SOLUTION PROPERTIES OF LIQUID DETERGENT MODIFIED WITH CARBOXYMETHYL CELLULOSE FROM BANANA PSEUDO STEM

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ABSTRACT

Objective: Carboxymethyl cellulose (CMC) can be used as thickener and rheology modifier in liquid detergents. In this research, liquid detergent of known concentration was prepared and the effect of CMC of different degrees of substitution (D.S) on the rheological properties and cleaning action of the liquid detergent was studied.
Research Method: The banana pseudo stems were converted to cellulose when pulped with sodium hydroxide (NaOH) solution bleached with sodium hypochlorite and dried. The cellulose was converted to CMC of different D.S by reaction with different amounts of chloroacetic acid in the presence of NaOH as alkalizing agent. Detergent was prepared by neutralizing 2-dodecylbenzene sulphonic acid with NaOH in the molar ratio of 2:1. The liquid detergent (1%, w/v) was modified with CMC of different D.S. The liquid detergent was characterized in terms of pH, lather volume, foam capacity, rheology and cleaning action.
Findings: The CMC prepared had D.S in the range of 0.67 to 0.91. The pH of 1% (w/v) aqueous detergent was 6.12. The lather volume and foam capacity of 1% (w/v) liquid detergent were 70.20mL and 3.51 respectively in distilled water and 51.30mL and 2.57 respectively in hard water. The rheological behaviors of the liquid detergent modified with CMC of different D.S were non-Newtonian.
Originality: The liquid detergent modified with CMC had better cleaning action and increased with D.S. Liquid detergent with known concentration was produced and CMC from banana pseudo modified the rheological properties of liquid detergent with increased D.S. The CMC also increased the cleaning action of the liquid detergent.
Keywords: Carboxymethyl cellulose, Degree of substitution, Liquid Detergent, Rheology

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1. INTRODUCTION

Liquid detergents are gaining popularity around the world. This is not only as a result of their ease of dissolution in wash water, but also because they outperform existing soap (Naganthran et al., 2017). The cleaning effectiveness of a detergent is greatly influenced by its viscosity. In order to effectively distribute its cleaning chemicals, perfect detergent should have the right viscosity. A detergent with an excessively low viscosity may not be able to keep its stability or remove dirt and stains off surfaces, while an excessively high viscosity may make the product more difficult to flow. Carboxymethyl cellulose (CMC) is a cellulose derivative, a biodegradable, water soluble anionic polymer. CMC can be synthesis from natural biomass. CMC acts as anti-redeposition agent and as thickener in liquid detergents. The thickening ability of CMC in liquid detergents is measured as a function of its viscosity. A single-point viscosity measurement method had been used to assess the viscosity of liquid detergents (McGregor, 1999). This approach comprises measuring the liquid detergent's viscosity using only one shear condition or averaged shear. The technique may no longer reflect a fundamental understanding of the CMC modified liquid detergent's underlying flow behavior (Herh et al., 1998). Problems become much more complex when working with non-Newtonian fluids since the product behavior may alter significantly as the flow rate varies. Flow characteristics, such the viscosity based on the shear rate, have an impact on the quality of the product and are therefore crucial control parameters.

Rheology plays a crucial role in the performance of liquid detergents. There are several distinct types of rheology modifiers which a formulator can utilize to achieve the appropriate flow characteristics. Cellulose gum, Guar gum, Xanthan gum, Hydroxyethylcellulose, methylcellulose, polyethylene glycols, clays (Karsheva et al., 2007) are various examples of thickeners used in cosmetics. CMC is a rheology modifier with unique properties through its associations with other components in a formulation. Another important property of CMC than aids its flow characteristics in liquid detergent is its degree of substitution (D.S) which is the average number of carboxymethyl group per anhydroglucose unit (Sittana, 2015).

Quantifying the concentration of liquid detergent can enhance the product quality control and formulation efficacy in the detergent manufacturing industry. Rheological measurements can be used to customize the flow parameters of liquid detergent to satisfy customers' practical and aesthetic requirements (Holland, 1991). The aim of this study was to prepare liquid detergent of known concentration modified with CMC of different D.S and determine the solution properties.

2. MATERIALS

Banana pseudo stem as feedstock for extraction of cellulose, Analytical grade reagents used were sodium hydroxide, chloroacetic acid, iso-propanol, methanol, ethanol, acetone, hydrochloric acid, 2-dodecylbenzene sulphonic acid.

2.1 SAMPLE PREPARATION AND EXTRACTION OF CELLULOSE FROM BANANA PSEUDO STEM

Banana pseudo stems were collected from plantain plantation in Ibadan, Oyo State, Nigeria. The pseudo stems were cleaned by washing with water, manually cut into smaller pieces and were air dried. These were reduced into powder form with the aid of blender and sieved to remove particles with large sizes. The extraction of cellulose was achieved according to the method reported by Adinugraha et al, (2005) with slight modification. 20g of pseudo stem powder was soaked in hot water for 1h. The solution was thereafter filtered using muslin cloth. The residue obtained was heated in an aqueous solution of 8% NaOH at sample to solvent ratio of 1:20 (w/v) for 3 h at 100^{o}C. The resulting mixture was then filtered and washed using distilled water. It was then bleached using 4% alkaline NaOCl for 3 h at 30^{o}C to improve the colour of the cellulose. The material was then washed with sufficient distilled water to completely remove the hypochlorite and dried at 60^{o}C.

2.2 SYNTHESIS OF CMC FROM CELLULOSE

The synthesis of CMC was carried out by the procedure described by Rachtanapun et al., (2012). The experiment was accomplished basically by two main reaction steps which include:

Alkalization reaction: 10 g of cellulose from Pseudo stem of banana was weighed into a 250 ml beaker, 100 ml of iso-propanol was added with continuous stirring to have homogenous mixture. The mixture was heated at 60oC for 1h while 30 ml of 30% NaOH solution (w/v) was added dropwise.

Etherification reaction: Chloroacetic acid (6 g, 8 g, 10 g and 12 g, respectively) was dissolved in 10 ml iso-propanol and was added into the reaction mixture while stirring mechanically over a period of 5 min. The reaction mixture was kept alkaline by adding drops of 0.1M NaOH and the mixture was kept at 60oC for 1 h. The carboxymethylation reaction is shown in Reaction 1.

$$\text{Cell-OH+ Cl-CH}_2\text{-COOH} \xrightarrow{\text{NaOH}} \text{Cell-O-CH}_2\text{-COONa + NaCl} \qquad \text{(Reaction 1)}$$

Cell-OH represents cellulose

After the reaction time, the solution was neutralized using acetic acid. It was then filtered and washed with 70% (v/v) aqueous ethanol. It was finally washed with 70% (v/v) methanol and filtered. The obtained CMC was dried at 60°C in an oven and stored for further characterizations.

2.3 DETERMINATION OF DEGREE OF SUBSTITUTION

The D.S of the CMC was determined using the standard method (ASTM 2005). 2g of dry CMC was weighed into a beaker and was then dispersed in acetone by stirring with a glass rod. Then, 6mL of standard 6 N HCl was added with continued stirring for 30 min. and the dispersion was then filtered to eliminate the excess acid. The obtained H-CMC was washed with 80% aqueous methanol (v/v). The H-CMC was also dispersed in acetone, filtered, and then oven dry. The H-CMC obtained was used for the degree of substitution determination.0.5g of the H-CMC sample was dissolved in 20 mL of standard 0.20 M NaOH and 50 ml of distilled water was added. The solution was transferred into a 100 mL volumetric flask, which was filled up to the mark with distilled water. Then, 25 mL of the solution was transferred to a 250ml beaker and 100 mL of distilled water was added. The excess of NaOH was back-titrated with standard 0.05N HCl using phenolphthalein as the indicator. Before the titration the phenolphthalein indicator showed a pink colour and it was changed to colourless.

The titration was repeated three times and the value of the HCl volume consumed was used for the calculations. The milli-equivalents of used acid/g of the sample (CMC) (A) was calculated using equation 1 while the degree of substitution was determined using equation 2.

$$\mathrm{A} = \frac{BC-DE}{F} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.(1$$

$$\text{Degree of Substitution} = \frac{0.162\ X\ A}{1-(0.058\ X\ A)} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.(2)$$

Where:
A = milli-equivalents of consumed acid per gram of specimen
B = volume of NaOH added
C = molar concentration of NaOH added
D = volume of consumed HCl
E = molar concentration of HCl used
F = specimen grams used
162 the mean gram molecular weight of the anhydroglucose unit

58 is the net increment in the anhydrous glucose unit for every substituted carboxymethyl group.

2.4 SWELLING CAPACITY

The swelling capacity measurement of the CMC was carried out using the method by okhamafe et al. (1991). 0.2g of each modified CMC was added into a 10mL graduated cylinder and distilled water was added to reach the 10mL mark. The mixture was allowed to stay overnight without shaking the content. This was done in triplicates.

Swelling Capacity was calculated using the formula: (V2-V1)/VI X 100

Where;
V1 = 0.2mL
V2 = Final volume of carboxymethyl cellulose overnight

2.5 FOURIER TRANSFORM INFRARED SPECTROSCOPY

The functional groups present in cellulose, CMC and H-CMC were investigated using the Infrared spectroscopy spectrum (EQUINOX 55, BRUKER, Germany). Pellets were made using KBr. Transmission levels were measured for wave numbers of 4000-400 cm^{-1}.

2.6 PREPARATION OF DETERGENT

The detergent production was carried out according to the method by Oluwasina (2018). The detergent was produced by the neutralization reaction between sodium hydroxide solution and 2-dodecylbenzene sulphonic acid in ratio 1:2. The pH of the detergent was adjusted to 6.12 with few drops of equal molar sodium hydroxide and 2-dodecylbenzene sulphonic acid. The reaction is a neutralization reaction and it is shown in Eq. 2.

$$\mathbf{CH_3\,(CH_2)_{11}C_6H_4SO_3H + NaOH \longrightarrow CH_3\,(CH_2)_{11}C_6H_4SO_3Na + H_2O}$$

(Reaction 2)

The formed detergent was thereafter precipitated using sodium chloride. 10mL of the detergent was added to 250mL beaker and solid sodium chloride was added into the detergent in the ratio of 2:1. The recovered precipitate was freeze dried. The detergent was re-constituted into the liquid form by dissolving in distilled water. 1% concentration of the liquid detergent was prepared by dissolving the detergent in distilled water in the detergent to water ratio of 1:100 (w/v). This prepared liquid detergent was stored for other characterizations.

2.7 CHARACTERIZATION OF LIQUID DETERGENT

2.7.1 DETERMINATION OF PERCENTAGE ACTIVE DETERGENT

The percentage active detergent was determined using the ISO method. This was achieved by determining the active ingredient (2-dodecylbenzene sulphonic acid). 5.2 g of the detergent was weighed into a 250 mL round bottom flask with ground glass neck. 25 mL of the standard 0.8M sulphuric acid solution was added and reflux in a water condenser. The solution was refluxed for 90 min. The source of heat was removed and the flask was cooled. A few drops of the phenolphthalein were added to the solution and the solution was titrated with standard 0.9M sodium hydroxide solution.

A blank test was conducted by titrating 25 mL of the standard 0.8M sulphuric acid solution with the standard 0.9M sodium hydroxide solution.

The purity of the 2-dodecybenzene sulphonic acid is expressed as a percentage by.

$= 32.65(V_1-V_0)\ M_O$ ………. . . . . ………………………………. Eq (3) a

Where,
V0 =Volume, in millilitres, of sodium hydroxide solution used for the blank test;
V1=Volume, in millilitres, of sodium hydroxide solution used for the sample;
m1=mass, in grams, of the sodium 2-dodecyl benzene sulphonate used and
M0=exact molarity of the sodium hydroxide solution.
326.5 = molar mass of 2-dodecybenzene sulphonic acid
Percentage Active Detergent denoted by M1 is determined by

$$M1 = \frac{m1 \text{ x purity x}100}{326.5}$$ ……………………………………………… Eq (3) b

2.7.2 DETERMINATION OF PH OF LIQUID DETERGENT

The pH of 0.1% liquid detergent was determined using Jaway 3505 pH meter. The pH meter was calibrated using buffer 4.01 and buffer 7. 10mL of the liquid detergent was diluted with 100mL of distilled water. The electrode of the pH meter was inserted in the solution and the pH will be recorded.

2.8 MODIFICATION OF DETERGENT WITH CMC

The liquid detergent was modified with CMC according to the method used by Oluwasina (2014). 2% (w/v) solution of CMC was prepared and 20% of this solution was then added to 500mL of 1% liquid detergent and mixed thoroughly in order to obtain homogeneous solution. The liquid detergents were named according to the D.S of the CMC and then stored in different labelled plastic for further analysis.

2.9 DETERMINATION OF LATHER VOLUME

The lather volume was determined using Uganda Standard DUS 1624-1 method (Uganda Standard, 2015). Firstly, standard hard water was prepared by dissolving 0.220 g of calcium chloride dihydrate and 0.246 g of magnesium sulphate monohydrate in distilled water. Distilled water was added to make it up to 5 L. 1mL of the 1% liquid detergent was measured into a 100-mL beaker, after which 10 mL of the standard hard water was added. The beaker was covered with a watch glass and allowed to stand for 30 min while the solution was stirred with a glass rod. The mixture was transferred into a 100mL graduated cylinder ensuring that not more than 2 mL foam was produced. The transfer of the residue left in the beaker was repeated with further 5mL of standard hard water ensuring that all the matter in the beaker was transferred to the cylinder. The solution in the graduated cylinder was adjusted to 20 mL by adding standard hard water to make up to the mark. The solution in the cylinder was stirred with a glass rod to ensure a uniform suspension and warmed. When the temperature of the solution in the cylinder reached 30 □C, the cylinder was removed and shakes vigorously. The cylinder was allowed to stand for 5 min. This was done in triplicate for each liquid detergent.

The following readings were taken:

Foam plus water (V1 mL) and water only (V2 mL).

$$\text{Foam volume} = V_1 - V_2 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{Eq (4a)}$$

$$\text{Lather Capacity} = \frac{V1-V2}{V2} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{Eq (4b)}$$

2.10 DETERMINATION OF LIQUID DETERGENT RHEOLOGY

The viscosities of the liquid detergent with and without CMC were determined at 25oC using an 8-speed electronic viscometer, model 800 (SN 03-857, OFI Testing Equipment Inc., Houston, USA) (Rotor radius 1.84 cm, bob radius 1.73 cm, bob height 3.8 cm, shear gap 0.1 cm). The viscometer bob, sleeve and cup were cleaned and dried. The viscometer was operated in air for 2 min to loosen up the bearings and gears. The cup was filled to the scribed line with the liquid detergent sample and placed on the viscometer stage. The stage was moved upward until the sample level is to the fill line on the sleeve. The liquid detergent was missed on the STIR setting for 10 s. The knob was rotated to the 600 speed setting. When the dial reading stabilized, the reading was then recorded. This step was repeated for 300, 200, 100, 60, 30, 6 and Gel (3) speed setting. For measuring the gel strength, as soon as the sleeve stopped rotating, the knob was rotated to GEL. After 10 s, the maximum dial deflection was recorded. This is the 10 s gel strength. The concentration of the liquid detergents with CMC used was 1% concentration. This was carried out in triplicate. The viscosity, Ŋ, (mPa.s) was calculate using (Eq 5).

$$Ŋ = \frac{KF\Theta}{RPM} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{Eq 5}$$

K= Machine constant for the Bob and Rotor combination, (300)
F= Spring Factor (1.0)
θ = Dial Reading
RPM = Rotational speed
Apparent Viscosity (AV), mPa.s = 600RPM reading/2

2.11 CLEANING ACTION OF LIQUID DETERGENT

The cleaning action of the liquid detergent was determined by the method used by Oluwasina (2018). A 0.1% (v/v) liquid detergent solution was prepared using distilled water. A 150 mL of this 0.1% liquid detergent solution was measured into 250 mL beaker. A dry clean fabric was weighed (wo) and then soiled with dirty. After this, the weight of the soiled fabric was also weighed (w1) and recorded and this was suspended in the liquid detergent solution. It was then agitated for 5 min at 120 rpm in a mechanical shaker and then allowed to stand for 15 min. The fabric was then removed and suspended in 100 mL of distilled water for 10 min. The fabric was removed and dried at room temperature. The weight of the dry fabric was weighed (ws2) and recorded. A control sample was prepared using 150 mL of tap water without detergent solution and all previous washing steps repeated. The weight after drying was given as wc2. The cleaning action was calculated using the following equation;

$$CA\% = 100\left(1 - \frac{T}{B}\right) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{Eq 6}$$

Where:
CA is cleaning action
T is the weight of soil remaining in the cloth sample after washing = ws1 – ws2
B is the weight of soil remaining in the control sample after washing = wc1 – wc2

3. METHODOLOGY

The percentage yield of cellulose was 33.37±0.12%. Alabi et al., (2020) reported cellulose yield of 30.43-37.03% for M. paradisiaca and 58.20% for Tithonia diversifolia stalk. The percentage yield of CMC increased with increasing amount of chloroacetic acid (Table 1). It was due to the substitution of hydroxyl group of cellulose molecules with carboxymethyl group which lead to a higher mass (Tasaso, 2015). 12g of chloroacetic acid gave the highest percentage yield of CMC which was 64.10±0.17%. Alabi et al., (2020), also in their work obtained CMC yield of 33.21% (M. paradisiaca (unripe peel), CMC), 41.37% (Musa paradisiaca CMC) and 62.57% (Tithonia diversifolia stalk CMC). It had been reported that yield of CMC production could be affected by reaction temperature, concentration of sodium hydroxide used and the etherifying reagents (chloroacetic acid) (Silva et al., 2004).

Table 1. Result Data for synthesis and characterization of CMC

Cellulose Yield (%)	33.37±0.12			
CMC Yield (%)	51.17±0.22	59.5±0.71	63.17±1.41	64.10±0.17
CMC D.S	0.67±0.01	0.76±0.02	0.87±0.00	0.91±0.014
Swelling Capacity of CMC (mL/mL)	550±0.24	550±0.24	850±0.43	926.67±8.16

*Values are means of three replicates ± standard deviation

3.1 CHARACTERIZATION OF LIQUID DETERGENT Cellulose and CMC Yield

The percentage yield of cellulose was 33.37±0.12%. Alabi et al., (2020) reported cellulose yield of 30.43-37.03% for M. paradisiaca and 58.20% for Tithonia diversifolia stalk. The percentage yield of CMC increased with increasing amount of chloroacetic acid (Table 1). It was due to the substitution of hydroxyl group of cellulose molecules with carboxymethyl group which lead to a higher mass (Tasaso, 2015). 12g of chloroacetic acid gave the highest percentage yield of CMC which was 64.10±0.17%. Alabi et al., (2020), also in their work obtained CMC yield of 33.21% (M. paradisiaca

(unripe peel), CMC), 41.37% (Musa paradisiaca CMC) and 62.57% (Tithonia diversifolia stalk CMC). It had been reported that yield of CMC production could be affected by reaction temperature, concentration of sodium hydroxide used and the etherifying reagents (chloroacetic acid) (Silva et al., 2004).

3.2 CHARACTERIZATION OF LIQUID DETERGENT

The degrees of substitution of CMC produced in this work were in the range of 0.67-0.91 as shown in Table 1. As shown in this table, the D.S of CMC increased by increasing amount of chloroacetic acid, this result is similar to that of Nwokocha et. al, (2008). The higher amount of chloroacetic acid produces more carboxy groups in the reactants. Adinugraha, et al. (2005) synthesized CMC from pseudo stem of banana with D.S in the range of 0.26-0.75. According to Asi et al., (2017) the part of the solvent in the cellulose etherification is to offer miscibility and accessibility of the etherifying reagent (chloroacetic acid) to the reaction centers of the cellulose chain rather than glycolate formation. Chloroacetic acid as an etherifying group partakes in reaction and offer carboxymethyl groups for substitution at C-2, C-3 and C-6. It must be noted that degree of substitution value is affected by cellulose source.

3.3 CHARACTERIZATION OF LIQUID DETERGENT

Table 1 shows the swelling capacity for each modified form of CMC. The CMC with D.S 0.91 had swelling capacity of 926.67±8.16, followed by CMC with D.S 0.86 with swelling capacity of 850±0.43, CMC with D.S 0.77 had swelling capacity of 750±0.90 and CMC with D.S 0.67 had swelling capacity of 550±0.24. The swelling capacity obtained by Alabi et al., (2020) were 350.14±0.13 (M. paradisiaca (unripe peel), CMC), 553.37±0.11 (Musa paradisiaca CMC) and 687.01±0.17 (Tithonia diversifolia stalk CMC). Abe et al., (2018), reported swelling capacities of 748.17g/g and 801.73g/g for C. gigantea CMC and G. sepium CMC respectively. Latif et al., (2005) reported that D.S of CMC is directly proportional to swelling capacity. Increase in degree of substitution increases the swelling capacity of CMC. The swelling volume might have been strongly influenced by D.S (Waring and Parsons 2001). The swelling capacity could be affected by the source of cellulose.

3.4 CHARACTERIZATION OF LIQUID DETERGENT

Fourier Transform Infrared Spectroscopy (FT-IR) shows the functional group present in the polymer and the chemical changes in the various forms of the polymer structures. Cellulose have some prominent functional groups with absorption bands in FT-IR. These functional groups include hydroxyl groups (-OH stretching) at 3200-3600 cm-1, hydrocarbon groups (-CH2 scissoring) at 1400-1450 cm-1, ether groups (-O-) at 1000-1200 cm-1. Cellulose etherification with chloroacetic acid causes the OH groups (at position 2, 6, and 3) in cellulose to be replaced with CH2COO- group which causes changes in the absorption spectrum of related bands. This lead OH groups to weaker peak and creates a new peak. However, from Figure 1, the differences can be observed in CMC absorption bonds, by the presence of a strong absorption band at 1565 cm-1 which indicate the presence of carboxyl group (-COO-). This shows that the hydroxyl group in the cellulose has been substituted with carboxymethyl group during carboxylation reaction (Hutomo et al., 2012). Muhammad et al., (2015), reported that an absorption band at 1596.56 cm-1 is due to the carboxymethyl group, which confirms the substitution of the hydroxyl group in the cellulose.

The FT-IR spectrum of acidified CMC (H-CMC) as shown in Figure 1 confirms the carboxylation reaction due to the loss of the absorption band at 1565 cm-1 and formation of new peak at 1741 cm-1 which correspond to carbonyl of the undissociated acid (-COOH). The shift in absorption band to higher wavenumber after acidification confirms the presence of the carboxylate ion of carboxymethyl group.

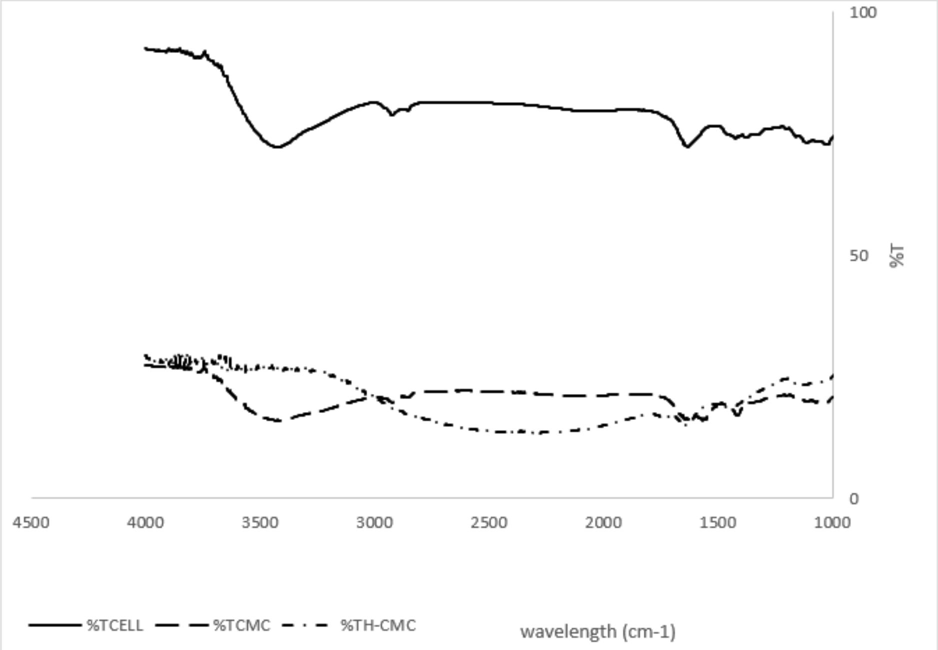

Figure 1. FT-IR spectral of cellulose, carboxymethyl cellulose and acidified carboxymethyl cellulose

3.5 DETERGENT YIELD AND PERCENTAGE ACTIVE DETERGENT

The yield of the detergent in this work was 79.30±6.02%. The percentage active detergent in this work was 21.00±0.73%. Active detergent is used to measure the activity or detergency of the sample and it is the sodium -2-dodecyl benzene sulphonate in the detergent. Azeez and Abegunde reported percentage active detergent of 23.83% for liquid detergent produced with caustic potash from the ash of cocoa pods, 18.62% (liquid detergent produced with caustic potash from the ash of plantain peels) and 17.86% (liquid detergent produced with alkaline obtained from maize cobs ash). The obtained percentage active detergent in this work though higher than some of their percentage active detergent values, their higher percentage active detergent values could be as a result of them using more than one surfactant.

3.6 LATHER VOLUME OF 1% LIQUID DETERGENT

The lather volume and foam capacity of the detergent deals with foaming ability of the detergent. It was determined that the lather volume and foam capacity of detergent with distilled water were 70.20mL and 3.51 respectively which when treated with hard water were 51.4mL and 2.57 respectively. Similarly, the detergent modified with CMC of different degrees of substituion with hard water have lather volumes and foam capacities of 51.4mL and 2.57 each which were the same with that obtained from liquid detergent and hard water. These values for liquid detergent with distilled water were the same with that obtained from morning fresh liquid detergent which had lather volume (70.40mL) and foam capacity (3.52). This observation shows that CMC had no significant effect on the lather volume and foam capacity. The lower values obtained when hard water was used were as a result of the presence of Ca2+ and Mg2+ ions in the hard water which form scums and reduce lather volume. The lather volume is a function of the active detergent, this is the sodium-2-dodecyl benzene sulphonic acid in the detergent. The higher the active detergent percentage in the liquid detergent, the more the foaming and the lather volume of the detergent. Azeez and Abegunde (2016), reported lather volumes in the range 3.162 to 4.218. The higher values obtained in their work could be as a result of them using more than one surfactant. It therefore means that carboxymethyl cellulose does not increase lather volume or increase foaming ability of detergent but rather stabilizes the foam produced.

Table 2. Result Data for Production, Modification and Characterization of Liquid Detergent

Parameter	Physicochemical Property				
Detergent Yield (%)	79.30±6.02				
Active Detergent (%)	21.00±0.73				
Ph	6.12				
Liquid Detergent modified with CMC	Liquid Det. Thickened with 0.67 D.S	Liquid Det. Thickened with 0.76 D.S	Liquid Det. Thickened with 0.86 D.S	Liquid Det. Thickened with 0.91 D.S	Liquid Det. Without CMC
Lather volume in Distilled water (mL)	70.20±0.04	70.20±0.14	70.20±0.06	70.20±0.11	70.20±0.10
Foam capacity in distilled water	3.51±0.05	3.51±0.09	3.51±0.01	3.51±0.04	3.51±0.00
Lather volume in hard water (mL)	51.30±0.09	51.30±0.17	51.30±0.43	51.30±0.14	51.30±0.43
Foam capacity in hard Water	2.57±0.009	2.57±0.009	2.57±0.02	2.57±0.01	2.57±0.02
Viscosity (mPa.s)	110±0.00	616.66±81.65	1833.33±18.67	2750±0.00	43.33±8.16
Power law index	0.460	0.445	0.631	0.663	0.756
Cleaning action (%)	48.8±1.98	51.27±0.91	51.60±2.04	53.46±0.86	32.47±4.60

*Values are means of three replicates ± standard deviation

3.7 LIQUID DETERGENT pH

The measured pH for the liquid detergent was 6.12. This means that the liquid detergent was weakly acidic. Oluwasina et al., (2018) produced liquid detergent with pH 6.5 in their work.

3.8 LIQUID DETERGENT RHEOLOGY

The viscosity of the 1% concentration liquid detergent was determined by the process described above using 8-speed rotational viscometer. From Table 2, at fixed shear rate of 10.21 sec-1, the liquid detergent thickened with 0.91 D.S had the highest viscosity value of 2750 mPa.s, followed by liquid detergent thickened with 0.86 D.S which had viscosity of 1500 mPa.s, then by liquid detergent thickened with 0.76 D.S with viscosity value of 650 mPa.s, then by liquid detergent thickened with 0.67 D.S with 110mPa.s and lastly liquid detergent without carboxymethyl cellulose which had 40mPa.s. The viscosity values were lower compared to viscosity obtained from morning fresh liquid detergent (5250 mPa.s). The lower value could be affected by the D.S of carboxymethyl cellulose used. Smulders, 2002, has reported that CMC acts as a thickening agent and as such are used in various industries. Oluwasina (2018), reported in his work viscosities of liquid detergent fortified CMC; Chromolaena odorata -CMC-Detergent had 954cP, Penniseteum purpureum -CMC-Det had 968cP, Ananas comosus -CMC-Det had 850cP, while Detgrade-CMC-Det had 1024cP. The degree of substitution is directly proportional to viscosity. The liquid detergent thickened with 0.91 D.S higher viscosity which could be linked to its higher degree of substitution, as swelling ability is a function of the degree of substitution, (Latif et a., 2005). Also, according to Heinze and Koschella (2005) the higher the degree of substitution the more soluble and swelling. The CMC with 0.91 D.S have more of the hydroxyl group been substituted by the carboxymethyl group with increase both the swelling ability and the solubility of the CMC with lead to a more entangled network leading to the observed increased viscosity (Fijan et al., 2007, Gong et al., 2012).

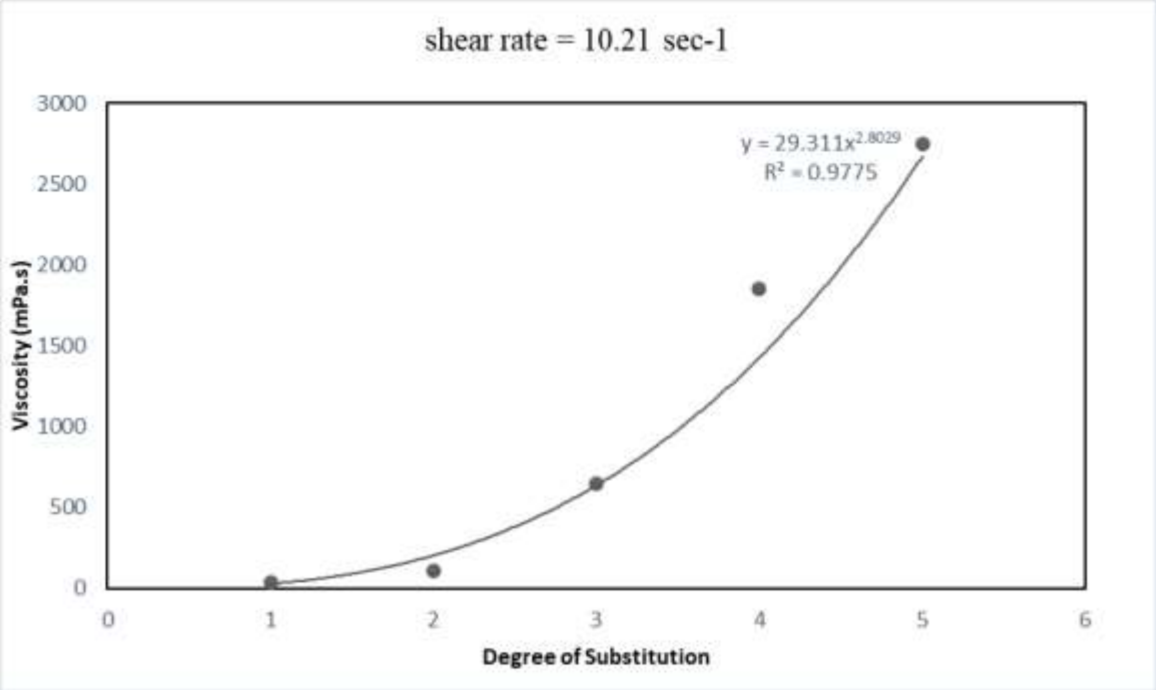

Figure 2. Effects of degree of substitution on viscosity of 1% liquid detergent

The viscosity decreases with increase of shear rate, which can be characterized by Non-Newtonian behavior as shown in Figure 3 and given by the power law in Table 2. For higher shear rate, disruption predominates over formation of new entanglement, molecules align in the direction of the flow and the viscosity decreased with increased shear rate. The shear rate responsible for the change from Newtonian flow to shear-thinning behavior goes to lower as the degree of substitution increases. The polysaccharide chains of CMC can produce a network by intertwining with each other making the solution have certain viscosity (Morris et al., 1981). Such networks can be disrupted rapidly during shear, which may be the sole reason for the shear-thinning nature observed in the detergent. Changes in the plotted graph noted for the liquid detergent modified with CMC of varying D.S may be associated with the polydispersity of the polymer. Xiquan et al., (1990) demonstrated in X-ray diffraction experiments that the CMC aqueous solution for D.S less than 0.82 the derivative crystalline regions are present, i.e the polymer chains are aggregated by hydrogen bonds. It follows that an inter-chain hydrogen bonds exist mainly between OH and CH2OOH. As D.S increases, there is a decrease in the number of OH group and an increase in the number of CH2OO- groups, the presence of which may lead to the destruction of inter-chain hydrogen bonds and the disappearance of aggregates. Consequently, at high D.S values, CMC is molecularly dispersed in water (Lopez et al., 2015). The difference in the shear thinning obtained from liquid detergent thickened with 0.67 D.S and 0.76 D.S show that the lowering of the D.S leads to the cross-linking of the polyion molecules. This led to the lower shear-thinning properties in 0.86 D.S and 0.91 D.S liquid detergents as shown in figure 3.

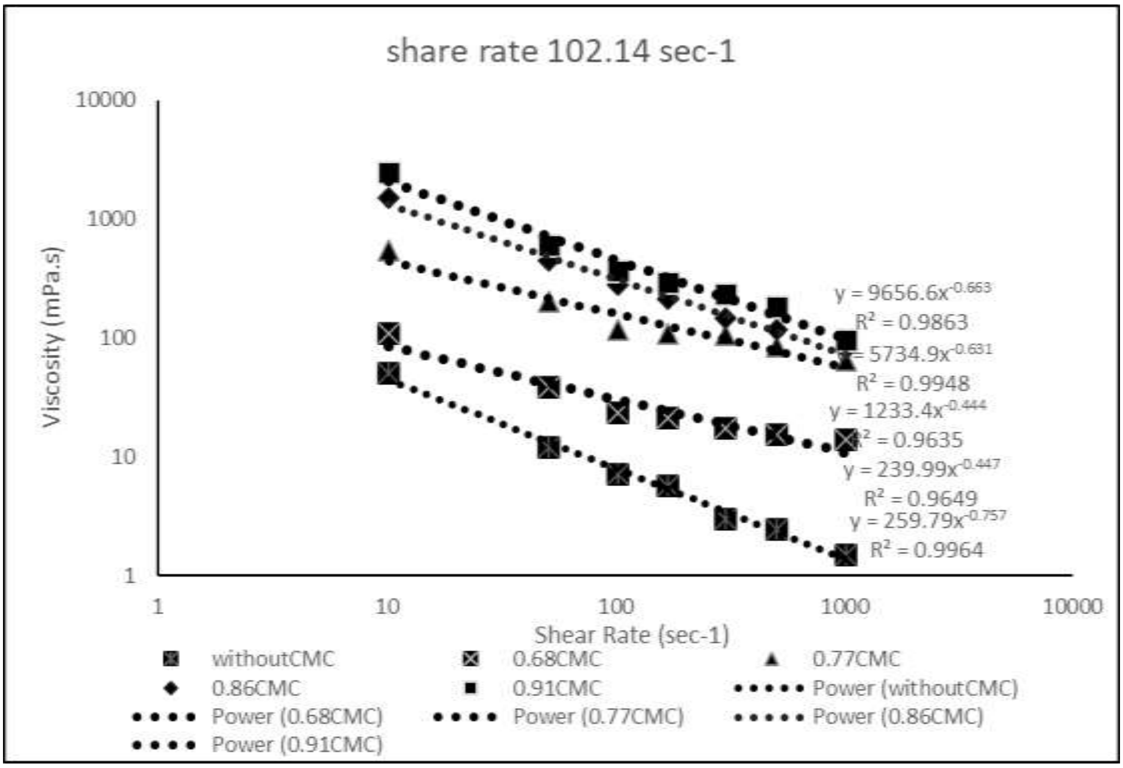

Figure 3. Effects of time on viscosity of 1% liquid detergent at fixed shear rate (102.14 sce-1)

3.9 CLEANING ACTION OF 1% LIQUID DETERGENT

The cleaning action of the liquid detergent shows that carboxmethyl cellulose had a great influence in the cleaning action of the liquid detergent since liquid detergent solution with CMC was able to record higher values than detergent without CMC. The result showed that liquid detergent thickened with 0.91 D.S had the highest cleaning action of 53.46±0.86, followed by liquid detergent thickened with 0.86 D.S with cleaning action value of 51.60±2.04%, which was then followed by liquid detergent thickened with 0.76 D.S with 51.27±0.91%, liquid detergent thickened with 0.67 D.S with 48.80±1.98%, and lastly detergent without CMC which is 32.47±4.60% as shown in table 4.6. The increased cleaning action of the CMC based detergent could be as a result of anti-redeposition action of carboxymethyl cellulose (Smulders, 2002), which would have prevented the dirt from been re-deposited on the fabric. Oluwasina (2018), reported cleaning action of liquid detergent as follows, 25.67%, 25.48%, 25.21%, 25.00% and 17.50%. Abe, et al., (2018), have also reported cleaning action of liquid detergent modified with CMC as 46.517%, 42.623%, 44.016% and 25.466%. The performance of liquid detergent modified with carboxymethyl cellulose would probably have been influenced by the added carboxymethyl cellulose. The higher cleaning action could be as a result of the percentage of active detergent and possibly the higher degree of substitution of the carboxymethyl cellulose. Also, the cleaning action of morning fresh liquid detergent (61.50%) determined was higher compared to the cleaning action obtained. The difference could probably be that the carboxymethyl cellulose used had higher-ups D.S. The difference in the cleaning action between liquid detergent modified with carboxmethyl cellulose and liquid detergent without carboxymethyl cellulose could be that the added carboxymethyl cellulose has assisted in the precipitation of the hard water ions (calcium and magnesium ions), thus promoting the surfactant ability of the 2-dodecylbenzene sulphonic acid in soil removal, because it has been reported by Abeliotis et al., (2015) that hard water affects the performance of detergent, this might have caused the low performance of detergent without carboxymethyl cellulose. Also, the sodium- 2-dodecylbenzene sulphonate would perhaps dissolve in the soil as it comes in contact with the soil and then might form a layer around the soil. This formed layer might be repelled by another soil droplet because of their negative charges and thus drop down inside the water, this would be aided by agitation. The carboxymethyl cellulose on the other hand is the anionic carboxymethyl ether of cellulose (Basavaraja et al., 2013) which would have attached to the soiled fabric and might have ionized in the water to produce negatively charged fabric. The negatively charge fabric would repel negatively charge soil dirt of the hydrophobic end of the detergent causing it not to get re-attached. This might be the reason why liquid detergent modified with CMC has higher soil removal.

4. CONCLUSION

This study emphasis on the synthesis of liquid detergent of known concentration and the rheological behaviors of liquid detergent modified with CMC of different D.S from banana pseudo stem. Within the range of explored parameters, our investigation reveals that the viscosities of the liquid detergents modified with CMC were greater than that of liquid detergent without CMC. The various liquid detergents produced exhibit non-Newtonian behavior as a result of decrease in viscosity as the share rate increases. Also, the cleaning properties of the liquid detergent were higher with liquid detergent modified with CMC which also varies with the D.S. This is attributed to the anti-redeposition properties of CMC. This investigation has proven that addition of CMC has been shown to be beneficial. Nevertheless, the process by which the rheological behavior of the liquid detergent can be used for quality control was not examined and further work is needed. Additional factors affecting the behavior of liquid detergents formulations, such as temperature variations and the role of individual ingredients, need to be further investigated.

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