac{W_1 - W_0}{W_0} \times 100$$

where W₁ and W₀ are the weights of the methylcellulose graft copolymer and the original methylcellulose, respectively.

Grafting Efficiency: Grafting efficiency (GE) shows the fraction of monomer grafted onto cellulose among the amount of monomer converted to graft polymer plus the homopolymer, in other words, the fraction of polymer which is grafted to cellulose in total polymer, and it is calculated by the equation given below:

Grafting Efficiency %GE =

$$\frac{\text{Weight of polymer grafted} \times 100}{\text{Weight of polymer grafted} + \text{Weight of homopolymer}}$$

$$= \frac{(W_1 - W_0)}{(W_1 - W_0 + W_2)} \times 100$$

where W₁, W₀, and W₂ are the weights of the methylcellulose graft copolymer, the original methylcellulose, and the PMA respectively. The weight of homopolymer (W₂) can be calculated by subtracting the amount of grafted polymer plus the amount of unreacted monomer from the initial amount of monomer.

Instrumental Analysis

A Perkin Elmer Fourier transform infrared spectrophotometer (FTIR) was used to record the IR spectra of the dried powdered samples of Napier grass cellulose, methyl cellulose and grafted sample. The samples were

prepared using a mixture of the material with KBr at a proportion of 1:100 (m/m). This technique was used to keep track of the modifications in the intensity of the characteristic bands of functional groups present before and after the methylation reaction of the prepared Napier grass cellulose. The $^1\text{H-NMR}$ analysis of the homopolymer (polymethylacrylate), methylcellulose and the grafted product was carried out on a HM Ready PRO 60 spectrometer operating at 60 MHz for proton. All the chemical shifts were reported in parts per million (ppm) using tetramethylsilane (TMS) as the internal standard and acetone as the solvent for the samples.

III. RESULTS AND DISCUSSION

Grafting Parameters: Grafting percentage and grafting efficiency were 43.3% and 72.2% respectively. The amount of homopolymer is quantified according to the following relationship:

$$\% \text{ Homopolymer} = 100 - \% \text{ grafting efficiency}$$

$$\% \text{ homopolymer was } 27.8\%$$

FTIR of Isolated cellulose fibers

Figure 1 shows the chemical changes that took place during the alkali treatment of cellulose. The broad peak at 3347.00cm^{-1} shows the presence of O-H stretch band of hydrogen bonded hydroxyl group vibrations. This peak can undergo substitution reaction by reacting with SOCl_2 , PCl_5 and PCl_3 . It will therefore form a major starting material for the formation of several useful organic materials such as incorporation of amino ethanediol into cellulosic material. This peak has also been reported to be the point of attack for different modifications of cellulose. Kraissig in 2015 also established that the primary hydroxyl group in cellulose reacts about five times as rapidly as the secondary group when it reacts with acetic anhydride-acetic acid mixture at 100°C . The high intensity and sharp peak indicates higher hydrophobicity of the fibers. The peak at 2916.75cm^{-1} corresponds to the saturated C-H stretching vibrations in lignin, cellulose and hemicelluloses. A strong peak at 1638.07cm^{-1} corresponds to the hemicellulose present in the cellulose fibers. From Table 1, Peaks at 1430.15cm^{-1} , 1372.39cm^{-1} and 1318.04cm^{-1} are attributed to CH_2 bending, C-H asymmetric deformation and CH_2 wagging vibrations in cellulose and hemicelluloses respectively. The results indicated a high purity of polysaccharides in the treated fibers. The peaks at 1162.16cm^{-1} , 1112.40cm^{-1} and 1060.02cm^{-1} represents the C-O stretch band and deformation in cellulose, residual lignin and hemicelluloses. An increase in the cellulose content upon alkali treatment of elephant grass (Napier grass) has been similarly reported by Reddy *et al.*, 2014.

Methylated Napier Grass Cellulose

The Methyl cellulose (MC) produced from Napier grass cellulose is a white purified fine uniform powder. The

MC spectrum in Figure 2 has a broad absorption band at 3431.98cm^{-1} and 2919cm^{-1} which correspond to stretching vibrations of -OH groups and C-H stretching vibrations respectively. From Table 1, it is observed that there is increase in the hydroxyl and C-H stretch peak of methyl cellulose. This is due to chemical modification of the hydroxyl groups to methyl group. The absorption bands at 1635.05cm^{-1} , 1457.64cm^{-1} and 1372.10cm^{-1} corresponds to the CH deformation in methyl, methylene, and methoxyl groups of lignin. The absorption bands at 1210.61cm^{-1} corresponds to the OCH_3 stretch of methyl cellulose and 1061.10cm^{-1} corresponds to the axial asymmetric strain of C-O-C in ether group of the lignin. A similar observation was reported by Maheswari *et al.* in 2012 and Li *et al.* in 2016.

The ether band results from mercerization which alters the chemical structure of the cellulose fiber. This serves as a major evidence for the methylation of the cellulose. The structure of the fiber inter-converts from alpha-cellulose and beta-cellulose mixture to a thermodynamically favorable cellulose polymorph. The absorption bands at 1414.00cm^{-1} , 1372.10cm^{-1} , 1004.10cm^{-1} , 1061cm^{-1} and 879cm^{-1} were related to the CH_2 bending vibration, C-O-C pyranose ring skeletal vibrations, C-O stretching, OCH_3 stretch and C-H rocking vibrations from the cellulose respectively. It has been reported by Winstein and Henderson in 1994 that the peak representing the OCH_3 can participate in solvolytic displacement reactions. The C-O-C pyranose ring can undergo cleavages to produce biohalogenoalkanes, such reactions include substitution reactions with reagents like phosphorus pentachlorides and sulphur dichloride. Modifications to these halogenolakanes can result into the synthesis of amines and amides. Therefore, the new functional group can make the methylcellulose a useful feedstock for producing important industrial chemicals.

FTIR analysis of Methyl acrylate and Polymethyl acrylate

The FTIR spectra of methyl acrylate in Figure 3 showed a peak at 1754.11cm^{-1} due to the presence of ester carbonyl group (C=O) stretching vibration in methyl acrylate. The peak at 1202.30cm^{-1} and 1281.95 are due to the presence of ester C-O-C stretching vibration. The band at 2963.83cm^{-1} and 3012.00cm^{-1} are due to presence of C-H stretching vibrations in the methyl acrylate. These bands altogether confirm the ester functional group in the methylacrylate. The sharp peak at 1637.71cm^{-1} is due to the C=C stretch in methyl acrylate. The peak confirms that the MA has unsaturated moieties within its structure that can undergo addition polymerization. Peaks at 993.15cm^{-1} , 820.48cm^{-1} and 690.00cm^{-1} are due to phenolic and unsaturation. Figure 4 shows the IR spectra of the homopolymer (poly methyl acrylate) from the methylacrylate. The spectrum showed a peak at 1747.37cm^{-1} due to the presence of ester carbonyl group (C=O) stretching vibration. The broad peaks at 1202cm^{-1} and 1374.33cm^{-1} in PMA is due to the presence of ester C-O-C stretching vibration. The broad band at 2929.13cm^{-1} and 2960.52cm^{-1}

which occurs as a doublet is due to the presence of C-H stretch of ester in the PMA. These bands altogether confirm that the homopolymer still retain the ester functional as found in the starting material (Figure 3). This confirms that the polymerization did occur at the carbonyl group of the methylacrylate but at the vinyl groups present in the MA monomer. The peaks at 835.00cm^{-1} to 606.72cm^{-1} and 740.26cm^{-1} confirming C-H bending of aromatics (acrylic).

Figure 3 indicated that the vinyl bands present in the monomer (MA) are fewer than those found in poly methyl acrylate (PMA). This serves as evidence that polymerization occurred at the vinyl part of the methyl acrylate monomer. Similar results were reported by Akinsanoye and Omotoso in 2018; Gupta and Sahoo, 2000; Ibrahim, 2002.

FTIR Analysis of Copolymer

The spectra of the grafted sample in Figure 5 showed a major absorption band of hydroxyl group around 3446.24cm^{-1} . Peaks at 1638.47cm^{-1} , 1564.01cm^{-1} and 1383.80cm^{-1} in the spectrum of copolymer results from C=C stretch of polymethylacrylate. The peaks confirm that the vinyl bonds found in the PMA homopolymer are still present in the copolymer. The peak at 1746.05cm^{-1} resulted from the C=O bond from PMA. This peak appears very weak and disappearing in the spectrum (Figure 5). The disappearance of this peak is an evidence that the grafting of PMA to the methylcellulose backbone occurred at the carbonyl parts of the monomers involved. This accounts for the broad and prominent O-H peak found in the spectrum of the copolymer at 3446.24cm^{-1} (Table 1). This kind of reaction is usually found in bayer-villiger oxidation reactions. The peaks at 1415.29cm^{-1} , 1338.80cm^{-1} resulted from the C-H bending in methyl cellulose, peak at 1268.00cm^{-1} and 1122.87cm^{-1} resulted from C-O-C stretching of methyl cellulose. The peaks at 928.48cm^{-1} , 839.73cm^{-1} and 619.47cm^{-1} resulted from C-H rocking vibrations of methyl cellulose and PMA (Zhe *et al.*, 2011). The observed differences between the FTIR spectra of methylcellulose and the copolymer confirm the copolymerization process.

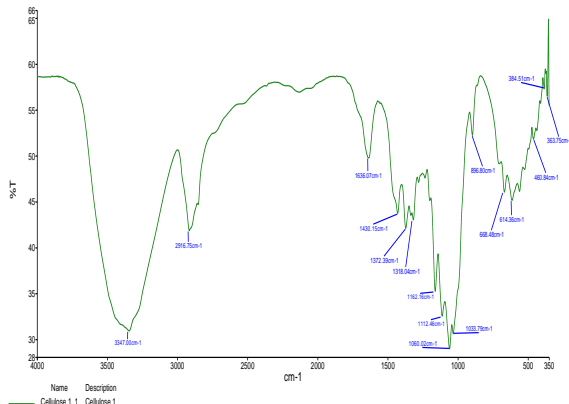


Figure 1: IR spectra of elephant grass (Napier grass) Cellulose (NGC).

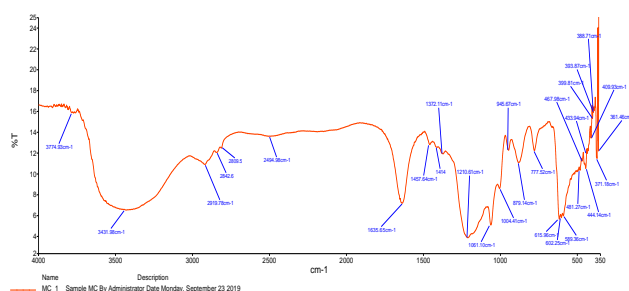


Figure 2: IR Spectra of Methyl Cellulose

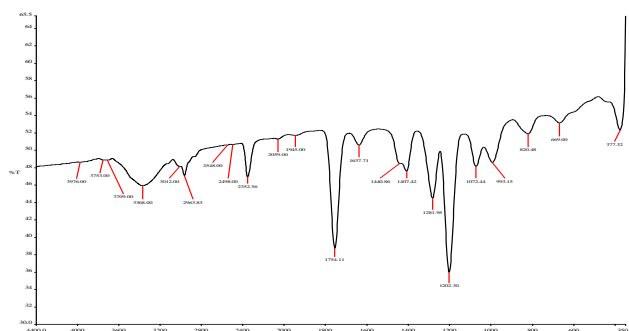


Figure 3: IR spectra of Methyl acrylate

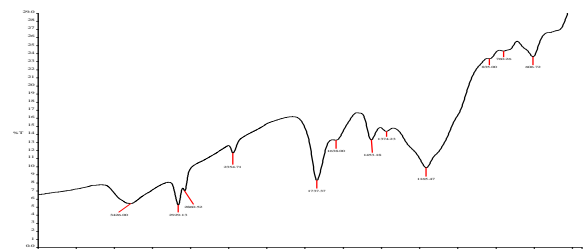


Figure 4: IR Spectra of Polymethylacrylate (PMA)

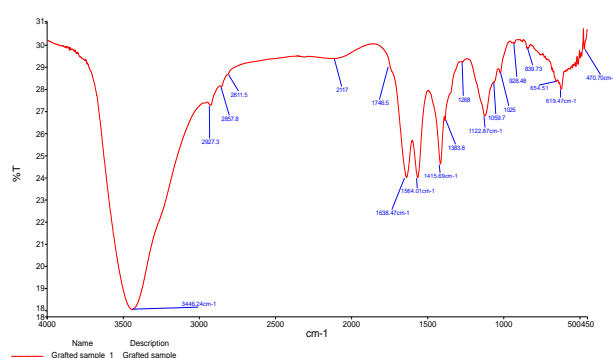


Figure 5: IR spectra of copolymer

¹H-NMR spectra of Methyl cellulose

Figure 6 shows the ¹H-NMR spectrum of the methylcellulose. The protons occurring at 3.66ppm and 3.81ppm are due to the methoxyl (O-CH₃) group in the methylcellulose. These protons resulted from the mercerization of cellulose into methyl cellulose. The peaks found at 2.12ppm and 2.28ppm are due to protons on carbon next to carbonyl group of the cellulose. They resulted from the modification of napier grass cellulose into

methylcellulose. The peak at 4.64ppm and 4.97ppm are due to anomeric effects. This peak serves as a distinct $^1\text{H-NMR}$ signature peak for carbohydrates in a region that is separated from other protons and usually produces a well resolved signal. The anomeric proton is spin-coupled to the proton of the methyl groups resulting in a doublet. The peak is an evidence for the presence of highly reactive sites in the methylcellulose. Peaks at 9.23ppm, 9.17ppm, 9.08ppm are due to heavily deshielded aldehyde protons. Peaks at 8.23ppm, 8.38ppm, 8.44ppm, 8.52ppm, 8.55ppm, 8.57ppm, 8.63ppm, 8.66ppm, 8.75ppm, 8.84ppm, 8.89ppm, 8.99ppm, 9.08ppm showed that methylcellulose were evidences of glycopyranoside ring or acetal ring of the methylcellulose. They showed that the methylcellulose has become cyclic. They also suggest that oxidation occurred. During this oxidation reaction, the aldehyde groups are converted into hemiacetals. This was also confirmed by the appearance of peaks at 4.97ppm and 4.64ppm. Similar results were reported for hemiacetals in oxidized methyl glycopyranoside (Bergo *et al.*, 2008; Arceo, 2006; Chami and Robert, 2013).

$^1\text{H NMR}$ spectra of polymethylacrylate

Figure 7 is the proton NMR spectrum of polymethylacrylate. The peak at 6.64ppm serve an evidence for the existence of acrylic proton in the homopolymer molecule. The peaks at 5.86ppm, 5.77ppm, 5.34ppm and 4.72ppm confirmed vinyl protons. They showed that the homopolymer contains a high level of unsaturation. Similar result was obtained from the FTIR The FTIR for MA and PMA however suggest that the vinyl protons were decreased to show that the polymerization process occurred. Peaks at 4.32ppm, 4.29ppm, 4.22ppm, 4.15ppm, 4.05ppm are due to O-CH_3 . These peaks suggest that the homopolymer contains an ester functional group which was in agreement with the FTIR of the methylacrylate monomer. The peaks at 3.42ppm, 3.36ppm, 3.29ppm, 3.24ppm, 3.20ppm, 3.15ppm, 3.10ppm, 3.06ppm, 3.04ppm, 3.00ppm are due to protons on carbon next to carbonyl group and it establishes the ester functional group. Peaks at 2.05ppm and 1.96ppm confirm the presence of methine protons. They indicate the presence of the vinyl protons. The peaks at 1.26ppm and 0.81 ppm are saturated peaks. They indicate that some of the vinyl protons have been polymerized.

$^1\text{H NMR}$ Spectra of Copolymer

Figure 8 is the proton NMR spectrum of the copolymer. The peak resonating at 3.62ppm confirm methoxyl proton of methylcellulose. Peak at 3.00ppm found in the PMA spectrum also appears in the copolymer spectrum. This proton confirm the presence of a carbonyl peak in the copolymer. Although the FTIR showed this peak but it was already disappearing. Peaks at 1.98ppm confirm allylic proton. Peaks found at 1.38ppm, 1.25ppm, 0.94ppm, 0.92ppm, 0.89ppm, 0.84ppm and 0.75ppm indicate the presence of the saturated protons from PMA. The peak resonating at 12.42ppm is absent in the PMA and methylcellulose spectrum, it appears as a new peak in the

proton NMR of the copolymer. This peak results from the hydrolysis of either the ester moiety in the methyl cellulose or PMA via the acidified KMnO_4 with H_2SO_4 playing the catalytic role. This proton peak is responsible for the formation of carboxylate salts when reacted with a base, the proton peak is usually available for replacement by a metal cation to form corresponding salts.

The new peak confirm O-H bond of carboxylic acid. The peak suggest that the new copolymer has a new reactive group that can undergo several reactions such as reaction with alkalis to produce corresponding salt, combination with SOCl_2 , PCl_5 and PCl_3 to undergo substitution reactions that can lead to formation of acyl chlorides. These can result into amides and amine. The new CO_2H functional group in the copolymer therefore confirm the new product as a viable precursor for producing useful industrial chemicals. The CO_2H reactive group showed that the copolymer material has new functional part that differentiated it from the starting monomers. The copolymer confirm that elephant grass could be important raw material in developing useful chemicals that can be useful in wide range of applications. These include organic solvent, emulsifiers and heavy molecular weight bio-lubricant. The Proton NMR spectrum of the copolymer suggests that grafting occurred between the methyl cellulose and PMA to produce the needed copolymer.

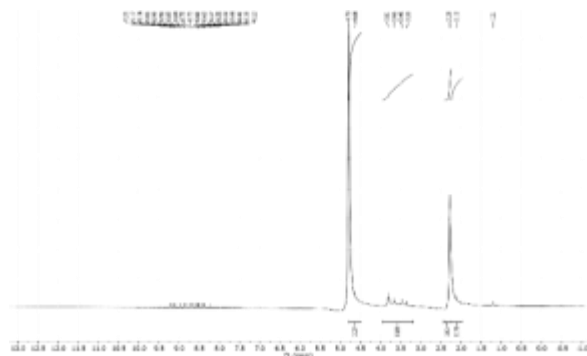


Figure 6: $^1\text{H NMR}$ peak of methylcellulose

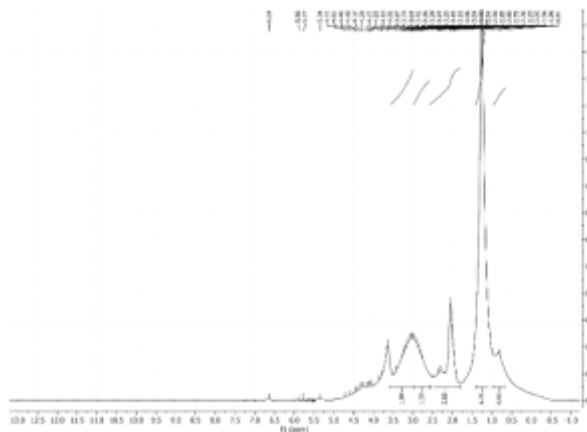


Figure 7: $^1\text{H-NMR}$ peak of poly methylacrylate.

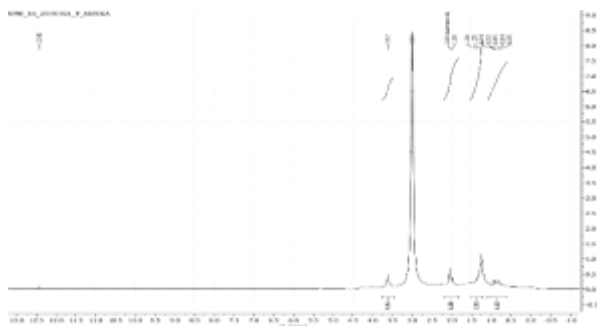


Figure 8: ¹H-NMR peak of copolymer

IV. CONCLUSION

Cellulose extracted from elephant grass was used to develop a gel biopolymer. The cellulose was treated chemically using NaOH. This was immediately followed by bleaching and acidic treatment. The cellulose was further modified to produce methylcellulose using dimethyl sulphide (DMS) as an alkylating agent. PMA was grafted to the methylated cellulose backbone to obtain a copolymer. The cellulose, methylcellulose, MA, PMA and the novel copolymer were characterized using FTIR and proton NMR to monitor the trend in the various phases of reactions and polymerization processes.

The FTIR result showed that the methylation of the cellulose occurred. It also confirmed that the MA was homopolymerized. The proton NMR result confirm that grafting of PMA onto the methylated cellulose actually occurred by showing a new peak at 12.42 ppm. This peak correspond to CO₂H peak. It is an evidence that the new copolymer will be a good gel polymer material because of the polar nature of CO₂H group. It can also be modified to produce other useful industrial chemical. It is also biodegradable and hence satisfied some good aspects of the green chemistry policies.

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