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Preparation and Characterization of Carboxymethyl Cellulose (CMC) from Cassava peels, Irish Potato, Yam peels

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***ABSTRACT**: The rise in the application of cellulose derivatives (Carboxymethyl Cellulose (CMC)) in the oil and gas industry has increased the search for cellulose based raw materials. CMC are in high demand as additives in drilling mud for viscosity and fluid loss control. Therefore, potential source of local raw materials for its preparation will help in reducing cost. In this work, raw materials such as Cassava peels, Irish potato and Yam peels were processed and Cellulose was extracted using sodium hydroxide (NaOH) solution. The cellulose extracted was converted to CMC with different concentrations of NaOH and etherified with monochloroacetic acid(MCA).The yield of CMC from Cassava peels, Irish potato and Yam peels was 0.080g ,0.547g and 0.995g with a viscosity of 21.2cp, 40cp and 35cp respectively. The result shows that increase in the concentration of NaOH increases the yield of CMC, degree of substitution with Yam peels having the highest yield.*

***KEYWORDS**: Cassava peels, Irish potato, Yam peels, Carboxymethyl cellulose, degree of substitution,Yield*

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I. INTRODUCTION

Cellulose derivatives have recently found its application in different fields. Carboxymethyl Cellulose (CMC), one of the most common derivatives (modified cellulose) with a linear, long-chain and an anionic polysaccharide prepared by reacting monochloroacetic acid(MCA) with alkali cellulose is widely used in the oil and gas industry for different application. CMC are of different grades and ranges of colour (white, cream, brown) and are tasteless and odorless powder(Mario et al.2005).CMC preparation are in two reaction steps, mercerization and etherification by slurry process(Heinze and Koschella,2005). In the slurry method, cellulose is suspended in Sodium Hydroxide (NaOH) solution with an excess of alcohol(Ethanol or Isopropanol) at 20^{o}C to30^{o}C(Fink et al.,1995). This suspension and treatment forms alkali cellulose(Na-cellulose) which is reacted with monochloroacetic acid and an etherification agent at about 50^{o}C to 70^{o}C and NaOH reacts simultaneously with the acetic acid to form sodium glycolate and chloride(Ambjornsson et al.,2013). The slurry process enhances uniform mixture of the components in the reactor with the alcohol facilitating even distribution of the chloroacetate in the reaction which enriches NaOH in the cellulose and decreases supramolecular order causing uniform etherification. CMC quality depends on the number of carboxyl groups attached to the cellulose. The number of carboxyl groups attached to the powder is the Degree of Substitution (DS) and its value is affected by the ratio of sodium monochloroacetate and the powder material(Spychaj et al.,2013). The higher the sodium monochloroacetate-powder ratio with an increase in carboxymethylation temperature, the higher the degree of substitution (DS) and reduction in the reaction efficiency (Distantina et al.,2018). Gulati et al.(2014) studied the production of water-soluble CMC and found that DS increased on increasing the concentration of NaOH and MCA with maximum DS of 0.5 obtained with 20% NaOH and 20%MCA concentration at 50^{o}C with 1.28g CMC/g cellulose optimized. Hong(2013) observed that the absolute degree of substitution(DS_{abs}) of CMC prepared from sugarcane Baggasse increases with increasing concentrations of NaOH up to 25% and decreased at a higher concentration of NaOH. Other properties such as water vapor permeability, molecular weight and mechanical properties were found to have similar trend with DS_{abs} and attributed to the crystalline cellulose becoming more amorphous. Jia et al.(2016) observed that alkalizing microcrystalline cellulose from corncob at 30^{o}C for 50min and etherifying at 65^{o}C for 3hours with 85% ethanol as solvent yielded optimum value of carboxymethylation cellulose with molar ratio of cellulose/NaOH/MCA as 1:1:1.Optimum reaction of alkalization was attained at 20%NaOH and etherification at the mass fraction ratio of MCA to cellulose of 1.0 with the highest degree of substitution and solubility(Sunardi et al., 2017). Due to the wide application of CMC in various industries, many research and studies have been done to produce CMC from different sources such as durian rind(Rachtanapun et al.,2012), sago waste(Pushpamalar et al.,2006), sugar beet pulp(Togrul and Arslan,2003), papaya peel(Rachtanapun et al.,2007), mimosa pigra peel(Rachtanapun and Rattanapanone,2011). In this work, other sources of cellulose based materials such as Cassava peels, Irish potato and Yam peels were examined to produce CMC with their Degree of Substitution (DS).

II. MATERIALS AND METHOD

2.1 Materials and Apparatus

Cellulose based materials used in this research are Cassava peels, Irish potato and Yam peels. Other chemicals/reagents are Sodium Hydroxide(NaOH), Monochloroacetic acid(MCA), Chloroethanoic acid, Isopropanol, Methanol, Ethanol, Distilled water, Acidified Sodium Chlorite($NaClO_2$), Hydrochloric acid(HCl), Acetone, Hydrogen Peroxide(H_2O_2), $HNO_{3,}$ Potassium Bromide(KBr) .The apparatus are Beaker, flask, graduated cylinder, test tubes, volumetric pipettes, burettes, glass and petri dish, porcelain evaporation dish, filter paper, digital scale, oven, centrifuge, thermometer, bursen burner, soxhlet, blender, vacuum pump, water bath, pH meter, stirrer, rotational viscometer, funnels

2.2 Procedure and Preparation of CMC

2.2.1 Preparation from Cassava Peels

- White cassava peels were sundried for twenty four (24) hours and grinded in to powder and sieved with a 100µm size screen.
- 5.5 grams of the powder was measured and reacted with 9.5 mol of aqueous Sodium Hydroxide(NaOH).
- The solution was stirred for 30 minutes at room temperature, filtered and washed with 78% ethanol and distilled water to remove the alkali.
- The residue(cellulose) was heated at 60^{o}C and 3.5 grams of acid Sodium Monochloroacetate reacted with 3grams of heated residue(sodium cellulose) and dissolved in 100ml of deionize water.
- 2ml of Isopropanol was added to the solution and heated for one hour at a temperature of 70^{o}C.
- The solution was allowed to cool for fifteen(15) minutes , filtered and washed with 70% ethanol for three(3) times with deionize water and residue(CMC) heated to 60^{o}C until dried.

2.2.2 Preparation from Irish Potato

- Irish Potato peels were sliced and dried for two days, grinded and sieved with a 100µm size screen.
- 4 grams of the powder was measured and reacted with 10.5 mol of aqueous NaOH.
- The solution was stirred for one hour at room temperature, filtered with residue (cellulose) washed twice with75% ethanol and distilled water to remove alkali.
- The residue(cellulose) was heated at 60^{o}C and 3 grams of the heated residue (cellulose) dissolved in 250ml of distilled water with 6 grams of sodium monochloroacetic acid.
- 2ml of Isopropanol was added to the mixture and heated to 75^{o}C for four hours
- The solution was stirred, filtered and residue washed with 75% ethanol and deionized water and residue (CMC) placed in an oven of a temperature of 70^{o}C for 24 hours.

2.2.3 Preparation from Yam peels

- White yam peels were sliced and dried for three (3) days, grinded and sieved with a 100µm size screen.
- 4 grams of the powder was mixed with 7.5 mol of aqueous NaOH.
- The mixture was stirred for one hour at room temperature, filtered and washed with 95% ethanol and distilled water to remove alkali
- The extracted cellulose was dried in oven at 60^{o}C and 3 grams of the cellulose mixed with 100ml distilled water with 15 ml glacial acetic acid, 2 grams of sodium chlorite and 6 grams of sodium monochloroacetic acid added.
- The mixture was stirred and heated at 75^{o}C
- The residue was filtered and washed with 95% ethanol and distilled water and residue(CMC) dried in an oven at 60^{o}C for 24hours.

2.3 Purification of CMC

5grams of the synthesize CMC produced was dissolved in 100ml of distilled water, heated at 80^{o}C and stirred for several minutes. The CMC was centrifuged for one minute at 4000rpm. The dissolved CMC were reprecipitated in 100ml of acetone. The recovered CMC was filtered and dried in a 60°C oven until a constant weight was attained.

2.4. Degree of Substitution (DS) of CMC

The Degree of Substitution (DS) of the CMC produced was determined by back titration. 4grams of the CMC powder was stirred in 75ml of 95% ethanol for 5 minutes with 5ml of HCl added to convert the CMC to its acid form (H-CMC). The solution was stirred for 10minutes after boiling and the mixture separated into two parts, solid and liquid phase. The solid phase was washed with 20ml of 80% ethanol at 60°C with the precipitate washed with a small quantity of anhydrous methanol, filtered, and dried at 100°C for 3 hours and cool in desiccators for 30minutes. 0.5grams of H-CMC was measured and dissolved in 25ml of 0.3M NaOH with 100ml of distilled water added and stirred. The mixture was heated for 10 minutes, and after the products dissolved, the mixture was titrated with 0.3MHCl and Phenolphthalein added as indicator. The titration was repeated for three times and the average volume of the HCl was recorded with the blank also titrated.
The number of COOH was determined with equation (1)

$$nCOOH = \frac{(V_b - V_0)\times M \times 0.059 \times 100}{ms}$$

(1)
The Degree of Substitution was determined using equation (2)

$$Ds = \frac{162 \times nCOOH}{5900 - (58 \times nCOOH)}$$

(2)
Where; Vb = Vol. of HCl for titration of the blank (mL)
Vo= Vol. of HCl for titration of the samples (mL)
M = molar concentration of HCl(mol/L)
ms = mass of sample(g)
molar mass of anhydroglucopyranoze unit ($C_6H_7O_2(OH)_3$) = 162gmol^{-1}
molar mass of CH_2COOH = 59gmol^{-1}

2.5 Fourier Transform Infrared Spectroscopy (FTIR)

Molecular groups of the cellulose were determined using Fourier Transform Infrared Spectrometer. The samples were dried in an oven at 60°C and Potassium Bromide added and compressed to form pellet. The infrared spectra of the samples were measured in the transmission of a wavelength number range of 4000 – 400cm^{-1}.

2.6 Viscosity

2.7grams of the Produced CMC from cassava peels, Irish potato and yams peels were measured and dissolved in 90ml of distilled water in a 100ml beaker. Their viscosities were measured at 25°C and 3rpm with a rotational viscometer.

2.7 Yield Measurement

Product yield, Cellulose yield and CMC yield were determined from equation (3),(4) and (5) respectively.

$$Product\,yield = \frac{Weight\,of\,dried\,CMC}{Dry\,weight\,of\,Cellulose}$$

(3)

$$Yield\,of\,Cellulose(\%) = \frac{Weight\,of\,Cellulose}{Weight\,of\,sample} \times 100$$

(4)

$$Yield\,of\,CMC\,(\%) = \frac{Weight\,of\,dried}{Dry\,weight\,of\,Cellulose} \times 100$$

(5)

III. RESULTS AND DISCUSSION

3.1 Yield of Cellulose and Carboxymethyl Cellulose(CMC)

Cellulose and CMC yield from the three raw materials (Cassava peels,Irish potato, Yam peels) calculated using equation(3), (4), and (5) are presented in Table1.0. Cassava peels have the least cellulose and CMC yield with Yam peels as the highest.

Table 1: Yield of Cellulose and CMC

Samples	Mass (g)	Na cellulose or hemicellulose (g)	C.M.C obtained (g)	Yield of cellulose (%)	Yield C.M.C (%)
Cassava	5.50	3.618	0.080	65.78	2.21
Irish potato	4.00	4.763	0.547	119.00	11.48
Yam	4.00	9.183	0.995	225.00	10.84

3.2 Properties of CMC from Cassava Peels, Irish Potato, Yam Peels

The viscosity, colour, solubility capacity and film formation ability of the CMC produced are shown in Table 2.0. CMC produced from Irish potato has the highest viscosity with cassava source as the least. The viscosity obtained from the three sources is within the commercial range for low viscosity CMC of 20 - 50cp in 3% concentration of the solution. The low viscosity is due to the presence of some amount of NaOH and degradation of polysaccharide.

Table 2: Properties of CMC

CMC Source	Colour	Form	Viscosity at 25^{o}C	DS	Solubility in water	Film formability	RPM
Cassava Peels	Brown	Powder	21.2cp	0.705	Soluble	Able to form	3
Irish Potato	Light Brown	Powder	40cp	0.45	Soluble	Able to form	3
Yam peels	Colourless	Powder	35cp	0.60	Soluble	Able to form	3

3.3 Degree of Substitution (DS)

The value of DS is a determinant in the water solubility of CMC. It is fully soluble when above 0.4 and insoluble below 0.4. The Degree of Substitution (DS) value from this work calculated from equation (2) is within the range of acceptable DS for solubility and is presented in comparison with those of other sources in Table 3.0. CMC from Cassava peels have the highest DS with Irish potato the least.

Table 3: DS value for CMC from this work and other sources of cellulose

Sources of Cellulose	Degree of Substitution(DS)	References
Irish potato, Yam peels and cassava peels	0.45 – 0.705	This work
Sugar beets pulp	0.11 - 0.67	Togrul and Arslan(2003)
Cotton fiber	0.15 – 0.70	Heydarzadeh et al.(2009)
Water hyacinth	0.24 – 0.73	Barai et al(1996)
Sago waste	0.33 – 0.82	Pushpamalar et al.(2006)
Lamtan Camera	0.20 – 1.122	Varshney et al.(2006)
Banana pseudo stems	0.26 – 0.75	Adinugraha et al.(2005)

IV. CONCLUSION

Cellulose was extracted from Cassava peels, Irish potato, and Yam peels through alkali treatment and successfully converted to Carboxymethyl Cellulose (CMC) using Sodium Hydroxide (NaOH) and etherified with monochloroacetic acid(MCA). The degree of substitution determined from the three raw materials were above 0.4 and within the range of water solubility of CMC. The viscosity of the CMC produced is within 20 - 50cp, an acceptable range for fluid loss control additive in drilling mud.

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