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Cocoa husks: a sustainable resource for alkali production

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ABSTRACT

Nigeria has no commercial alkali plant and most of her alkali requirements are imported. Thus the sustainability of using cocoa husks as resource for alkali production was investigated. Cocoa husks collected from three locations in Edo State; (CH₁), (CH₂) and (CH₃) were separately burnt to ashes. Moisture content of ashes ranged from 72.25 ± 1.92% to 74.75 ± 4.11%, dry matter from 25.26 ± 4.11% to 27.76 ± 1.92%, while ash content ranged from 20.29 ± 3.00% to 23.01 ± 3.71%. Alkali was extracted from the ashes by leaching with water at room temperature and CH₁ had highest alkaline content (0.84 ± 0.01 M) while CH₂ had the lowest (0.78 ± 0.02 M). Conductivity of the extract was 72.45 ± 0.03 s/m, 71.02 ± 0.02 s/m and 71.64 ± 0.01 s/m, while the pH was 11.655 ± 0.02 s/m, 11.40 ± 0.01 s/m and 11.42 ± 0.02 s/m respectively for CH₁, CH₂ and CH₃. Metal analysis revealed that they contain appreciable potassium (CH₁ = 43.54%, CH₂ = 41.15% and CH₃ = 41.67%) and sodium (CH₁ = 34.78%, CH₂ = 37.55% and CH₃ = 34.86%) ions, thus can be used to generate alkali as alternative to foreign alkali, reduce Nigerian dependence on foreign alkali and providing environmental solution to their disposal problem.

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INTRODUCTION

Cocoa (*Theobroma cacao*) farming is an important part of the global economy with high potentials for employment generation and poverty alleviation. For example, an estimate of 800,000 farm family are employed by cocoa farming in Ghana alone and also generating about \$ 2 billion annually in foreign exchange (Adi- Dako et al., 2016). Cote d'Ivoire Coast makes an average annual production of 1.2 million tones of commercial cocoa (Sahore et al., 2015) while over 200,000 tons is produced annually in Cameroon (Mahob et al., 2014). Furthermore, about 185,000 metric tons are produced annually in Nigeria (CAN, 2006).

The crop is grown in tropical areas such as West African, South America, and Central America (Adi- Dako et al., 2016; Noble, 2017). In Nigeria, the crop is grown in the Eastern, Southern and Western parts of the country. The economically useful part of the crop is the fruits (cocoa pods) where the seeds (or beans) are removed, amounting for about 25% of the total weight of the fruit (Karim et al., 2014). The seed processing, results to the generation of huge amount of cocoa husks (67% of the pod), amounting for an estimated 10 tons per every ton of dry seeds processed (Campos-Vegas et al., 2018). As a result of inadequate knowledge about waste treatment and

managements, these wastes are usually discarded in concentrated heaps around the farm areas to rot, resulting to environmental degradation, soil infertility, foul smelling and disease causing conditions around the farm areas. This can also lead to the spread of botanical diseases (Mansur et al., 2014). These conditions could endanger the lives of inhabitants around the neighborhood. However, concept of wastes as useless materials is rapidly changing to that of a valuable resource (Kwaghe et al., 2011) because of its valuable chemical component with nutritive, energetic and fertilizing properties (Liang-Qiao and Wu, 2009) that are usually lost by improper waste management methods.

A proper option to which cocoa husk can be put is in the production of ash derived alkali as alternative to inorganic sodium hydroxide (NaOH) and potassium hydroxide (KOH). This option remains largely unexploited and up till now Nigeria do not have a commercial alkali plant. Therefore, most of her alkali requirements are imported. In 1985, about 26,000 tons of sodium hydroxide and potassium hydroxide were imported (Onyegbado et al., 2002). This amount has increased tremendously as result of increasing population, thereby increasing the pressure on importation of inorganic alkali

However, when properly managed these waste could be used to generate alkali solution as alternative to inorganic alkali. Thereby, adding more value to the crop, promoting the creation of new economic activities associated to cocoa farming, increasing the income levels of cocoa farmers and life in rural areas (Sahore et al., 2015). And above all, the nation dependence on imported alkali will reduce considerable if not halted. Also, in line with the Federal Government of Nigeria call to improve on agricultural waste disposal policies and to as much as possible replace imported raw materials with locally sourced raw materials, makes study - Cocoa husks: a sustainable resource for alkali production even more attractive. Also, studies estimating the mass of hydroxide contained per

was of ash extract are lacking. It is on these bases that the study is conducted.

MATERIALS AND METHODS

Sample collection

Cocoa Husks (CH) obtained from three locations; Mr Usman farm in the Nikohole area of Auchi (CH₁), Mr. Ayoola farm, in Usen (CH₂) and Papa Kemi farm in Ogbogui (CH₃) all in Edo state in triplicates between October to December 1999. The samples collected were washed separately with distilled water, drained and weighed. Thereafter, they were sun dried for three days, after which they were dried at 100°C in an oven to attain constant weight (FAO, 2006).

Moisture content (MC) and dry matter content (DM) determination

The determination of the moisture content (MC) of the samples was done using standard methods FAO (2006) with little modification. The dry matter content was also done using standard methods (Adewuyi, 2008).

$$\text{Moisture content (MC)} = \frac{M_0 \times 100}{M_1}$$
$$\text{Dry matter content (DM)} = \frac{M_2 \times 100}{M_1}$$

Ashing and determination of ash content (AC)

Known weights (M₂) of the bone dried samples were placed separately in an open combustion pan made from aluminum and heated until it ignited and turned into ashes. While heating, a metallic rod with a wooden handle was used to turn the sample to ensure uniform combustion. The ash obtained was left to cool at room temperature and weighed again (M₃). The ash content was determined according using standard methods (Radojevic and Bashkin, 2006) with little modification.

$$\text{Ash content (AC)} = \frac{M_3 \times 100}{M_2}$$

Extraction of alkali from sample ashes

100.00 g of each ash sample was weighed into a 1litre capacity beaker and 800 ml water added and the resulting solution agitated thoroughly. Also, the ash solution was

left for 72 hours at room temperature in an attempt to maximize the alkaline extraction. Finally, the solution was decanted to obtain the extract.

Determination of the alkaline concentration

25 ml of the extract was pipette and titrated against 1.35 M hydrochloric acid solution (HCl), using methyl orange as indicator. The titration was done in triplicate and the average titre was used to calculate the alkali content of the extract, using the expression;

$$M_1V_1 = \text{mole ratio}$$

$$M_2V_2$$

Mole ratio = 1:1

Extract pH and conductivity determination

The pHs of the extracts were determined using the jenway 3020 pH machine. The machine was calibrated using buffer solution of 4 and 9. The conductivity was determined by using TDS (total dissolve oxygen) meter, Hannah instrument.

Metal analysis of the extract

The spectrophotometric analysis of the metallic ions present in the extract was determined using an atomic absorption spectrophotometer (AAS), model- sola 969 unicam series. The flame used was acetylene flame.

Estimated masses of NaOH and KOH (g) obtained from the ash extract

The estimated masses (g) of NaOH and KOH obtained from the ash extract were calculated, considering that 100.00 g of each ash was extracted by using 800 ml water by using the mathematical expression:

Estimated mass of hydroxide (g) =

$$\frac{\text{Alkali Content} \left(\frac{\text{mol}}{\text{dm}^3} \right) \times \text{Molar mass} \left(\frac{\text{g}}{\text{mole}} \right) \times \% \text{ composition of elements} \times \text{dm}^3}{125 \%}$$

RESULTS

Properties of the ash obtained from the samples

The results obtained from moisture content (MC %), dry matter content (DM %) and ash content (AC %) (Table 1) reveals the values are not significantly different ($p < 0.005$). The pH values varied significantly ($p < 0.005$) with CH₁ having the highest value which was significantly different from CH₂ and CH₃. The

Alkali content and conductivity values were significantly different with CH₁ having the highest value while CH₂ had the lowest for both.

Atomic adsorption spectrophotometric analysis of some metals in the alkali extract.

The metal concentration analyzed varied significantly among the samples (Table 2). However, the result indicates that potassium and sodium are the main metallic ions present in the ash extract of all the samples, which is distantly followed by magnesium and calcium. Lead was barely present in CH₂ and was the highest value which was significantly different from CH₁ and CH₃ were lead was not present.

Estimated masses of NaOH and KOH from 100g ash extract

Estimates of the masses of NaOH and KOH from 100g ash extract from samples reveals that CH₁ had the highest NaOH and KOH content. CH₂ had the lowest KOH content while CH₃ had the lowest NaOH content. Comparing the total mass of NaOH and KOH content that could be obtained from the extracts indicates that CH₁ had the highest mass of both hydroxides, followed by CH₃ while CH₂ had the lowest mass.

Table 1: Moisture content (MC), Dry matter content (DM), ash content (AC) Alkali Content, pH and Conductivity (s/m) of samples.

SAMPLPES	CH ₁	CH ₂	CH ₃
Moisture content (MC %)	72.25 ± 1.92 ^a	74.75 ± 4.11 ^a	73.83 ± 2.14 ^a
Dry matter content (DM %)	27.76 ± 1.92 ^a	25.26 ± 4.11 ^a	26.17 ± 2.14 ^a
Ash content (AC %)	23.01 ± 3.71 ^a	20.29 ± 3.00 ^a	22.07 ± 1.74 ^a
Alkali Content/ Molarity (mol/dm ³)	0.84 ± 0.01 ^c	0.78 ± 0.02 ^a	0.81 ± 0.01 ^b
pH	11.65 ± 0.02 ^b	11.40 ± 0.01 ^a	11.42 ± 0.02 ^a
Conductivity (s/m)	72.45 ± 0.03 ^c	71.02 ± 0.02 ^a	71.64 ± 0.01 ^b

Results are expressed as mean of triplicate determinations. (The superscripts a, b and c represents statistical significance). Values with the same superscript letters on the same row do not differ significantly at p < 0.05

Table 2: Atomic Adsorption Spectrophotometric analysis/Concentration and Percentage Composition of some Metals in the Alkali Extract.

Metal	Conc. of CH ₁ ppm (mg/litre)	CH ₁ % composition elements	Conc. of CH ₂ ppm (mg/litre)	CH ₂ % composition elements	Conc. of CH ₃ ppm (mg/litre)	CH ₃ % composition elements
K ⁺	217.12 ± 1.00 ^a	43.54	184.37 ± 0.02 ^b	41.15	202.75 ± 0.05 ^c	41.67
Na ⁺	168.43 ± 0.03 ^b	34.78	168.22 ± 0.11 ^a	37.55	169.61 ± 0.01 ^c	34.86
Mg ²⁺	51.03 ± 0.05 ^b	10.24	42.82 ± 0.10 ^a	9.56	51.77 ± 0.05 ^c	10.64
Ca ²⁺	33.77 ± 0.01 ^b	6.77	30.15 ± 0.05 ^a	6.73	35.57 ± 0.01 ^c	7.31
Cu ²⁺	21.51 ± 0.02 ^b	4.31	18.34 ± 0.01 ^a	4.09	21.65 ± 0.01 ^c	4.45
Fe ³⁺	5.11 ± 0.00 ^c	1.02	2.79 ± 0.00 ^a	0.62	4.04 ± 0.01 ^b	0.83
Zn ²⁺	1.59 ± 0.01 ^c	0.32	1.33 ± 0.00 ^b	0.30	1.17 ± 0.01 ^a	0.24
Pb ²⁺	0.00 ± 0.01 ^a	0.00	0.02 ± 0.01 ^b	0.01	0.00 ± 0.00 ^a	0.00
Total	498.56	100.98	479.84	100	486.56	100

Results are expressed as mean of triplicate determinations. (The superscripts a, b and c represents statistical significance). Values with the same superscript letters on the same row do not differ significantly at p < 0.05.

DISCUSSION

The moisture content (MC), dry matter (DM) and ash content (AC) obtained for all the samples were not statistically different. The MC obtained in this study CH₁ (72.25 ± 1.92^a %), CH₂ (74.75 ± 4.11^a %) and CH₃ (73.83 ± 2.14^a %) were similar to the 76.00 ± 2.00% obtained by (Akindejoye, 2017) but lower than the 80.9 – 86.7% obtained by (Babayemi et al., 2010), respectively for cocoa pods and plantain peels in similar studies. The variations in values for plantain peels could be because the crops are different. Ash content was high (20.29 ± 3.00% - 23.01 ± 3.71%) compared to 11.62 ± 3.00% obtained by (Akindejoye, 2017) for cocoa pods in a similar study. Climatic variations, seed species, and geological locations could be responsible for the deviations. The high ash content for cocoa husks obtained in this study is likely attributed to their high mineral content. The molarities of the ash extracts were 0.84, 0.78 and 0.81 for CH₁, CH₂ and CH₃ respectively. The molarities of the ash extract were higher than the 0.23 M and 0.45-0.49 M obtained respectively by (Onyegbado et al., 2002) and (Olabanji et al., 2012) using plantain peels ash/banana and plantain peels ash in similar studies. Higher concentrations obtained in this study could be attributed to difference in plants and the use of lower volumes of the extraction solvent and allowing the extraction solution to stand for a longer period (72 hours).

The pH values of the samples were not considerably different, while conductivity values obtained for CH₁ was highest.

Table 2 reveals that the main metallic ions present in the ash extracts were potassium and sodium. Potassium was higher than sodium in all the samples with CH₁ containing the highest percentage of potassium ion (43.54%) and CH₂ recorded the lowest (41.15%). The amount of metallic ions content in the extract followed the same trend of K > Na > Mg > Ca > Cu > Fe. This observation is consistent with some research findings (Akindejoye et al., 2017; Ayeni, 2010) while (Olabanji et al., 2012) had a different trend.

However, highest total metal content was recorded by CH₁ (498.56 mg/liter) while CH₂ (479.84 mg/liter) had the lowest. The heavy metal ions under study (Cu, Fe, Zn and Pb) constituted less than 6%, with Pb which is known to cause different kinds of adverse environmental and health conditions (Eze et al., 2013) was almost not present in the samples, suggesting that alkali extract from the will not pose any pollution threat.

Figure 1 shows the estimated masses of NaOH and KOH (g) obtained from 100g ash extract. From the result it is observed that potassium hydroxide was higher in all the samples with the highest hydroxide obtained by (CH₁). CH₁ also had the highest mass for sodium hydroxide. The highest hydroxides obtained for CH₁ could be attributed to the fact that it had the highest ash content, suggesting high mineral content. Previous studies (Ooi, et al., 2012) reported that high ash content was a result of high-value of mineral composition.

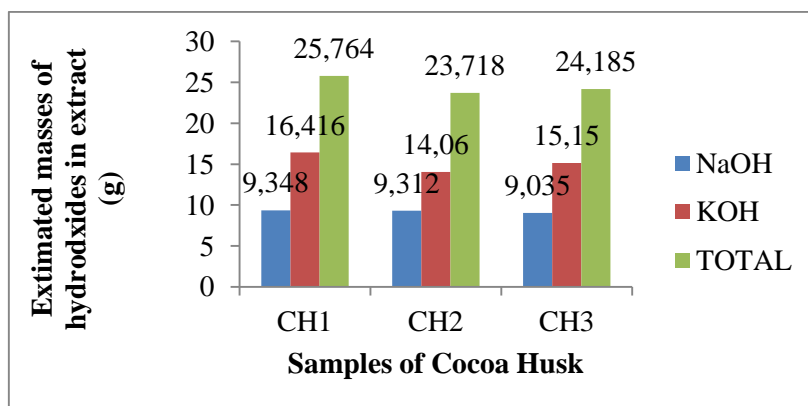


Figure 1: Estimated masses of NaOH and KOH (g) from 100g ash extract.

Conclusion

Results from this study reveal that these agricultural wastes contain appreciable amount of alkali. It estimated that more than 20 g of alkali hydroxide can be obtained per 100 g of ash, so when properly harnessed can serve as raw material for different industrial and analytical use. More research in the study, particularly in the area of extract purification would make these agricultural wastes more useful and also cutting down on or eliminating the country's importation requirement for alkali.

COMPETING INTERESTS

The authors declare that they have no competing interests.

AUTHORS' CONTRIBUTIONS

MM: Conceptualization methodology, formal analysis, investigation and writing – original draft. IHI: conceptualization, supervision and SOO: validation, resources, review and editing.

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