



## SODIUM HYDROXIDE-ANTHRAQUINONE AND SODIUM HYDROXIDE-ANTHRAQUINONE-ETHANOL PULPING AND THEIR PREPARED CARBOXYMETHYLCELLULOSE

O.O. Oluwasina\*, L. Lajide and B.J. Owolabi

Department of Chemistry, Federal University of Technology, Akure, Ondo State, Nigeria

\*Corresponding author: oluwasinagbenga@yahoo.com

### ABSTRACT

Alpha-cellulose of 49.44 % to 52.83% was isolated from waste agricultural plants: *Pennisetum purpureum*, *Ananas comosus*, and *Chromolaena odorata*, using sodium hydroxide-anthraquinone and sodium hydroxide-anthraquinone-ethanol mixture as pulping liquors. The results revealed a gradual reduction in the ash, silica and pentosan content from pulp sample to the alpha-cellulose. It was observed that, though with smaller fraction value, the materials obtained using sodium hydroxide-anthraquinone-ethanol mixture as pulping liquors had slightly better properties than those obtained with sodium hydroxide-anthraquinone. Pulp, bleached pulp and alpha-cellulose obtained through sodium hydroxide-anthraquinone-ethanol pulping liquor had lower silica and ash content, but higher yield, viscosity, degree of polymerization and molecular weight. The yields of the prepared Carboxymethyl cellulose ranged from 80.71 % to 91.10 %, the pH ranged from 6.30 to 6.73, ash content of 0.40 to 0.43 %, sodium chloride content of 0.14 to 0.16 %, with moisture ranging from 4.67 to 4.83. The results of the analysis of carboxymethyl cellulose CMC indicated that most of their determined properties were within the specified range of standard recommended such as United State Pharmacopeia and British Pharmacopoeia.

**Keywords:** Pulping, Alpha-cellulose, Carboxymethyl-cellulose; *Pennisetum purpureum*; *Ananas comosus*; *Chromolaena odorata*;

### INTRODUCTION

*Chromolaena odorata* (L.) King and *Pennisetum purpureum* (Schumach) are invasive weedy plants. They are majoreconomic and ecological burden to many tropical and subtropical regions of the world. They are environmental menace due to the danger they pose to crops and forage species (Uyi *et al.*, 2014). The threat of these weeds to agriculture has been of global concern and there is need to find alternative means of utilizing them. Pineapple, *Ananas comosus* (Linn.) Merr., belongs to the family *Bromeleaceae*. Wastes from pineapple leaves

are either composted or burned by farmers thus causes environmental pollution and wasting a potential source of good fibers (Wan and Zainuddin, 2013). The aforementioned plants and other agricultural plants are sometimes considered wastes because of their over production and they have been associated with environmental pollution arising from decaying, littering and burning. In all these agricultural waste abounds cellulose, the most abundant and cheapest natural polymer with annual production of about one trillion tonnes, making it virtually an inexhaustible source of raw materials (Kim *et*

*al.*, 2007; Israel *et al.*, 2007). Cellulose fibre is a class of potential raw materials not only for pulp and paper industries, but also other allied industries that convert cellulose to its derivatives. Being biodegradable, recycling of these products gives it other practical advantages over the petroleum based products in various applications (Johansson, 2012)

Carboxymethyl cellulose is also one of the most important cellulose derivatives. Carboxymethyl cellulose (CMC) uses are based on levels of purity. Unpurified CMC is used for technical applications and highly purified CMC is used for pharmaceutical – and food grade- applications. In its initial application, CMC is used as soil fertilizer, carrier and redeposition inhibitor in detergents (Mohanty *et al.*, 2003). In deep-well drilling, CMC is used as flotation aid in drilling mud (Dolz *et al.*, 2007). Purified products are used in surface coatings, for example in paper industry (Fijan *et al.*, 2009). Together with gelatin, CMC is used as a coacervate to encapsulate ink in the production of non-carbon copy papers (Xiaoji *et al.*, 2009). In food-grade purity, NaCMC is commonly known as cellulose gum or as food additive E 466. In food applications, CMC improves consistency and emulsion stability, controls and provides freeze-thaw stability of deep-frozen products (Heinze and Koschella, 2005; Seiichi and Shosuke, 2000). Carboxymethyl cellulose have been prepared from various agricultural wastes such as water hyacinth, coconut shells (Gaonkar and Kulkarni, 1987), sugar cane bagasse (Tang *et al.*, 1996; Castro and Bueno, 1996), ramie (Castro and Bueno, 1996), wheat and rice straws (Chen *et al.*, 1996), jute (Abdullah, 1991), flax fibers, flax straw (Bochek *et al.*, 2003), soybean husk (Nelson *et al.*, 2000), orange peel (Yasar *et al.*, 2007), papaya peel (Rachtanapun *et al.*, 2007), banana pseudo stem (Hattori *et al.*, 2004) and sago waste (Pushpamalar *et al.*, 2006).

However, there is paucity of information on research work on preparation of carboxymethyl cellulose and its physicochemical properties from the agricultural materials reported in this work. It is our aim to prepare carboxymethyl

cellulose from *Pennisetum purpureum*, *Ananas comosus*, and *Chromolaena odorata*, by using sodiumhydroxide-anthraquinone and sodium hydroxide-ethanol-anthraquinone as pulping liquor. We also aim to ascertain literature claim that addition of certain chemicals to sodium hydroxide could improve pulping ability of liquor. According to Mclaughan (2000), adding ethanol to a caustic soda cook greatly improves its selectivity and degradation of lignin and prevents lignin condensation. (Chai *et al.*, 2007) also ascertains that the presence of sodium hydroxide improves the delignifying ability of ethanol. Adding anthraquinone as catalyst in sodium hydroxide system increases the pulp yields, decreases the kappa numbers, and improves the strength properties (Valladares *et al.*, 1984).

## MATERIALS AND METHODS

The specimens (Pineapple (*Ananas comosus*) leaves, Siam weed (*Chromolaena odorata*) stems and Elephant grass (*Pennisetum purpureum*) stalks) that were used for this research were collected from south western part of Nigeria. All the samples were authenticated at the Department of Crop, Soil and Pest Management, Federal University of Technology, Akure, Ondo State, Nigeria. Stalks were harvested at 10 cm above the ground level. All samples were cleaned to remove dust, sand, dirt and contaminations. They were then cut into chips of about 2-4cm and sun-dried. The samples were milled, screened through 425 µm and stored separately in labeled polyethylene bags for subsequent experiments at room temperature.

### Hot Water Prehydrolysis

Hot water pretreatment was carried out in a 15-litre reconstructed (THR -280B), thermostatically controlled, electrically heated oil bath autoclave digester with an inner stainless steel cooking container at 150 °C with a pressure of 15 psi using 100g plant sample for 90 mins, with solid to liquor ratio of 1:25. The liquor was drained after prehydrolysis and the sample dried to a constant weight at 105°C in an oven.

### Pulping Procedure

Pulping experiments were performed in a 15-litre reconstructed (THR -280B), thermostatically controlled, electrically heated oil bath autoclave digester with an inner stainless steel cooking digester with an inner stainless steel cooking container. Two sets of pulping chemicals were employed. The first had the following pulping conditions parameters: Liquor to fibre ratio was 25:1 (v/w), Temperature was 170°C, Pressure was 15psi, Cooking time was 90 mins and anthraquinone was 0.1% based on the solid fiber content. The second pulping method had in addition to the above parameters, 40% ethanol (95%) based on the liquor. After digestion, the pulp was obtained through filtration. The pulp was thoroughly washed with water until free of residue alkali. The pulp yield was determined gravimetrically as percentage of oven-dried raw materials after drying at 105°C to a constant weight. At the end of the pulping experiment, two sets of pulps were obtained: NaOHAQPulp- pulp obtained from sodium hydroxide and anthraquinone mixture and NaOHAQEtOHPulp obtained from sodium hydroxide, anthraquinone and ethanol mixture. Thus, the pulps obtained are designated as follows, based on the fibre source and pulping method used:

COSA-P: *Chromolaena odorata* NaOHAQPulp,

COSAE-P: *Chromolaena odorata*

NaOHAQEtOHPulp,

PPSA-P: *Peninisetum purpureum* NaOHAQPulp,

PPSAE-P: *Peninisetum purpureum*

NaOHAQEtOHPulp

ACSA-P: *Ananas comosus* NaOHAQPulp,

ACSAE-P: *Ananas comosus*

NaOHAQEtOHPulp

### Bleaching and Isolation of Alpha-Cellulose

The method used for the bleaching and isolation of alpha-cellulose has been described by Oluwasina *et al.* (2014)

### Synthesis of Sodium Carboxymethyl Cellulose

The carboxymethyl cellulose was synthesized according to the method described by Ruzene and Goncalves (2007), as follow; a 5 g alpha-

cellulose was transferred to 500 mL two-necked flask with 92.5 g ethanol and 3.7 g water. A solution of sodium hydroxide (5 g of NaOH and 8 g of water) was added to the mixture, within the addition time of 30 min, under mechanical agitation in a water bath at  $20 \pm 5^\circ\text{C}$ . On completion of the addition, the mixture was agitated for 1h, maintaining the water bath between 15-25°C. After the alkalization, a solution of monochloroacetic acid and ethanol (6.5 g of monochloroacetic acid and 6.5 g of ethanol) was added within 30 min. At the end of the addition, the sample was heated at 60°C and agitated for 3h. The mixture was drained and the solid phase was suspended in 70 % (v/v) methanol and neutralized while in suspension with 90 % (v/v) acetic acid. The suspension was filtered and the precipitate washed repeatedly with ethanol (80 %) and absolute methanol to remove the reaction side products (NaCl), until the filtrates gave negative response to silver nitrate test of chloride. The slurry obtained was suspended in acetone, stirred for 30 min and dried in an oven at  $50 \pm 5^\circ\text{C}$  for 12 h to constant weight. The prepared carboxymethyl celluloses were named after their plant sources as follows: *Peninisetum purpureum*-carboxymethyl cellulose (PP-CMC) *Ananas comosus*-carboxymethyl cellulose (AC-CMC) and *Chromolaena odorata*-carboxymethyl cellulose (CO-CMC). The percentage yield of CMC was calculated based of the weight of oven dried material.

### Determination of the Pulp, Bleached pulp and Alpha-cellulose Properties

Chemical analyses were carried out using standard methods to determine the properties of the pulp, bleached pulp and alpha-cellulose. The yield was determined gravimetrically at percentage of oven-dried raw materials after drying at 105°C to constant weight. Also, the materials were analyzed for moisture, ash, silica, water soluble (cold- and hot- water solubility), 1% soda solubility, ethanol-benzene extractable, acid-insoluble- and acid soluble-lignin, holocellulose, cellulose, kappa number and pentosan in accordance to the following standards: T550om-03, T211om-93, T244om-93, ASTM, 1994, T212om-98, T204om-97,

T222om-98, TUM250, ASTM, 1994, T236CM-85, Al-Showiman, 1998 respectively. Others are beta- and gamma – cellulose of bleached pulp (T550om-03) viscosity (T230om-99, Ibrahim *et al.*, 2010), degree of polymerization (Morton 1996) and molecular weight (Hong *et al.*, 1978) with full details in Oluwasina *et al.* (2014).

#### **Determination of physicochemical properties of CMC**

Physicochemical analysis of the CMC were determined using standard methods; moisture content (United States Pharmacopeia, 2006), ash (Pomeranz and Meloan, 1994), swelling (Okhamafe *et al.*, 1991), degree of substitution (ASTM, 2005) and sodium chloride content (ASTM, 1995; JECFA 1998).

#### **Statistical Analysis**

The data obtained in triplicate were analysis by Probit Analysis using Duncan's Multiple Range Test (DMRT) and Analysis of Variance (ANOVA)

### **RESULTS AND DISCUSSION**

#### **Pulp Pretreatment**

The result of samples pretreatment showed that *C. odorata* had the highest yield of 90.28%, followed by *P. purperum* with 89.34 %, and *A. comosus* had 88.23%, making it the least of all. Liquid hot water has been used to remove simple sugar hemicelluloses from lignocellulose (Verma *et al.*, 2011; Xiao *et al.*, 2011; Mosier *et al.*, 2005), thus the lowest yield obtained from *A. comosus* could be suggestive of the removal of much of hemicellulose sugars.

#### **Pulp sample**

Different physico-chemical properties are obtained from pulp using sodium hydroxide-anthraquinone-ethanol and sodium hydroxide-anthraquinone pulping chemical (Table 1). The pulp yield (Table 1) results revealed that hydroxide- anthraquinone-ethanol pulp had values ranging from 65.2 for ACSAE-P to 67.51 % for COSAE-P, while sodium hydroxide-anthraquinone pulp had yield ranging from 64.30 to 67.20 % .The result showed that there was no much difference in the pulp yield

obtained from the two pulping liquors. Although, literature has it that the addition of anthraquinone and ethanol, separately or in combination to sodium hydroxide cooking could increase pulp yield (Valladares *et al.*, 1984; Janson and Vuorisalo, 1986), this was not the case in this study. The result obtained compared favorably with that of Jahan *et al.* (2007) using soda/AQ vapour phase pulping and soda/AQ pulping liquor under various conditions recorded a yield of 66.2 %, 67.9 % and 69.1 % for Jute fiber, 59.2 %, 59.7 % and 60.2 % for Jute cutting, while 55.8 %, 56. 2% and 56.9 % were recorded for Jute caddies. On the other hand, the ash and silica contents of all materials obtained for sodium hydroxide-Anthraquinone-ethanol pulping chemical were lower than those of sodium hydroxide-anthraquinone. For example, ash content ranging from 3.20 to 3.87% were recorded for COSA-P, PPSA-P, and ACSA-P, Lower values ranging from 2.93 to 3.47% were recorded for COSAE-P, PPSAE-P, and ACSAE-P, respectively. These lower values might be due to the ability of ethanol to swell up the fibre, thereby exposing it to sodium hydroxide penetration, thus solubilize the ash (inorganic substance) and reducing the content in the pulp obtained. The reduction in ash and silica content after pulping recorded in this work was in agreement with the work of Punsuvon *et al.* (2008), Kirci and Akgul (2002), though using different pulping chemicals recorded reduction in ash and silica content of the pulp sample as compared with the original sample. The pentosan content of sodium hydroxide-anthraquinone-ethanol pulping was higher than those of sodium hydroxide-anthraquinone pulping. This could be attributed to the combined effect of the addition of ethanol and anthraquinone which prevented the breaking down of the glucose units in the plant material (Chai *et al.*, 2007), thereby preserving the pentosan present. According to the pentosan result, 0.08 to 0.11% was obtained for sodium hydroxide-anthraquinone pulps, while 0.07 to 0.11% was obtained for sodium hydroxide-anthraquinone-ethanol pulps. Also, the low pentosan content recorded could be attributed to the prehydrolysis treatment. This supports the

claims of Ibrahim *et al.* (1996), that the prehydrolysis of plant materials helps in reducing pentosan content and that pulping would cause greater reduction. Kappa number obtained for Sodium hydroxide-anthraquinone-ethanol was fractionally lower than that obtained for Sodium hydroxide- anthraquinone. The Kappa number obtained for COSAE-P was 14.70 lower than 15.28 of COSA-P, PPSAE-P had 16.10 lower than PPSA-P with 16.50. ACSAE-P 17.56 had lower than ACSA-P having 18.13. Although, there were no much differences in the Kappa number recorded using the different liquor, it might be that the

combination of ethanol and anthraquinone had influence in the reduction. This is because it has been reported that the combination of ethanol and anthraquinone has the ability to remove much of lignin from the pulp, than when either is added alone (Janson and Vuorisalo, 1986). Kappa numbers reported in this study were within the range of those reported by other researchers. For example, Kappa number of 11.9., 21.7., 35.2., 43.4 25.4., 16.00., 11.9., 13.10., and 10.40., are reported in soda/AQ vapour phase pulping of wheat straw at different conditions (Mckean and Jacobs, 1997).

**Table 1: Physicochemical Analysis of Pulp Sample**

Sample	Parameters					
	Yield (%)	Moisture (%)	Silica (%)	Ash (%)	Pentosan (%)	Kappa number
COSA-P	66.38	5.10 <sup>ab,c</sup> ±0.17	1.45 <sup>b</sup> ±0.01	3.20 <sup>b,c</sup> ±0.10	0.08 <sup>b</sup> ± 0.00	15.28 <sup>ab,c</sup> ±0.01
PPSA-P	67.20	5.33 <sup>ab,c</sup> ±0.34	1.54 <sup>c</sup> ±0.02	3.60 <sup>e,f</sup> ±0.10	0.11 <sup>d</sup> ± 0.00	16.50 <sup>c</sup> ± 0.01
ACSA-P	64.30	5.33 <sup>ab,c</sup> ±0.34	1.83 <sup>d</sup> ±0.01	3.87 <sup>f</sup> ± 0.06	0.11 <sup>d</sup> ± 0.00	18.13 <sup>c</sup> ± 0.01
COSAE-P	67.51	4.89 <sup>a</sup> ±0.19	1.30 <sup>a</sup> ± 0.01	2.93 <sup>a</sup> ± 0.06	0.11 <sup>d</sup> ± 0.00	14.70 <sup>ab</sup> ± 0.01
PPSAE-P	67.34	5.33 <sup>ab,c</sup> ±0.00	1.27 <sup>a</sup> ± 0.06	3.20 <sup>b,c</sup> ± 0.10	0.10 <sup>c</sup> ± 0.00	16.10 <sup>ab,c</sup> ±0.01
ACSAE-P	65.20	5.22 <sup>ab,c</sup> ±0.19	1.83 <sup>d</sup> ± 0.06	3.47 <sup>d,e</sup> ± 0.06	0.07 <sup>a</sup> ± 0.00	17.56 <sup>b,c</sup> ± 0.01

Values are means of three replicate ± standard deviation. Column means followed by different letters are significantly different at P< 0.05

*COSA-P: Chromoleana odorata NaOHAQPulp,*  
*PPS-P: Peninisetumpurpurem NaOHAQPulp,*  
*ACSA-P: Ananas comosus NaOHAQPulp,*

*COSAE-P: Chromoleana odorataNaOHAQEtoHPulp,*  
*PPSAE-P: PeninisetumpurpuremNaOHAQEtoHPulp*  
*ACSAE-P: Ananas comosus NaOHAQEtoHPulp*

Table 2: Properties of Bleached Sample

Sample	Parameter											
	Yield (%)	Pentosan (%)	Silica (%)	Ash (%)	kappa number	Beta cellulose (%)	Moisture (%)	Gamma cellulose (%)	Viscosity (cP)	Alpha cellulose (%)	Degree of Polymerization	Molecular weight (g/mol)
COSA-BP	59.84 <sup>ab</sup> ±0.02	0.02 <sup>a</sup> ±0.00	0.90 <sup>d</sup> ±0.10	1.07 <sup>abc</sup> ±0.06	3.49 <sup>b</sup> ±0.01	3.61 <sup>c</sup> ±0.44	4.78 <sup>ab</sup> ±.19	4.40 <sup>c</sup> ±0.04	6.15 <sup>c</sup> ±0.17	51.83 <sup>c</sup> ±0.03	1026.67 <sup>c</sup> ±30	166000 <sup>c</sup> ±45
PPSA-BP	59.96 <sup>ab</sup> ±0.04	0.03 <sup>b</sup> ±0.01	1.02 <sup>d</sup> ±0.01	1.20 <sup>d</sup> ±0.01	4.08 <sup>d</sup> ±0.10	3.95 <sup>d</sup> ±0.05	5.00 <sup>ab</sup> ±.33	4.51 <sup>d</sup> ±0.00	7.75 <sup>b</sup> ±0.011	51.50 <sup>bc</sup> ±0.01	1270.20 <sup>ab</sup> ±21	205667 <sup>ab</sup> ±25
ACSA-BP	55.34 <sup>c</sup> ±0.06	0.04 <sup>c</sup> ±0.00	1.17 <sup>c</sup> ±0.06	1.37 <sup>e</sup> ±0.06	5.41 <sup>e</sup> ±0.10	4.38 <sup>e</sup> ±0.06	4.89 <sup>ab</sup> ±.19	4.63 <sup>e</sup> ±0.00	5.20 <sup>f</sup> ±0.17	46.33 <sup>a</sup> ±0.06	857.67 <sup>c</sup> ±31	138667 <sup>c</sup> ±31
COSAE-BP	60.80 <sup>c</sup> ±0.02	0.02 <sup>b</sup> ±0.00	0.53 <sup>a</sup> ±0.06	0.97 <sup>a</sup> ±0.06	3.32 <sup>a</sup> ±0.10	3.38 <sup>c</sup> ±0.03	4.67 <sup>b</sup> ±0.00	4.44 <sup>c</sup> ±0.03	7.75 <sup>b</sup> ±0.21	52.98 <sup>a</sup> ±0.01	1270.07 <sup>a</sup> ±20	205667 <sup>ab</sup> ±25
PPSAE-BP	60.09 <sup>c</sup> ±0.03	0.03 <sup>b</sup> ±0.00	0.77 <sup>bc</sup> ±0.06	1.10 <sup>bc</sup> ±0.00	3.95 <sup>c</sup> ±0.04	3.25 <sup>a</sup> ±0.04	5.00 <sup>ab</sup> ±.00	4.03 <sup>a</sup> ±0.03	8.07 <sup>a</sup> ±0.12	52.81 <sup>d</sup> ±0.02	1310.13 <sup>a</sup> ±20	213000 <sup>a</sup> ±55
ACSAE-BP	57.14 <sup>a</sup> ±0.03	0.04 <sup>c</sup> ±0.01	0.87 <sup>c</sup> ±0.06	1.17 <sup>c</sup> ±0.06	5.28 <sup>d</sup> ±0.02	3.35 <sup>ab</sup> ±0.09	4.78 <sup>ab</sup> ±.19	4.35 <sup>b</sup> ±0.02	5.75 <sup>d</sup> ±0.17	49.44 <sup>ab</sup> ±0.04	957.33 <sup>d</sup> ±29	155000 <sup>d</sup> ±32

Values are means of three replicates ± standard deviation. Column means followed by different letters are significantly different at P< 0.05

COSA-BP-*Chromolaena odorata* NaOHAQbleached-pulp,  
 PPSA-BP -*Peninisetumpurpurem* NaOHAQbleached-pulp,  
 ACSA- BP-*Ananas comosus* NaOHAQbleached- pulp,

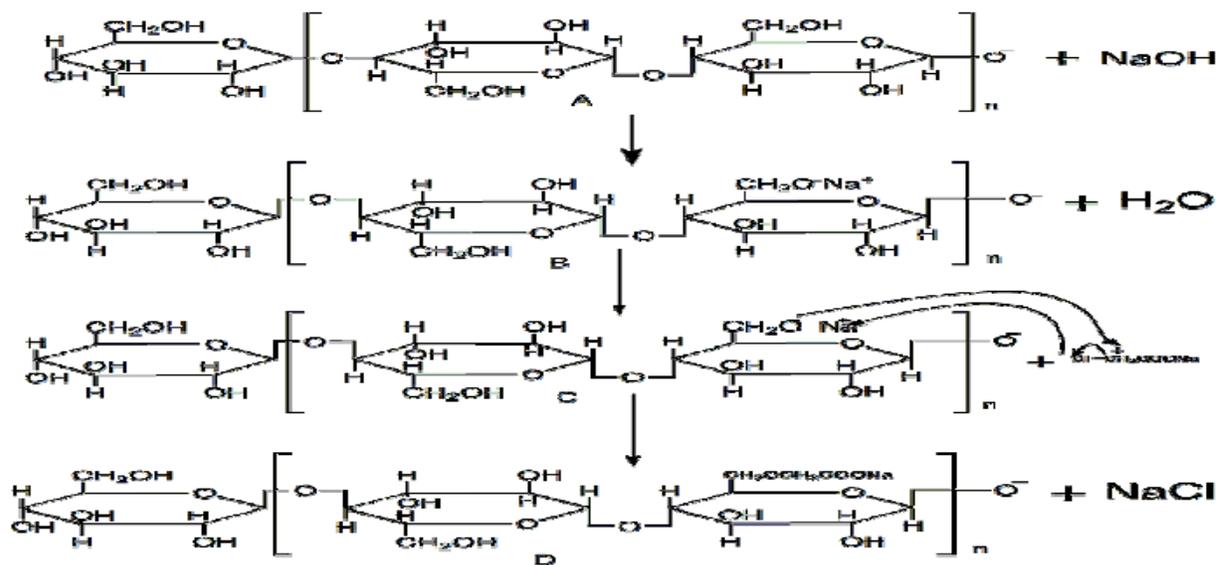
COSAE-BP-*Chromolaena odorata*NaOHAQEtOHbleached-pulp  
 PPSAE-BP-*Peninisetumpurpurem* NaOHAQEtOHbleached-pulp  
 ACSAE-BP- *Ananas comosus* NaOHAQEtOHbleached-pulp

Table 3: Physicochemical Properties of Alpha-cellulose

Parameter Samples	Parameters						
	Pentosan (%)	Silica (%)	Ash (%)	Moisture (%)	Viscosity (cP)	Degree of polymerization	Molecular Weight(g/mol)
COSA-AC	0.01 <sup>a</sup> ±.00	0.05 <sup>d,e,f</sup> ±0.01	0.57 <sup>b,c</sup> ±.03	4.11 <sup>a,b</sup> ±.02	5.53 <sup>c</sup> ±0.17	918.33 <sup>c</sup> ±30	148667 <sup>c</sup> ±31
PPSA-AC	0.01 <sup>a</sup> ±.00	0.06 <sup>f</sup> ±0.00	0.70 <sup>d</sup> ±.00	4.68 <sup>f</sup> ±.02	5.09 <sup>d,e</sup> ±0.06	837.00 <sup>d,e</sup> ±12	135667 <sup>d,e</sup> ±23
ACSA-AC	0.02 <sup>a</sup> ±.00	0.05 <sup>d,e</sup> ±.01	0.83 <sup>a</sup> ±.06	4.25 <sup>c</sup> ±.04	4.91 <sup>e,f</sup> ±0.11	801.00 <sup>e,f</sup> ±22	129667 <sup>e,f</sup> ±35
COSAE-AC	0.01 <sup>a</sup> ±.00	0.04 <sup>a,b,c</sup> ±.00	0.47 <sup>a</sup> ±.06	4.10 <sup>a</sup> ±.00	6.95 <sup>a</sup> ±0.06	1153.33 <sup>a</sup> ±11	187000 <sup>a</sup> ±32
PPSAE-AC	0.01 <sup>a</sup> ±.00	0.05 <sup>c,d,e</sup> ±.00	0.67 <sup>b</sup> ±.06	4.56 <sup>d,e</sup> ±.10	6.58 <sup>b</sup> ±0.11	1096.67 <sup>b</sup> ±30	177667 <sup>b</sup> ±41
ACSAE-AC	0.02 <sup>a</sup> ±.00	0.04 <sup>b,c,d</sup> ±.00	0.50 <sup>b</sup> ±.00	4.20 <sup>b,c</sup> ±.00	5.13 <sup>d</sup> ±0.11	844.00 <sup>d,e</sup> ±21	136667 <sup>d</sup> ±35

Values are means of three replicate ± standard deviation. Column means followed by different letters are significantly different at P< 0.05

COSA-AC-*Siam weed* NaOHAQAlpha-cellulose  
 COSAE-AC-*Siam weed* NaOHAQEtOHAlpha-cellulose  
 PPSA-AC-*Peninisetumpurpurem*NaOHAQAlpha-cellulose,  
 PPSAE-AC-*Peninisetumpurpurem*NaOHAQEtOHAlpha-cellulose  
 ACSA-AC-*Ananas comosus* NaOHAQAlpha-cellulose,  
 ACSAE AC- *Ananas comosus* NaOHAQEtOHAlpha-cellulose



Scheme 1: Reaction for preparation of CMC

Table 4: Physicochemical Properties of Carboxymethyl Cellulose

Parameters	Samples					
	COSA-CMC	PPSA-CMC	ACSA-CMC	COSAE-CMC	PPSAE-CMC	ACSAE-CMC
Yield (%)	80.71	81.84	86.84	87.99	91.10	87.99
NaCL (%)	0.16 <sup>a</sup> ±0.01	0.16 <sup>a</sup> ±0.01	0.16 <sup>a</sup> ±0.01	0.15 <sup>a</sup> ±0.01	0.15 <sup>a</sup> ±0.01	0.14 <sup>b</sup> ±0.01
DS	0.31 <sup>d</sup> ±0.01	0.30 <sup>b</sup> ±0.01	0.26 <sup>a</sup> ±0.01	0.34 <sup>e</sup> ±0.01	0.33 <sup>c</sup> ±0.01	0.28 <sup>b</sup> ±0.01
Ash (%)	0.43 <sup>b</sup> ±0.01	0.41 <sup>a</sup> ±0.01	0.44 <sup>b</sup> ±0.01	0.40 <sup>a</sup> ±0.01	0.40 <sup>a</sup> ±0.01	0.40 <sup>a</sup> ±0.00
Moisture (%)	4.75 <sup>b</sup> ±0.05	4.67 <sup>a</sup> ±0.03	4.83 <sup>c</sup> ±0.05	4.73 <sup>b</sup> ±0.03	4.65 <sup>a</sup> ±0.00	4.80 <sup>c</sup> ±0.00
pH	6.41 <sup>c</sup> ±0.01	6.62 <sup>e</sup> ±0.00	6.30 <sup>b</sup> ±0.01	6.50 <sup>d</sup> ±0.01	6.11 <sup>a</sup> ±0.01	6.73 <sup>f</sup> ±0.01
Viscosity(cP)	53.67 <sup>e</sup> ±1.15	47.33 <sup>d</sup> ±0.56	43.00 <sup>b</sup> ±1.0	46.67 <sup>d</sup> ±0.5	45.00 <sup>c</sup> ±1.00	41.00 <sup>a</sup> ±1.00
Swelling (%)	780.67 <sup>d</sup> ±1.5	669.33 <sup>c</sup> ±1.1	460.67	860.67	846.67 <sup>e</sup> ±1.5	526.67 <sup>b</sup> ±1.1
DP	976.00	851.00	757.00	837.00	801.00	711.67
	<sup>e</sup> ±20.78	<sup>d</sup> ±12.12	<sup>b</sup> ±22.00	<sup>d</sup> ±12.12	<sup>c</sup> ±22.00	<sup>a</sup> ±23.00
MWt g/mol (X10 <sup>5</sup> )	1.58 <sup>e</sup> ±3464	1.38 <sup>d</sup> ±1732	1.23 <sup>b</sup> ±3511	1.36 <sup>b</sup> ±2309	1.30 <sup>c</sup> ±3511	1.15 <sup>a</sup> ±4000

Values are means of three replicates ± standard deviation. Row means followed by different letters are significantly different at P< 0.05.

COSACMC-*Chromoleana odorata*NaOHAQ pulp carboxymethyl cellulose,  
 COSAECMC-*Chromoleana odorata*NaOHAQEtOH pulp carboxymethyl cellulose,  
 PPSACMC-*Pennisetum purpurem* NaOHAQ pulp carboxymethyl cellulose,  
 PPSAECMC-*Pennisetum purpurem* NaOHAQEtOH pulp carboxymethyl cellulose  
 ACSACMC- *Ananas comosus* NaOHAQ pulp carboxymethyl cellulose,  
 ACSAECMC –*Ananas comosus* NaOHAQEtOH pulp carboxymethyl cellulose

### **Bleached pulp**

Results obtained after the pulp samples were bleached (Table 2), indicated that those materials have different physico-chemical properties. The yield obtained revealed that all the bleached pulp from sodium hydroxide-anthraquinone-ethanol pulping and sodium hydroxide-anthraquinone counterparts are within the same value bracket. The alpha-cellulose content obtained showed that all the samples had more than 50 % alpha-cellulose. This suggests that they could be a good source of cellulose raw material. Though the yield obtained from sodium hydroxide-anthraquinone-ethanol pulping had fractional high values of 60.80, 60.09, and 57.14 %, for COSAE-BP, PPSAE-BP and ACSAE-BP respectively against 59.84, 59.96, and 55.34 %, for COSA-BP, PPSA-BP and ACSA-BP respectively, the result obtained for gamma cellulose which represents the degraded cellulose could be an indication that all the plant materials are good sources of strong fibre raw material that could be used in paper production and various syntheses. This is because the gamma cellulose obtained in this work was approximately 5 %, on the average, for each of the samples. This indicates that the materials were not greatly degraded by the pulping chemicals, having recorded 4.63 % for ACSA-BP as the highest, and 4.40 % for COSA-BP as the lowest value. The recorded ash and silica values showed that there was great reduction in the ash and silica contents of the bleached pulp as compared with that of the pulp samples. This could be as a result of the sequences of sodium chlorite treatment, sodium hydroxide extraction and water washing. All these treatments have led to the removal of lignin, extractive and degraded cellulose; all of which contain a level of inorganic matters. The result showed that bleached pulps obtained by sodium hydroxide-anthraquinone-ethanol pulping liquor have lower ash and silica content than those obtained from sodium hydroxide-anthraquinone pulping liquor. This might be due to the swelling effect of ethanol used during

pulping, which would have opened up the fiber inner core thereby allowing better dissolution of inorganic matter which invariably leads to a reduction in the ash and silica content. While COSAE-BP had the lowest ash (0.97 %) and silica content (0.53 %), COSA-BP had the second lowest ash content (1.07 %), with silica content of 0.90 %. PPSAE-BP had the second lowest silica content of 0.77 % but had the third higher ash content of 1.10 %. Bleaching result showed that there was reduction in the pentosan content of the bleached pulp as compared with the pulp sample. The pulp sample pentosan values ranged from 0.07 to 0.11 %, but the bleached sample value ranged from 0.02 to 0.04 %. This reduction in pentosan value could be suggesting that the various treatments given to the sample during bleaching had influenced the removal of the pentosan. The result of Kappa number indicated that pulp obtained using sodium hydroxide-anthraquinone-ethanol had better bleachability than those obtained by sodium hydroxide-anthraquinone, having recorded lower values than their corresponding sodium hydroxide-anthraquinone bleached pulp. The Kappa number ranged from the lowest value of 3.32 for COSAE-BP to 5.41 the highest for ACSA-BP. Viscosity allows an estimation of the degree of polymerization (DP) of pulp. The determination of the viscosity, degree of polymerization and the molecular weight of the bleached pulps has shown that the materials had undergone various degrees of degradation (decrease in cellulose molecular weight) resulting from the pulping and/or bleaching process. The result revealed that the bleached pulp obtained from sodium hydroxide – anthraquinone-ethanol pulping, has lower chemical degradation effect than those from sodium hydroxide-anthraquinone pulping, as indicated by their higher viscosity, degree of polymerization and molecular weight. It may probably be attributed to the effect of the ethanol and anthraquinone. Though within the groups of bleached pulp obtained by sodium hydroxide – anthraquinone-ethanol and sodium hydroxide –

anthraquinone pulping, there were different levels of degradation with PPSAE BP having the highest values for viscosity, degree of polymerization and molecular weight, indicating that it might not have been affected much by the pulping and bleaching chemical. This showed that within each group, the chemical composition of the plant materials might to some extent also affect the viscosity, degree of polymerization and the molecular weight, since viscosity is a relative measurement, which describes the increase in viscosity of a solvent when a polymer (or other materials) is dissolved in that solvent. It could therefore mean that those plant materials with chemical composition that allowed them to dissolve easily in the cupriethylenediamine may have higher value than any other (Gullihsen and Fogelholm, 2000).

#### **Alpha-cellulose**

The physico-chemical properties of the isolated alpha-cellulose revealed differences in the properties of the obtained materials (Table 3). The result showed that the silica content ranged from 0.04 % to 0.06 % and the ash content ranged from 0.47 % to 0.83 %. The result also revealed that the silica and ash contents of alpha-celluloses obtained from sodium hydroxide-anthraquinone-ethanol pulping were lower than those of the sodium hydroxide-anthraquinone pulping. The variation in the silica and ash content could be as a result of the different fibers' response to each of the pulping chemicals. For example, the alpha-cellulose obtained through sodium hydroxide-anthraquinone pulping, ACSA-AC (0.83 %) had the highest ash content while COSA-AC (0.57 %) had the lowest. It might be that ACSA-AC fiber was more resistant to the solubilisation effect of the pulping chemical thereby retaining much of its inorganic components, while COSA-AC might be vulnerable to the pulping chemical thus losing more inorganic components. This could also be applied to the sodium hydroxide-anthraquinone-ethanol alpha cellulose.

The ash content obtained in this work was higher than that of Alfred and Hurter (1998) which are: 0.04-0.15 % for bagasse, 0.06-0.11 % for bamboo and 0.10 -0.15 % for cotton. Also

0.14 % was reported for sugar cane bagasse (Ibrahim *et al.*, 1996), while 0.05 % has been reported for lower grade linter (Ass *et al.*, 2006). The pentosan value in the alpha-cellulose obtained from both the sodium hydroxide-anthraquinone-ethanol pulp and sodium hydroxide-anthraquinone pulp showed no significant difference. The pentosan ranged between 0.01 % and 0.02 %. The pentosan values obtained in this study were lower than the 4.0 to 6.0% reported for bagasse and 2.5 to 3.5% for bamboo alpha-cellulose (Alfred and Hurter 1998). This might be due to different processing method. The viscosity, degree of polymerization and molecular weight showed that extraction of the alpha-cellulose using 17.5 % sodium hydroxide had significant effect on the cellulose chain length of each of the cellulose. While the alpha-cellulose from sodium hydroxide-anthraquinone-ethanol pulping had viscosity range from 5.13 to 6.95, that of sodium hydroxide-anthraquinone pulping ranged from 4.91 to 5.53. The result suggested that the alpha-cellulose obtained from sodium hydroxide-anthraquinone pulping were more susceptible to chemical degradation when compared to those obtained from sodium hydroxide-anthraquinone-ethanol pulping. The result to some extent showed that COSAE-AC might have greater fiber strength than any other alpha-cellulose as observed in its viscosity, degree of polymerization and molecular weight. The viscosities obtained in this work were lower than 13.14 for bagasse and 31.90 for sisal (Alfred and Hurter, 1998), while degrees of polymerization in this work were lower than 1440 reported for cotton (Alfred and Hurter 1998). But the degree of polymerization of 1153 (COSAE-AC) and 1096 (PPSAE-AC) reported in this study were higher than 1026 to 1030 reported for bamboo (Alfred and Hurter 1998) but lower than 1169 and 1311 reported for Kraft softwood and Kraft hard wood alpha-cellulose (Iller *et al.*, 2002).

#### **Analysis of carboxymethyl cellulose**

The reaction mechanism between alpha-cellulose and monochloroacetic acid is shown in scheme 1. The main steps in the carboxymethylation reaction are as follows:

(A) mercerization reaction which involves the treatment of cellulose with sodium hydroxide in ethanol. This acts as swelling and impregnation steps thereby facilitating the accessibility of the reactants to the cellulose chain. (B) accessibility of sodium hydroxide to the cellulose chain resulted to the protonation of the most reactive hydroxyl group to produce reactive alkali cellulose (CELLULOSE METHYLOL) (C) etherification stage. Reaction between sodium hydroxide and monochloroacetic acid has already produced sodium salt of monochloroacetic acid (sodium monochloroacetate). This has a chloride ion which is negatively charge. This was abstracted by leaving sodium ion from the cellulose methylol to give a carbinium ion, a good electrophile. This electrophile then attacks oxygen of the methylol group of the cellulose to give ether (D).

#### Physicochemical analysis of CMC

The physicochemical properties of the various CMC are presented in Table 5. The yield obtained showed that all CMC prepared from alpha-cellulose obtained through sodium-anthraquinone-ethanol pulping chemical was higher than those from sodium-anthraquinone pulping chemical. For example PPSAE-CMC had the highest yield of 91.00 %, while COSAE-CMC and ACSAE-CMC had same value of 87.99 %, against 81.84 % for PPSA-CMC, 86.84 % for ACSA-CMC and 80.71 % for COSA-CMC. The higher yield recorded for PPSAE-CMC, COSAE-CMC and ACSAE-CMC could be attributed to the viscosity, degree of polymerization and molecular weight result of their alpha-cellulose. These present them with high anhydroglucose unit (cellulose monomer reacting unit) for etherification reaction thus leading to higher CMC yield. The moisture content ranged from the lowest value of 4.65 % for PPSAE-CMC to the highest value of 4.83 % for ACSA-CMC. The moisture content values

obtained in this work were higher than those reported by Latif *et al.*, (2005). The obtained results were still within the 12 % prescribed (RESOLUTION, 2009; ASTM 1995). The pH showed that PPSAE-CMC had the lowest value of 6.11 and 6.73 for ACSA-CMC with the highest value. Bono *et al.*, (2009), in their work records 6.5 to 8. The official recommended value was between 6-8.5 (RESOLUTION, 2009). The ash content value showed reduction from 0.05 % to 0.83 % reported for the alpha-cellulose and 0.40 % – 0.44 % for the CMC prepared. This, no doubt, could be attributed to the processing effect for producing CMC from the alpha-cellulose, since ethanol used as reaction medium for synthesis of CMC allows swelling of fibers, exposing the inner core of the fiber to chemical which can solubilize some of the inorganic components of the alpha-cellulose. The swelling characteristic indicated that COSAE-CMC had the highest swelling ability with 860.67 %. Others were ranked as follows: PPSAE-CMC (846.67 %) > COSA-CMC (780.67 %) > PPSA-CMC (669.33 %) > ACSAE-CMC (526.67 %) > ACSA-CMC (460.67 %). The results showed that pulping method could be a determining factor since nearly all sodium hydroxide-anthraquinone-ethanol pulp had higher alpha-cellulose; thus more anhydroglucose reacting unit for greater CMC yield which in turn gave high swelling ability. The result suggested that swelling ability is a function of degree of substitution (DS), since COSAE-CMC with highest swelling ability still had the highest DS value of 0.34. The others behave similarly. Latif *et al.*, (2005), showed that DS is directly related to the alpha-cellulose content, having reported that DS of 1.05, 0.94 and 0.74 respectively for cotton linter with 96.20 % alpha-cellulose, *Picea smithiana* wood with 93.7 % alpha-cellulose and *Eucalyptus globules* with 89.83 % alpha-cellulose. DS of 0.24 to 0.73 has been reported by Barai *et al.*, (1996) for CMC from water hyacinth, 0.33 to 0.82 for CMC from Sago waste (Pushpamalar *et al.*, 2006), 0.11 to 0.67 for CMC sugar beet pulp cellulose and 0.20 to 1.22 for CMC from *Lantana camara*. ACSAE-CMC had the lowest sodium chloride content

value of 0.14 %, COSAE-CMC and PPSAE-CMC had 0.15 % while all others had 0.16 %. Thus all the sodium hydroxide-anthraquinone-ethanol pulp derived CMC had lower sodium content than the sodium hydroxide anthraquinone pulp derived CMC. All the sodium chloride contents reported in this work were lower than 0.62 %, 0.29 % and 0.19 % reported by Latif *et al.*, (2005) for CMC from cotton linter, *Picea smithiana* wood and *Eucalyptus globules* respectively. The standard recommendation is that sodium chloride content must not be more than 5 % for anhydrous CMC obtained (RESOLUTION, 2009), thus the sodium contents obtained in this work are within the required limit. COSA-CMC had the highest viscosity of 53.67cP, a degree of polymerization (976.00) and molecular weight (158000 g/mol), while ACSAE-CMC had the lowest value of 41.00 viscosity, DP of 711.67 and molecular weight of 115,000 g/mol. The result could be an indication that the chain length of the sodium hydroxide –anthraquinone pulp CMC were not much affected by the sodium hydroxide degradation effect that occurred during the carboxymethylation reaction, this partially might be due to the fact they are not as pure as the sodium hydroxyl-anthraquinone-ethanol pulp, making chemical penetration difficult therefore reducing degradation and this was attested to by the low DS recorded for sodium hydroxyl –anthraquinone pulp CMC. Barba *et al.*, (2002) has reported molecular weight ranging from 150,900 to 328,700 for various CMC in their work.

## CONCLUSION

This experiment has revealed that alpha-cellulose with good yield which ranges from 55.34 % to 60.08 % are obtained from the different plant materials used. The result of the carboxymethyl cellulose shows that the yield varies from 80.71 % to 91.10 % and degree of substitution from 0.20 to 0.34. The results have demonstrated that with good practices, cellulose could be obtained from different agricultural plants and such could be used for preparation of various cellulose derivatives.

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