



Synthesis and Characterization of Carboxymethyl Cellulose from *Eichhornia crassipes* and *Pennisetum purpureum* as Potential Source of Sustainable Drilling Mud Additives

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Authors' contributions

This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

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ABSTRACT

Cellulose extracted from *Eichhornia crassipe* (Water hyacinth) and *Pennisetum purpureum* (elephant grass) yielded 21.88% and 31.39% respectively. Cellulose extracted was used to synthesize carboxymethyl cellulose (CMC) under heterogeneous condition with ethanol as the supporting medium. Effect of concentration of sodium hydroxide (NaOH) on the modification of cellulose to yield CMC was investigated. It was observed that percentage CMC yield increased with increase in NaOH concentration. Comparative studies of the two biomass samples through physico-chemical analyses in terms of degree of substitution (DS), water absorption capacity, water loss, pH, conductivity and analytical characterization using SEM-EDX, FT-IR and EDXRF spectroscopy of the extracted cellulose and synthesized CMC were done. The DS of CMC obtained by alkalization reaction of cellulose from *E. crassipe* and *P. purpureum* with monochloroacetic acid was in the

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range of 0.54-0.75 which showed that it is highly soluble. Fourier Transform-Infrared (FT-IR) spectrophotometer showed changes of functional group from cellulose to CMC. The absorption at 3283 cm^{-1} and 3320 cm^{-1} as observed in *E. crassipe* and *P. purpureum* spectra showed OH vibration of polymeric compounds. The presence of bands at 1592 cm^{-1} and 1417 cm^{-1} in *E. crassipe* spectrum and bands at 1566 cm^{-1} and 1410 cm^{-1} observed in *P. purpureum* spectrum showed the presence of $-\text{COO}$ group as a result of carboxymethylation reaction on cellulose during modification process. EDXRF was applied for quality control and product development due to the unavailability of the elemental composition of elephant grass and water hyacinth in the literature. The morphology and elemental compositions on the surface of the biomass were analyzed by SEM-EDX and among the chemical elements detected were C, O, Na, Mg, Al, S, Cl, K, Ca, Fe Si and Zr which confirms the elements identified with EDXRF spectroscopy. XRF spectra show high peaks at Fe, K and Sn for untreated *P. purpureum* samples and high peaks at Ca, Fe and Sr for untreated *E. crassipe* fiber. Both samples are rich in Iron (Fe). Samples were free from some toxic elements such as Pb, As, Hg, V and Ni which makes them safe for use as novel raw materials for industrial applications. Also very low concentration of Sulphur in the samples, make them safe to be considered as additives in drilling mud formulation.

Keywords: Cellulose; Carboxymethyl cellulose; *Eichhornia crassipes*, *Pennisetum purpureum*; Agrowastes; environmental friendly.

1. INTRODUCTION

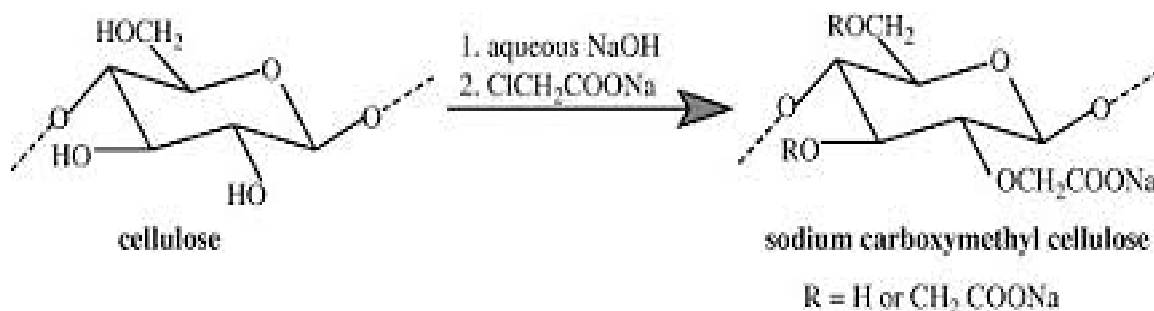
Cellulose is a homogeneous long chain polysaccharides comprised of β -D-glucose monomer units, of formula $(\text{C}_6\text{H}_{10}\text{O}_5)_n$, where n is the degree of polymerization. It is a linear and high molecular weight polymer that consists of anhydroglucose unit linked together through 1 and 4 carbon atoms with a β -glucosidic linkage [1]. Cellulose is obtained mainly from different plant sources that include woody matter, cotton fibers, bast fibers, straw, stalks, hulls, grasses and even marine plants [2]. It is a natural, renewable, and biodegradable material usually found in plant cell walls in combination with lignin, hemicellulose, pentosans and other materials [3]. Several chemicals and processes are used to separate cellulose from other undesirable compounds. From scheme 1 below, each anhydroglucose unit in cellulose structure (scheme 1) has six carbon atoms with three hydroxyl groups at C_2 , C_3 , and C_6 atoms, giving cellulose molecule a high degree of functionality [4].

Notwithstanding the number of hydroxyl groups, which are hydrophilic in nature, cellulose is insoluble in water, which is probably due to the presence of hydrogen and van der-Waals' intermolecular bonds [5]. Cellulose is also insoluble in common organic solvents, such as alcohol, ether, benzene, and petroleum ether. Efficient utilization of cellulose as a material source in chemical industries has been challenging due to its insolubility. The hydroxyl groups on the surface of cellulose make it

possible to undergo various chemical modifications. This makes cellulose a good starting material which is ecofriendly for the production of cellulose derivatives such as cellulose ether and cellulose ester used in many areas of industry and domestic life [6,7] Carboxymethyl cellulose (CMC) is an example of cellulose ether synthesized from cellulose and monochloroacetic acid (MCA) or its sodium salt with sodium hydroxide (NaOH) as the third essential ingredient (scheme 1 & 2) [8]. Alkalinization and carboxymethylation are two main steps involved in synthesis of CMC from cellulose. Cellulose is first treated with sodium hydroxide to cause swelling and to form alkali cellulose. This is a crucial step in the process to ensure that the cellulose is homogeneously converted to alkali cellulose and it's known as alkalinization or mercerization reaction [9]. The alkali cellulose formed is accessible and reactive towards monochloroacetic acid, which is added to the reactor either as free acid— monochloroacetic acid, or as its sodium salt— sodium monochloroacetate under controlled conditions. This second step is known as etherification or carboxymethylation reaction.

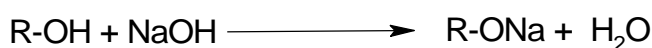
Where R is cellulose radical, R-ONa is alkali cellulose and R-O-CH₂-COONa is sodium carboxymethyl cellulose.

Sodium carboxymethyl cellulose (Na-CMC) is non-toxic salt, hydrophilic and dissolves when dispersed in water. Industrial application of CMC depends upon its purity, degree of polymerization (DP) and degree of substitution (DS) which govern the performance of the resulting products

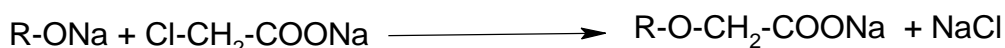


Scheme1. Hydrogen bonding (-) and carboxymethylation of cellulose [8]

Step one:



Step two:



Scheme 2. Schematic illustration for the synthesis of CMC

such as solubility, particle size, viscosity and rheological properties. Viscosity of CMC is proportional to the average chain length or the DP. Viscosity is a measure of a fluid's resistance to flow and defines the internal friction of a moving fluid. CMC is a polymeric material that provides a viscose solution in an aqueous medium due to its high solubility in water. Its viscosity increases with increasing degree of polymerization but decreases with increasing temperature. A lower viscosity-based CMC can be used with sodium bentonite as a viscosity modifier or dispersion media in a drilling mud system. The average chain length and the degree of substitution determine the molecular weight of the CMC grade. CMC products are of different grades: food-grade, pharmaceutical grade, and industrial grade which are based on purity and DS [10-11]. Degree of substitution is the average number of carboxymethyl groups per anhydroglucose unit. Theoretically, the maximum DS is 3 [12]. CMC wide applications and properties such as solubility, emulsibility, thickening property, acid resistance, viscosity, stability, and salt tolerance highly depend on the DS value [13]. For example, CMC polymer is entirely insoluble and swellable under the 0.4 DS value but it's fully soluble beyond DS value of 0.4 [14]. The normal DS range for commercially available CMC is approx. 0.4 - 1.4 (Huang et al., 2017). Arthur in [15] synthesized CMC with a DS value of 0.5–1.2. Higher DS improve the solubility of the CMC and enhance the viscosity

stability in the presence of salts or at low pH. CMC has many commercial applications, such as its incorporation in drilling muds as additive [16], its use as a thickening and dispersing agent in the manufacture of cosmetics and paints, its use as a food additive, its incorporation in soaps and detergents as a deterative action accelerator and its use in the pharmaceutical industry. CMC is made from specially selected cellulose raw material and manufactured under specific process conditions. Since cellulose constitutes the major part of a plant cell wall, it is important that those plants which have no industrial utilization, as well as the residual wastes from utilized plants should form a huge potential for its source [17]. Non-woody biomasses are very promising alternative materials because they are economical, environmentally friendly, biodegradable and renewable raw materials [18] that have been shown to exhibit equal or better physical and mechanical properties comparable to some commercial wood species. Saputra et al. [19] synthesized and characterized CMC from *E. crassipes* using ethanol-isobutyl alcohol mixture as the solvents. They observed that highest degree of substitution on the cellulose was with a mixture of 20% ethanol, 80% isobutanol and 10% NaOH. CMC synthesized by Barai et al. [20] from *Eichhornia crassipes* yielded highest DS in 10% aqueous NaOH when isopropyl alcohol was used as solvent. In this research, *Pennisetum purpureum* (Elephant grass) and *Eichhornia crassipes* (water hyacinth) which are non-woody

biomasses, agro-wastes, aquatic and terrestrial weeds were exploited as the starting raw materials for the synthesis of CMC. These agro-wastes are invaders, persistent and noxious weeds that impact aquatic and terrestrial environments negatively. Cellulose extracted from these samples was subjected to modification into CMC through mercerization and etherification processes. The extracted cellulose and synthesized CMC were characterized through physico-chemical analyses and some analytical methods such as Fourier-Transform Infra-Red (FT-IR) spectroscopy, Energy-Dispersive X-Ray fluorescence (ED-XRF) and Scanning Electron Microscopy-Energy-Dispersive X-ray (SEM-EDX) spectroscopy. Comparative studies of products from both samples and conventional CMC were carried out in this research to determine their suitability as additives in drilling mud formulation [21-22].

2. MATERIALS AND METHODS

2.1 Materials

Chemicals: All chemicals used were of analytical grade purchased from AccuStandard® obtained from Shanghai Fine Chemical Co., China. Sodium hydroxide (99%, 39.99g/mol), sodium-monochloroacetate (99%, 117.49g/mol), ethanol (99%, 46.069g/mol), methanol (99.8%, 32.04g/mol), glacial acetic acid (99%, 60.05g/mol), sodium hypochlorite (98%, 74.44g/mol), sodium bisulphite (98%, 104.06g/mol), potassium bromate (99.5%, 167.01g/mol), Sulphuric acid (98%, 98.079g/mol), methyl red (97%, 269.304g/mol), zinc chloride (98%, 133.867g/mol), potassium iodide (76%, 166g/mol), iodine (99.8%, 253.809g/mol) and distilled water.

Instruments and Apparatus: Beaker glass, round-bottom flask, graduated cylinder, volumetric pipettes, petri dish, porcelain evaporation lab dish, glass lab dish, filter paper, digital scale, fume-hood, oven, thermometer, Franz von soxhlet, vacuumed pump, pH meter, pH paper, water bath and stirring rod with motor, rotational viscometer, Fourier Transform-Infrared (FT-IR) spectrophotometer (Agilent Happ-Genzel), Scanning Electron Microscopy-Energy-Dispersive X-ray Spectroscopy (SEM-EDX) (Phenom-World), Standard Method Energy Dispersive X-ray fluorescence (EDXRF), weighing balance (Ohaus), Hannah pH meter (Hannah), heating oven (Memmert.), vacuum pump, stirrer, 3-necked round bottomed flask,

Beakers, 2500 standard sieve with mesh size of 5 µm, Whatman filter paper Grade 1, with diameter 24cm and pore size of 11 µm, funnel, filtration loss tester, thermometer, sonicator, autoclave, spatula, basin, measuring cylinder

2.2.1 Sample collection

Pennisetum purpureum and *Eichhornia crassipes* were collected from Miniorlu, Ada-George, Port Harcourt, Rivers State and a river in Ubuna, a community in Gbaran, Bayelsa State respectively. The samples were washed several times with tap water to remove extraneous impurities and sun dried for a week. The dried samples were cut into small pieces, ground with a blender and kept in a hot air oven for 24 hrs at 105°C to remove the moisture.

2.2.2 Isolation of cellulose

Cellulose isolation procedure was a modified method described by Murigi et al., [23]. 20 g of the samples were weighed each into a round bottomed flask placed on a water bath, 70% ethanol was added, stirred, heated and refluxed for 120mins at 85°C. The fluids were drained and residues rinsed with 50% ethanol to complete the degreasing processes. At this stage pectin, fats, waxy matters, and aqueous extracts were separated from the residues. The pretreated samples were further treated with 17.5% aqueous NaOH solution at room temperature for 60mins in a fiber to liquor ratio of 1:20 with occasional stirring to remove the hemicellulose. The mixtures were filtered and the residues washed with 5% acetic acid, tap water and subsequently with distilled water to neutralize the reaction. The residues were then bleached with 2% sodium hypochlorite (NaOCl) for 120mins at 30°C. At this stage, rich cellulose content was obtained from the pretreated samples of *P. purpureum* and *E. crassipes* by eliminating hemicellulose and lignin. The extracted cellulose from the two samples were filtered and dried in an oven at 105°C until constant weights were obtained. The percentage yield of the cellulose was calculated and samples kept in a desiccator for further use in synthesis of CMC.

2.2.3 Synthesis of carboxymethyl cellulose

Cellulose isolated from *E. crassipes* (water hyacinth) and *P. purpureum* (Elephant grass) samples were soaked in 95% ethanol as solvent in the solid to liquid ratio of 1:20 in a covered round-bottomed flask. After 30 mins, sodium

hydroxide (NaOH) of different concentrations (10%, 20%, 30%, 40%, and 50%) were added and stirred vigorously for 30 mins at room temperature to form alkali cellulose [19]. This is known as alkalization or mercerization reaction. After the alkalization reaction, etherification of alkali cellulose was achieved by drop-wise addition of aqueous monochloroacetic acid (ClCH₂COOH) at 55°C and stirred for 3 hrs. After cooling, the mixture was separated into two phases by filtration. The liquid phase was discarded and the solid phase suspended in methanol, and neutralized with 95% acetic acid (v/v). The residue was recovered by filtration and washed with ethanol/water (70/30 v/v). CMC obtained from the two samples were dried until a constant weight was reached. The dried CMC synthesized from the two samples were characterized using the following parameters: CMC yield, degree of substitution, conductivity, pH, water loss, and water absorption capacity, FT-IR, ED-XRF and SEM-EDX.

2.2.4. Cellulose and CMC yield

CMC yield was calculated on a dry weight basis. The net weight of dried CMC was divided by the weight of dried cellulose to get the yield value. Percentage yield of cellulose and CMC were determined using the formulae below according to [8].

$$\text{Cellulose yield, \%} = \frac{\text{Weight of cellulose obtained}}{\text{Weight of sample used}} \times 100$$

$$\text{CMC yield, \%} = \frac{\text{Weight of obtained CMC}}{\text{Weight of dried cellulose}} \times 100$$

2.2.5 Degree of substitution

0.5 g sample of dried CMC was weighed in a crucible. The sample was ignited over a small flame until it became charred, followed by 45 minutes in a kiln at 650 °C until ash was grayish white. Ash was dissolved in 100 ml of distilled water and 20 ml of the solution was titrated with 0.1N sulphuric acid using methyl red as an indicator. After the first end point, the solution was boiled and titrated to a sharp end point. The degree of substitution of the carboxymethyl group [24] was calculated as follows:

$$\text{Degree of Substitution (DS)} = \frac{0.162 \times B}{1 - 0.08 \times B}$$

Where $B = 0.1 \times \frac{b}{G}$ b is the volume (in ml) of 0.1 N sulphuric acid and G is the mass of pure CMC in grams.

Water absorption capacity: 2% of CMC film (6 cm × 4 cm) was prepared, weighed and immersed in distilled water for 15 hrs at room temperature. The film was wiped with tissue paper and weighed again. Water absorption capacity was determined by using a gravimetric method according to method described by El-Din et al., [25].:

$$\text{water absorption capacity, \%} = \frac{W_1 - W_0}{W_0} \times 100$$

Where, W_0 (g) is the weight before immersion and W_1 (g) is the weight after immersion.

FTIR Analysis: The infrared spectra were used to effectively identify changes in chemical compositions of the products and to confirm the substitution reaction in carboxymethylation. The FTIR spectra of powdered fibers, cellulose and synthesized CMC from *Eichhornia crassipes* and *Pennisetum purpureum* samples were studied. The infrared spectra were obtained using FTIR Spectrometer model Apodization: Happ-Genzel taken at a resolution of 8 cm⁻¹, with a total of 32 scans for each sample. The transmittance range of the scans was 4,000.00 - 650.00 cm⁻¹.

2.3 Scanning Electron Microscopy-Energy-Dispersive X-ray Spectroscopy Analysis

Scanning Electron Microscopy-Energy-Dispersive X-ray Spectroscopy (SEM-EDX) analysis with magnification ranging 225x – 500x was used to study and compare the morphology, composition and features of samples produced at different stages of the research. Imaging of each sample was done using Phenom-World scanning electron microscope at Mode: 15kV – Map with BSD Full detector.

2.4 X-Ray Fluorescence Analysis

Energy Dispersive X-Ray Fluorescence (EDXRF) analyzer was used for qualitative and quantitative determination of the elemental compositions of the samples and products. The samples were analyzed with biological calibration oxide in vacuum method, copper thin filter and linear analysis technique.

3. RESULTS AND DISCUSSION

3.1 Physico-chemical Parameters

Results of the physico-chemical analyses show that CMC yield (%), water absorption capacity and DS of *P. purpureum* and *E. crassipes* increased with increase in concentration of aqueous NaOH. It was observed that the water absorption capacity and DS for the conventional CMC were higher than that of the locally synthesized CMC. The DS of CMC obtained in this work was within the expected range of 0.54-0.75 as seen in Table 1 since CMC is fully soluble at DS above 0.4 and its hydro affinity increases with increasing DS [26]. DS determines water solubility and influences the effectiveness of CMC as a mud additive and for other applications. Drilling grade of CMC used in muds usually has DS around 0.80 to 0.96 [27] which suggests that the commercial CMC used for this study with DS 0.93 is a drilling grade and it's more soluble than CMC synthesized from *P. purpureum* and *E. crassipes*. The measured DS for CMC from *P. purpureum* and *E. crassipes* for this research are in good agreement with published values (0.4-1.4) for commercial CMC (Huang et al., 2017). Therefore CMC from *P. purpureum* and *E. crassipes* have high water solubility and could be good alternative additives for industrial applications.

CMC yield was higher than that of cellulose extracted from the raw materials; this could be as a result of swelling caused by alkalization reaction and the substitution of hydroxyl group with carboxymethyl group with higher molecular weight on addition of monochloroacetic acid during carboxymethylation or etherification reaction [28]. This showed that cellulose was successfully modified to cellulose ether, CMC. The results from Table 1 show that conductivity values increased with increase in percentage concentration of NaOH and percentage CMC yield which could be as a result of increase in the concentration of the product, Na-CMC after modification with more sodium metals. It was observed that percentage CMC yield is directly proportional to conductivity of the samples which could be as a result of higher concentration of sodium (Na) in Na-CMC and the by-product sodium chloride (NaCl) formed during the modification process (scheme 2). Also higher concentration of Ca, K and Na which was observed from SEM- EDX and EDXRF data for *E. crassipes* could have caused its higher ionic conductivity values than that of *P. purpureum* [20,19].

Percentage water loss is higher in water hyacinth than elephant grass which suggests that elephant grass sample could be a better raw material for synthesizing CMC used as fluid loss control agent in drilling mud formulation with 30% NaOH that yielded lowest value. CMC synthesized from both samples demonstrates that they have high water absorption capacity which confirms their hydrophilic characteristic. Conventional CMC used in this research has higher water absorption capacity and higher DS of 90 and 0.93 respectively than values obtained from locally available raw materials (Table 1) which suggests that it's more soluble than locally synthesized CMC. The data also show that CMC from *E. crassipes* has higher DS values than that from *P. purpureum* therefore has higher solubility and better modification to cellulose ether. Modification with 50% NaOH yielded higher DS values, which suggests that it's a better condition for modification contrary to other results from literature with different solvent media [19]. The pH values are slightly acidic which could be as a result of high chlorine (Cl) values from source materials or may require much washing for neutralization reaction to be complete [29].

3.2 Fourier Transform-Infrared Analysis

Structures and compositions of cellulose and CMC from *Pennisetum purpureum* and *Eichhornia crassipes* were established on the basis of spectroscopic data. Cellulose etherification with sodium monochloroacetate caused OH groups in cellulose extracted from *Pennisetum purpureum* and *Eichhornia crassipes* to be replaced with CH_2COONa which caused changes in the absorption spectra data shown in (Table 2). FT-IR spectra show the peaks corresponding to the backbone of the cellulose molecule at 3320 and 3283 cm^{-1} (broad absorption band due to stretching of -OH groups and inter-molecular and intra-molecular hydrogen bonds) in *P. purpureum* and *E. crassipes* respectively. *E. crassipes* shows absorption at 2921 cm^{-1} as a result of C—H str (asym.) of Ar- CH_2 while band at 2880 cm^{-1} observed in *P. purpureum* spectrum was as a result of symmetric C—H str. (del Ahmed, 2018). The bands between 1655 cm^{-1} and 1629 cm^{-1} observed in *E. crassipes* spectrum which was absent in *P. purpureum* indicates C=O group or presence of water molecules. The absorption bands at 1592 cm^{-1} and 1566 cm^{-1} corresponding to *E. crassipes* and *P. purpureum* respectively indicate C—O symmetric stretch corresponding

to —COO^- (Carboxyl group) seen in CMC products (del Ahmed, 2018). The peaks at 1417 cm^{-1} and 1410 cm^{-1} observed in *E. crassipes* and *P. purpureum* spectra respectively confirm the presence of CH_2COO group due to carboxymethylation process [30]. The band at 1320 cm^{-1} corresponds to C-H stretch in cellulose. The bands between $1200\text{--}1052\text{ cm}^{-1}$ indicate C—O stretch (C—O—C—O—C, cyclic acetal and O—H bending of cellulose (del Sills et al., 2012). Absorption band at 992 cm^{-1} was due to C—O valence vibration while band at 899 cm^{-1} was as a result of 1, 4- β glycoside of cellulose [31]. FT-IR spectra of CMC samples showed successful modification of cellulose into CMC.

3.3 SEM-EDX Analysis

Morphology and analysis of the elements present on the sample surface were made with Energy Dispersive X-ray analytical system (Energy Dispersive X-ray Spectrometer—EDX) coupled with SEM microscope (Phenom-World, The Netherlands). The micrographs of untreated, cellulose and CMC of *Pennisetum purpureum* and *Eichhornia crassipes* samples as seen in Fig.6 showed that after extraction and modification processes, the biomass presented significant changes and this suggested that the solvents, NaOH and monochloroacetic acid had removed most of the natural products, caused swelling and structural changes in the biomass. The micrographs also showed that *E. crassipes*

had dense morphology when compared with *P. purpureum* which agrees with the bulk density result. The EDX analysis was able to qualitatively and quantitatively identify chemical elements present on the surface of the *P. purpureum* and *E. crassipes* samples. EDX study showed very high weight percent concentration of Potassium (K) and chlorine (Cl) on both untreated samples. EDX study conducted on CMC synthesized from both samples showed high weight percent concentration of Cl, Ca, Ag, C and Na with low concentration of K, S, Si, P, Al, Mg and N. High concentration of C, O and Na should be as a result of the addition of sodium acetate (—COONa) on cellulose structure during modification process to form salt of Na-CMC. High value observed on Ag could be contamination. The data also showed that Fe, B, Ti, Zr and Y were totally absent in *E. crassipes* sample while Ti, Zr and Y were not observed in *P. purpureum* sample after modification. The greater abundance of Ca metal found in *E. crassipes* could be as a result of its marine environment. Higher concentration of Na observed in *E. crassipes* samples showed that mercerization and etherification reactions of cellulose to Na-CMC, was better with *E. crassipes* than *P. purpureum*. Toxic trace elements such as Vanadium, Nickel and toxic heavy metals such as Mercury and Lead are absent. The absence of these elements in both samples confirms that they are environmentally friendly [8].

Table 1. Physico-chemical data from *P. purpureum*, *E. crassipes* and Conventional CMC at different NaOH Concentrations

Samples	Parameters	NaOH Concentration (%)			
		20	30	40	50
<i>Pennisetum purpureum</i> (Elephant grass)	CMC Yield (%)	70.08	78.22	82.04	90.44
	Water loss (%)	54.00	47.02	69.33	73.15
	Conductivity (us/cm)	370	870	940	1330
	Bulk density (g/ml)	0.07	0.12	0.10	0.07
	pH	6.21	6.31	6.13	6.23
	Water absorption capacity	60	64	68	72
	Degree of substitution	0.54	0.57	0.61	0.68
<i>Eichhornia crassipes</i> (Water hyacinth)	CMC Yield (%)	66.84	76.28	80.80	88.62
	Water loss (%)	84.97	84.03	77.74	88.50
	Conductivity (us/cm)	130	540	1310	1410
	Bulk density (g/ml)	0.11	0.12	0.09	0.09
	pH	6.29	6.41	6.58	6.58
	Water absorption capacity	62	66	68	70
	Degree of substitution	0.66	0.69	0.70	0.75
Conventional CMC (Kermel)	Water absorption capacity	90			
	Degree of substitution	0.93			

Table 2. FTIR band assignments for water hyacinth and elephant grass samples

Elephant grass		Water hyacinth	
Band position (cm ⁻¹)	Band assignment	Band position(cm ⁻¹)	Band assignment
3320	Polymeric O-H stretch	3283	Polymeric O-H stretch
2880	C-H symmetric	2921	C-H asymmetric
1566/1410	-COO ⁻ carboxylate	1655-1629	Carboxyl C=O or absorbed water
1320	C-O stretch	1592/1417	-COO ⁻ carboxylate
1019	C-O-C stretch	1320	C-O stretch
899	1, 4-β glycoside of cellulose	1200-1052	Polysaccharides
676-992	O-H out-of-phase bending	676-836	C-O-C stretch C-H wag

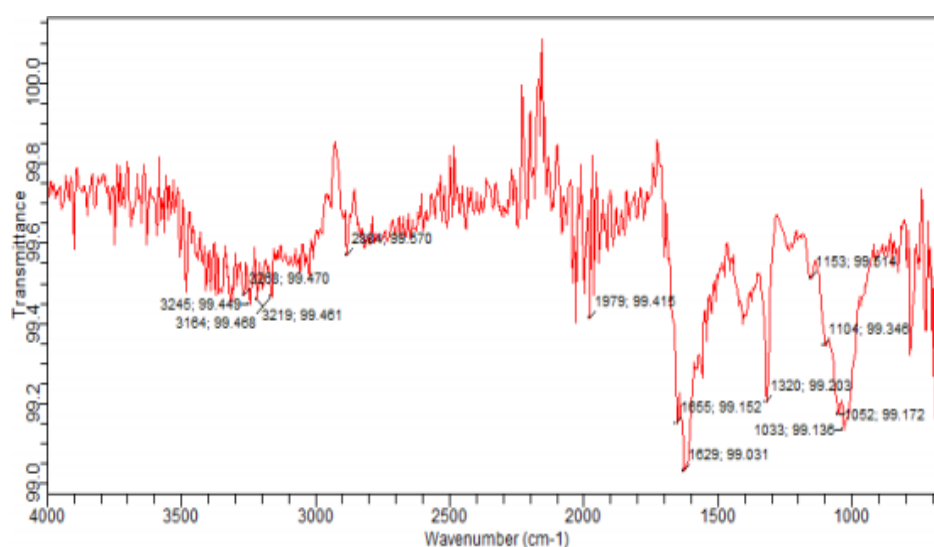


Fig. 1. FT-IR spectrum of extracted cellulose from water hyacinth sample

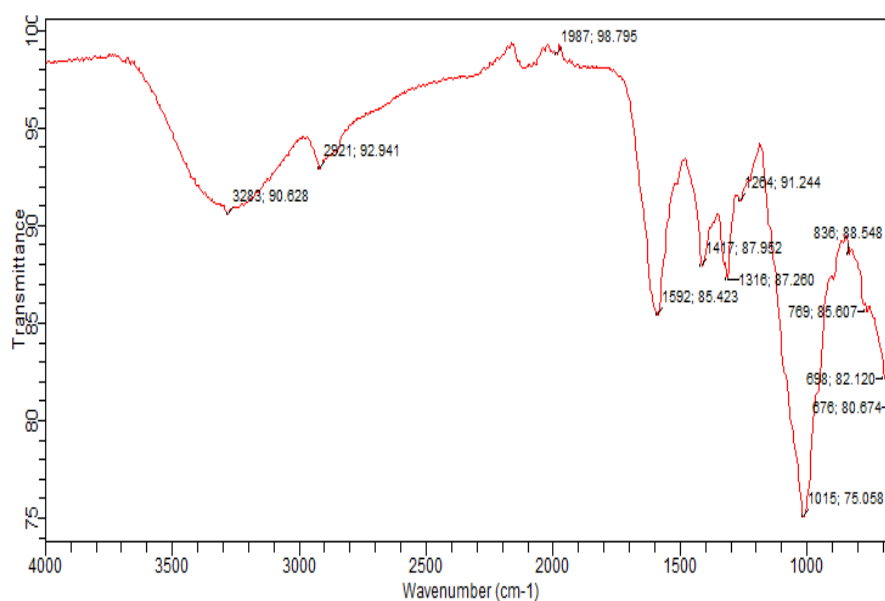


Fig. 2. FT-IR spectrum of synthesized CMC from water hyacinth cellulose sample

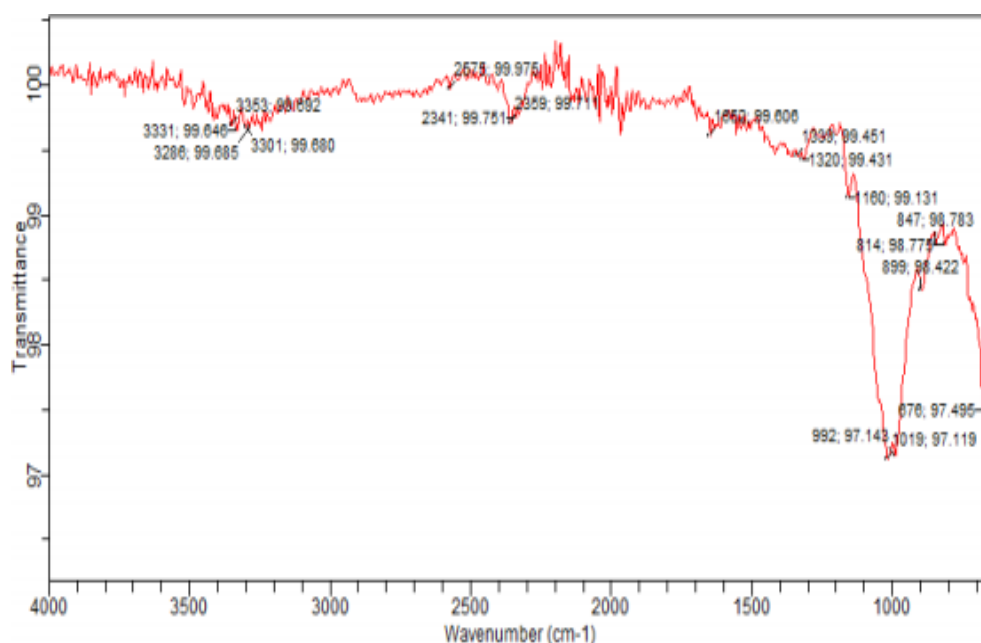


Fig. 3. FT-IR spectrum of extracted cellulose from elephant grass sample

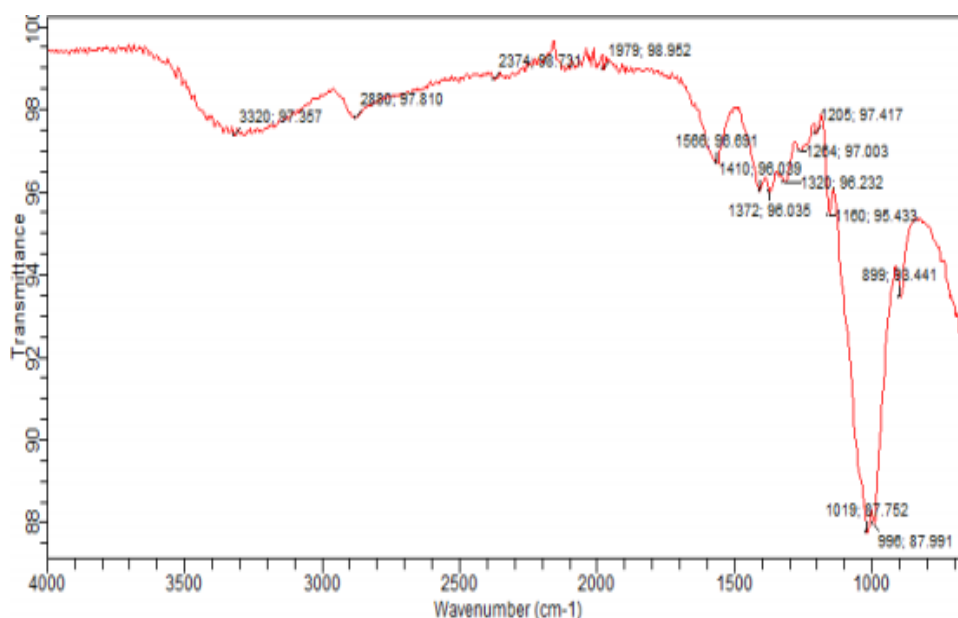


Fig. 4. FT-IR spectrum for synthesized cmc from elephant grass cellulose

3.4 X-ray Fluorescence (XRF) Analysis

XRF was used to determine the elemental composition of fibers, extracted cellulose and synthesized CMC from *E. crassipes* than *P. purpureum* samples. The result was used to complement the EDX data obtained. This was important in other to limit the usage of toxic chemicals as novel raw materials for industrial application and for the qualitative and quantitative analysis of the synthesized CMC

after the modification processes. XRF analysis of *E. crassipes* fiber reveals high weight percentage of oxides of phosphorus, calcium and potassium which could be as a result of its marine environment. There was a reduction on the weight percent of the metals except for calcium (Ca) after extraction and modification processes. Oxide of sodium (Na₂O) which was absent in the raw samples was observed in high concentration in CMC from both samples but higher in water hyacinth, this was expected as a result of the

modification of cellulose to sodium carboxymethyl cellulose. Oxygen observed in the biomass samples forming oxides with the metals are expected since fibers are composed mainly of Carbon(C), Hydrogen(H) and Oxygen (O) as observed from the structure of cellulose. It could also be as a result of biological calibration oxide in vacuum method used for the analysis. Chlorine (Cl) and Tin (Sn) were also in high weight percentage in water hyacinth specimen. Higher Chlorine (Cl) concentration on CMC could be as a result of contamination from by-product, sodium chloride. Other elements and oxides of metals were in small traces. This confirms that the raw materials and subsequent products are free from toxic elements and are environmentally friendly therefore could be recommended for

industrial applications. Sulphur is a hazardous element in crude oil and its low content in the products suggests that CMC synthesized from these samples, *E. crassipes* and *P. purpureum* can be used as additives in drilling mud formulation in oil and gas industries. The higher percentage concentration of sodium (Na) in water hyacinth proves that it was better modified than elephant grass fiber but the lower sulphur content in elephant grass suggests that elephant grass may be a better additive in oil and gas application especially as drilling mud additives [21]. XRF being the most important analytical method for the analysis of additives and impurities was used for precise and reliable analysis of the additives (CMC) at the minor and trace level as the key for high product quality.

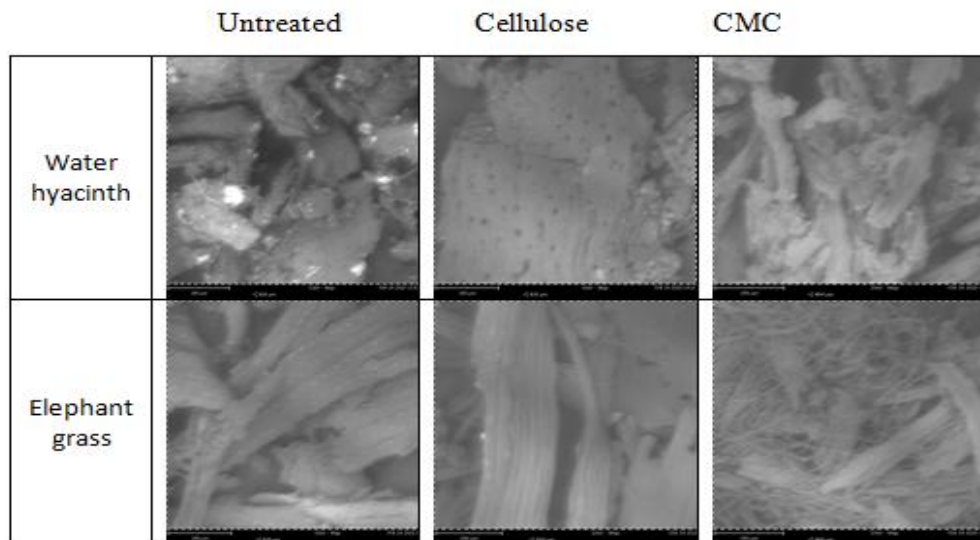


Fig. 5. SEM micrographs for CMC, cellulose, and untreated samples of water hyacinth and elephant grass. Water hyacinth (225 x 1.20mm x 15kv), Elephant grass sample (330 x 809 μm x15kv)

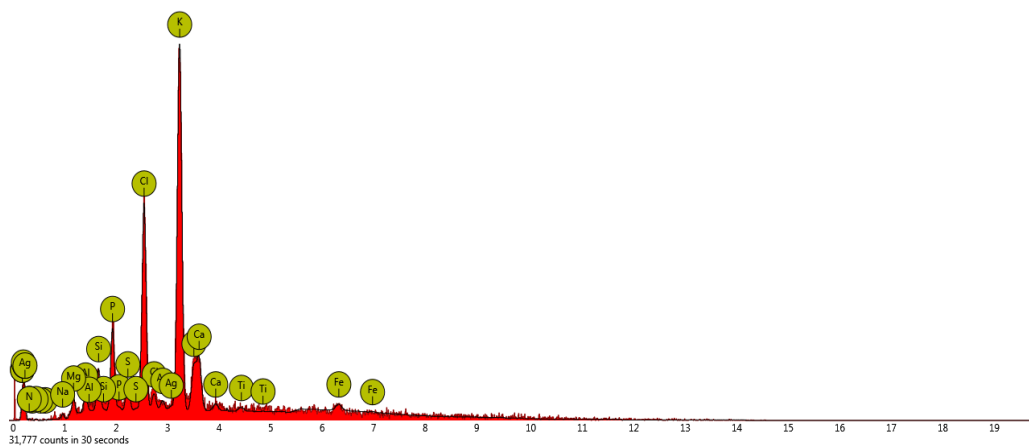


Fig. 6. EDX spectrum of untreated water hyacinth showing the detected chemical elements

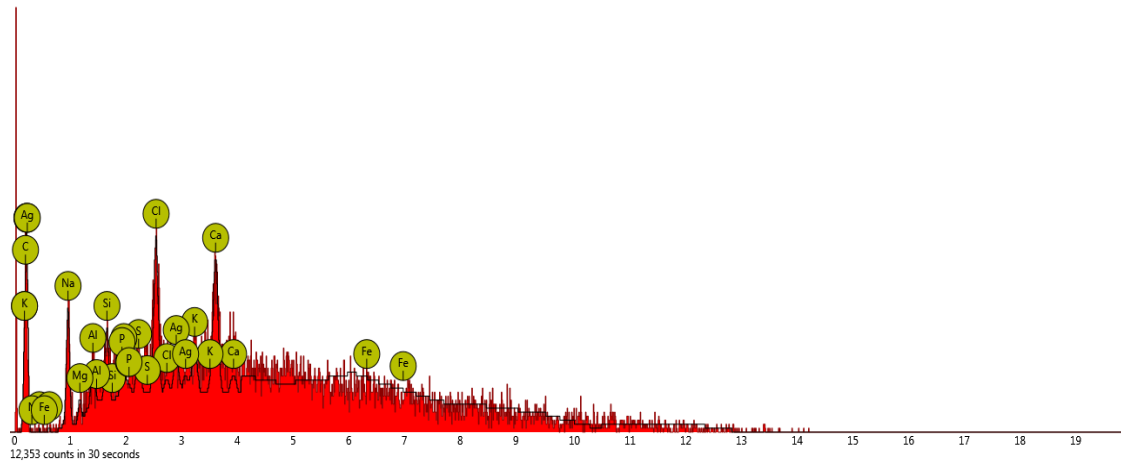


Fig. 7. EDX spectrum of synthesized CMC from Water Hyacinth showing the detected chemical elements

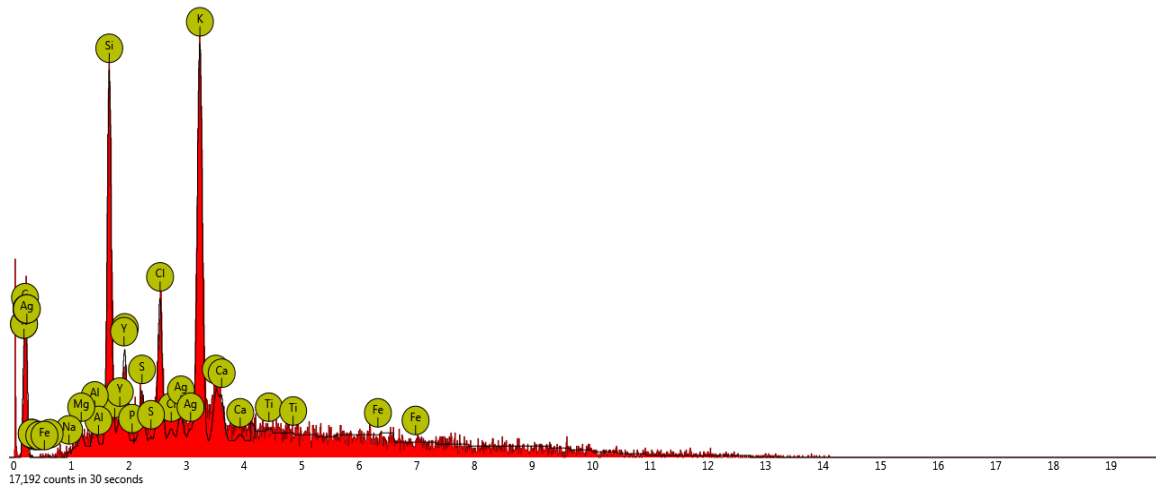


Fig. 8. EDX spectrum of untreated elephant grass sample showing the detected chemical elements

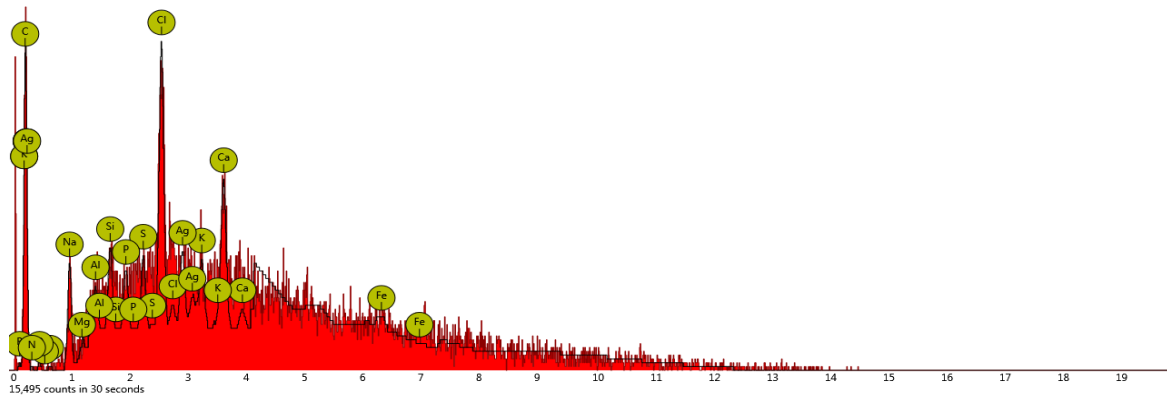


Fig. 9. EDX spectrum of Synthesized CMC from Elephant Grass Cellulose showing the detected chemical elements

Table 3. EDX Data for untreated biomass, cellulose and CMC from elephant grass and Water Hyacinth samples

Samples Element	Element Name	Elephant grass			Water hyacinth		
		Weight concentration (%)			Weight concentration (%)		
		Untreated	Cellulose	CMC	Untreated	Cellulose	CMC
Cl	Chlorine	11.07	9.37	19.42	19.89	4.57	15.78
Ca	Calcium	5.00	9.47	14.66	8.30	23.18	19.28
Ag	Silver	5.88	11.69	14.10	2.65	9.91	10.94
C	Carbon	7.11	19.67	13.11	2.58	11.67	11.22
Na	Sodium	0.30	1.31	10.11	0.73	20.07	15.24
K	Potassium	39.16	7.82	5.54	47.43	4.18	6.25
Fe	Iron	0.00	2.64	4.55	3.00	3.94	0.00
S	Sulfur	3.26	6.04	4.09	2.12	6.17	3.19
Si	Silicon	15.84	6.68	3.42	2.38	3.34	4.53
P	Phosphorus	5.06	4.32	3.24	6.07	2.23	1.31
O	Oxygen	0.42	0.79	2.6	0.82	1.24	1.43
Al	Aluminium	1.36	10.98	2.23	1.12	3.61	3.81
B	Boron	0.00	0.00	1.16	0.00	0.00	0.00
Mg	Magnesium	1.06	2.00	0.93	1.48	1.51	2.46
N	Nitrogen	0.47	0.72	0.84	0.00	0.41	0.81
Ti	Titanium	0.47	6.51	0.00	0.89	1.05	0.00
Zr	Zirconium	0.00	0.00	0.00	0.00	2.91	0.00
Y	Yttrium	3.55	0.00	0.00	0.00	0.00	0.00

Table 4. EDXRF data showing elements and oxides of metals on untreated fiber, cellulose and CMC from water hyacinth and elephant grass samples.

Sample Elements/Oxides of metals	Water hyacinth			Elephant grass		
	Concentration (%)			Concentration (%)		
	Untreated fiber	Cellulose	CMC	Untreated fiber	Cellulose	CMC
Fe ₂ O ₃	0.31	0.07	0.10	0.17	0.13	0.20
CuO	0.00	0.00	0.00	0.00	0.00	0.00
NiO	0.07	0.08	0.66	0.07	0.03	0.74
ZnO	0.02	0.00	0.010	0.00	0.00	0.00
Al ₂ O ₃	0.02	0.07	0.03	0.08	0.03	0.07
MgO	0.40	0.40	0.25	0.42	0.13	0.21
Na ₂ O	0.00	4.00	3.38	0.00	0.04	2.15
S	0.39	0.14	0.08	0.20	0.05	0.05
P ₂ O ₅	1.02	0.04	0.03	0.53	0.06	0.02
CaO	1.27	2.73	1.61	0.85	0.11	0.13
K ₂ O	4.69	0.03	0.01	2.64	0.00	0.00
MnO	0.04	0.03	0.02	0.02	0.00	0.00
Rb ₂ O	0.01	0.00	0.00	0.00	0.00	0.00
SrO	0.01	0.01	0.00	0.00	0.00	0.00
Br	0.01	0.00	0.00	0.00	0.00	0.00
Cl	2.71	0.03	0.19	0.82	0.15	0.34
Cr ₂ O ₃	0.00	0.00	0.02	0.00	0.00	0.02
V ₂ O ₅	0.00	0.00	0.00	0.00	0.00	0.00
Sn	2.28	0.150	0.10	0.80	0.26	0.07

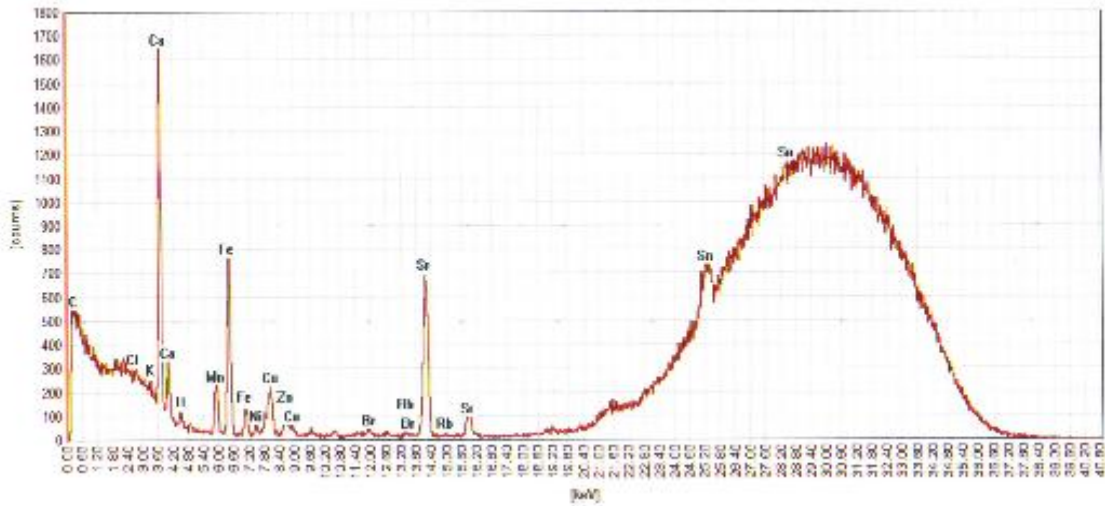


Fig. 10. EDXRF spectrum of untreated water hyacinth sample

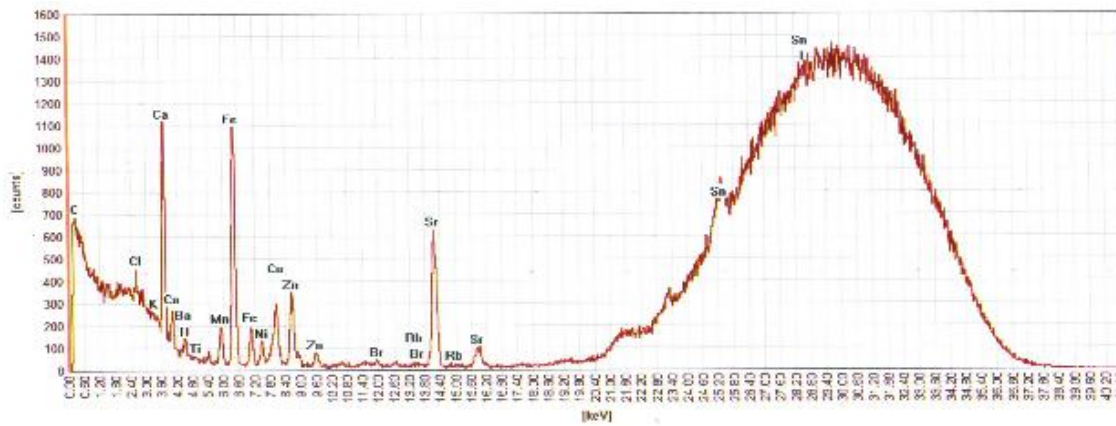


Fig. 11. EDXRF analysis of synthesized CMC from water hyacinth sample

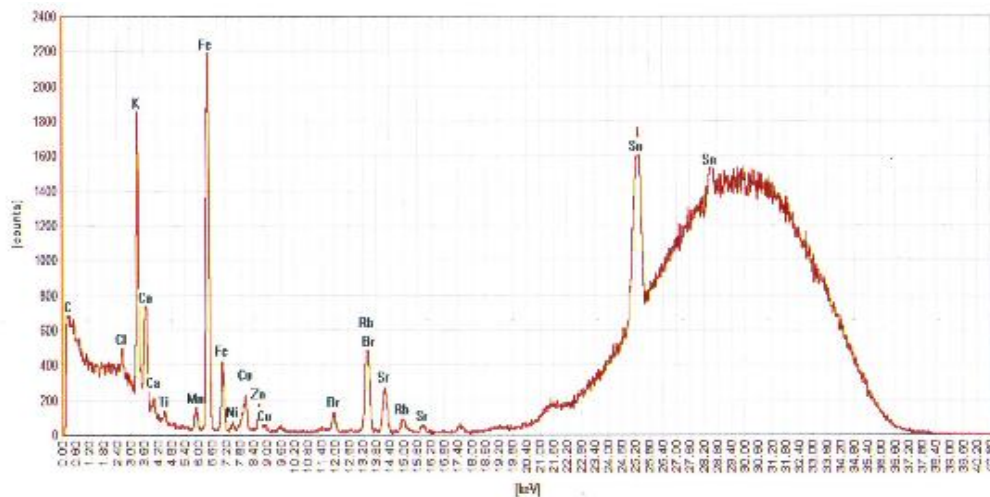


Fig. 12. EDXRF Spectrum of untreated elephant grass

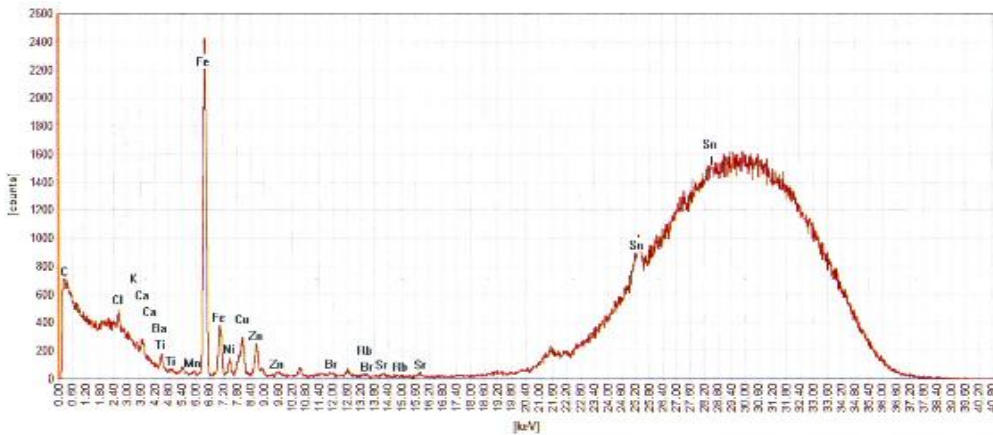


Fig. 13. EDXRF spectrum of Synthesized CMC from elephant grass Sample

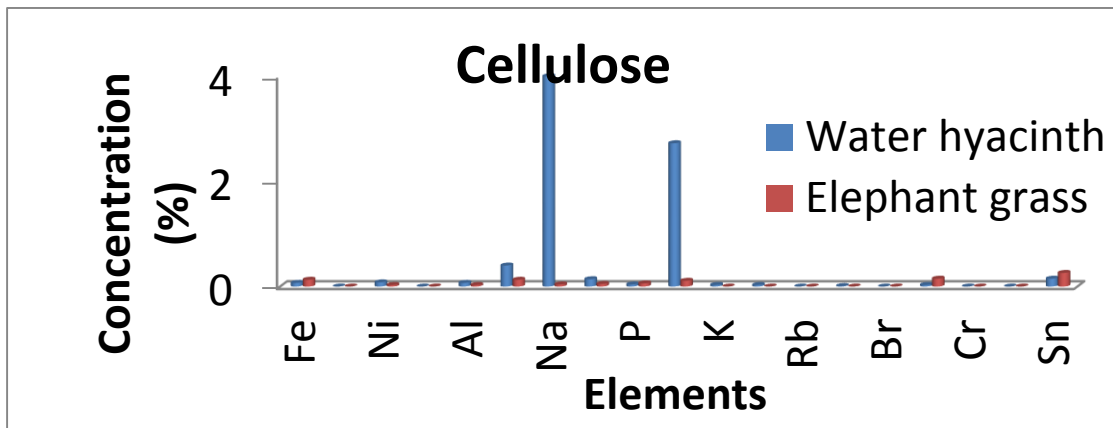


Fig. 14. Pictogram of percentage concentration of different elements in extracted cellulose from water hyacinth and elephant grass

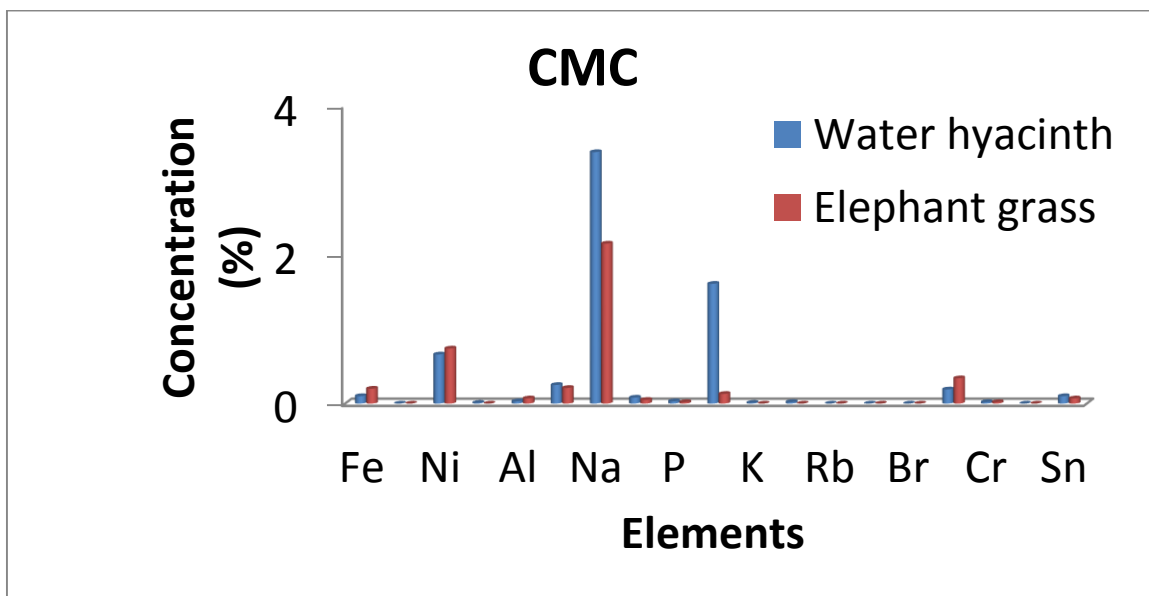


Fig. 15. Pictogram of percentage concentration of elements in the synthesized CMC from water hyacinth and elephant grass

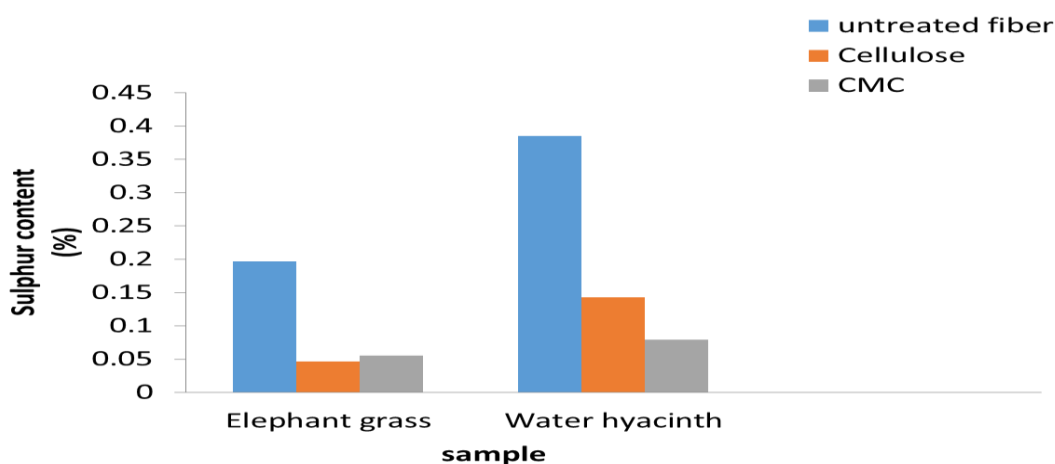


Fig. 16. Pictogram of Percentage Sulphur in the untreated fiber, extracted cellulose and synthesized CMC from both samples

4. CONCLUSION

Modifications in the morphology of *Eichhornia crassipes* (Water hyacinth) and *Pennisetum purpureum* (Elephant grass) were viewed with scanning electron microscopy (SEM). After the extraction and modification processes, the biomass presented significant changes and this suggested that the solvents, NaOH and monochloroacetic acid had removed some natural products generating structural changes in the biomass. The analysis of the images showed that *E. crassipes* had dense morphology when compared with *P. purpureum* which agrees with the bulk density result. Biomass fibers and products were characterized by analyzing elemental concentrations using XRF and EDX to determine their potentials as safe novel raw materials source for industrial applications. Scanning electron microscopy-energy-dispersive X-ray spectroscopy (SEM-EDX) provided spatially resolved element composition of the samples on the surface while XRF data was used for quality control. From the EDXRF studies of the two samples, the elemental composition agrees with the data from SEM-EDX analysis. The study showed that cellulose extracted from *E. crassipes* and *P. purpureum* gave a high percentage yield of non-toxic, hydrophilic cellulose ether (CMC) after modification with sodium hydroxide and monochloroacetic acid. Conventional CMC used for this research showed higher value for DS than the values obtained from locally synthesized CMC. CMC synthesized is safe for further use in industrial application especially in oil and gas as additives in drilling mud formulation.

DISCLAIMER

The products used for this research are commonly and predominantly use products in our area of research and country. There is absolutely no conflict of interest between the authors and producers of the products because we do not intend to use these products as an avenue for any litigation but for the advancement of knowledge. Also, the research was not funded by the producing company rather it was funded by personal efforts of the authors.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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