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Full Length Research Paper

Metal analyses of ash derived alkalis from banana and plantain peels (*Musa* spp.) in soap making

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The objective of this work was to determine the metal content of plantain and banana peels ash derived alkali and the possibility of using it as alternate and cheap source of alkali in soap industry. This was done by ashing the peels and dissolving it in de-ionised water to achieve the corresponding hydroxides with pH above 12. The solution was then analyzed using Atomic Absorption Spectroscopy (AAS). The analytical measurements were carried out in triplicate and the multi elemental solution was used for calibration of equipment. The abundance of essential metals was in these orders in both the banana and plantain alkalis: K > Fe > Ca > Mg > Mn > Zn > Na and Fe > K > Ca > Mg > Zn > Mn > Na, respectively. The presence of other metals besides K and Na at higher concentrations limits the foamability of the soaps but could be adapted as thickeners and emulsifiers in greases. The concentrations of elements with health risk in the ash derived alkalis are within the allowable range of the Commission of European Communities (2008) limit.

Key words: Banana, plantain, ash derived alkali, major elements, minor elements.

INTRODUCTION

Nigeria is one of the largest plantain producing countries in the world (FAO, 2006). Despite this large production, she does not export plantain because its production is largely consumed locally. The rise in cottage industries that made use of plantain for snacks (plantain chips) in the non-farming urban population coupled with the demand for easy and convenient foods made from plantain locally, made its consumption to be on the increase (Akinyemi et al., 2010). The high demand for plantain also generates wastes which are often discarded, and sometimes used for animal feeds. FAO (1988) estimated 5,879,000 metric tonnes of banana peels and 17,397,000 metric tonnes of plantain peels in African countries which could be put into use for generation of ethanol, alkali for soap production and other medicinal use.

Soap production started around 2500 BC with boiling of fats with ashes. The formula for soap consisting of water, alkali and cassia oil was written on a Babylonian clay tablet around 2200 BC (SDA, 1981; Willcox, 2000). In ancient times, lubricating greases were made by reacting lime with olive oil (Cavitch and Miller, 1995) these are non synthetic and agricultural based materials like banana peels, plantain peels, palm oil and palm kernel oil, and therefore agricultural wastes such as banana peels, plantain peels reacting with oil (palm oil and palm kernel) could also serve the same purpose.

In chemistry, soap is a salt of a fatty acid (IUPAC, 1997). Ester hydrolyzed in the presence of an alkali produces the carboxylates (salts of parent carboxylic acids) and alcohols. The reaction is irreversible and can be represented as shown below

$$RCOOR' + OH^- \rightarrow RCOO^- + R'OH$$

This reaction is used in the soap-making process, in which fats or oils (or triesters) are hydrolyzed to produce sodium carboxylates (soap) (Wong et al., 1998). The alkaline solution promotes what is known as saponifica-

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tion. Soaps for cleansing are obtained by treating vegetable or animal oils and fats with a strongly alkaline solution. Soap is mainly used for washing, bathing, and cleaning but soaps are also important components of lubricants. Therefore, it is important to note the metal constituents of the ash from agricultural waste for the production of locally made soaps.

Studies have been conducted on metal composition of personal care products, soaps and detergents and cosmetics in Nigeria (Ayenimo et al., 2010; Abulude et al., 2010; Oyedeji et al., 2011) but there was little or no information on metal constituents of locally made soaps or its alkali. The toxic effects of heavy metals on human health and ecosystem are well documented (Turkdogan et al., 2003; Kawata et al., 2007; Liu et al., 2009). At low concentration, some of these elements cause internal body organ damage in animals and humans, since metals' pollution is through ingestion, inhalation and skin contact, therefore, metals in agricultural waste could get accumulated in man through the above route and their by-products.

The abundance of plantain and banana peels could generate ash derived alkali solution as alternative to inorganic alkali, such as NaOH and KOH. Irvine (1965) stated that agricultural waste materials contain a good percentage of potash. These materials include palm bunch waste, cocoa pod, plantain peels, banana leaves, banana peels, maize cob, wood, sugar beet waste and many others. When these materials are burnt in air, the ashes contain oxides of potassium and sodium which when dissolved in water yield the corresponding hydroxides (Onyegbado et al., 2002) according to the equations:

$$Na_2O + H_2O \rightarrow 2NaOH$$

$$K_2O + H_2O \rightarrow 2KOH$$

Environmental factors can affect the quality of locally made soap, since they are made of raw or unprocessed materials from agricultural waste. Agriculture and aquaculture have been reported to affect the environment due to fertilizer, contaminated sewage and the use of herbicides (Falandysz et al., 2005). It is therefore pertinent to assess the composition of the ash-derived alkali and its suitability for human use. This will enable us to have information on the heavy metal that can be absorbed into the body through the use of the product made from the alkali and possible danger man may face through their use.

MATERIALS AND METHODS

Pretreatment and sterilization of apparatus

The beakers, volumetric flask, sample bottles, measuring cylinder, pipette, burette, stirring rod, spatula, were soaked with 10% HNO_3 and liquid soap for 48 h and rinsed with double distilled water after which they were left to dry in the oven at 105°C ± 2 (Ogunfowokan et al., 2005). Other materials used include an oven, a furnace, crucibles, weighing balance, a large shallow tray called "combustion pot" and a sieve set.

Reagents

All reagents used are of analytical grade. They include, alcoholic KOH, sodium carbonate, sodium chloride were all from BDH Chemicals Limited, Poole England, Hydrochloric acid (Riedel-de Haen).

Sample collection and preparation

Unripe plantains (*Musa balbisiana)* Figure 1 and unripe banana (*Musa acuminate*) Figure 2 were collected from the same farmland within Obafemi Awolowo University Ile-Ife, Nigeria. They were peeled and the peels were washed with double distilled water dried in an oven at 105°C ± 2 for two days to constant weight. The dried peels were ashed in a porcelain crucible placed in a Gallenkamp muffle furnace for 6 h by stepwise increase of the temperature up to 500°C (Crosby, 1977). The ashed samples (grey in colour) were homogenized in porcelain mortar and pestle and sieved. Sixty (60) g of each of the sample were weighed into poly ethylene buckets of 2000 L capacities and one liter of water were added (Kuye and Okorie, 1990; Onyegbado et al., 2002). They were covered to prevent contamination for 24 h for maximum extraction. The extracts were carefully decanted and double distilled water were added in ratios of 1:4 of sample to double distilled water and were analyzed by atomic absorption spectrophotometer (AAS) Buck Model 205 at the International Institute for Tropical Agriculture (IITA), Ibadan. These extracts were alkaline to litmus paper and gave yellow colour when two drops of methyl orange were added. The remaining extracts were used in the determination of molarities and in preparation of soaps.

Determination of molarities

Ten gram (10 g) of anhydrous Na_2CO_3 was placed in a crucible and heated between 250 to 270°C for 30 min in the oven and allowed to cool in desiccator. 2.65 g was weighed into 500 cm^3 standard flasks and double distilled water was added and shaken at interval until the salt dissolved and made to the mark. This solution was titrated against HCl using methyl orange as indicator to determine its molarity. The HCl of known molarity was titrated against each of the extract using Phenothpthalein indicator to determine its molarities.

Determination of pH and conductivity

The pH of the extracts were determined using Hannah instruments, pH 210 Microprocessor pH meter. The pH meter was calibrated using buffer solutions of pH 4, 7 and 9, the pH meter of each extract subsequently determined. The conductivity meter (CD210, WPA, UK) model was calibrated following the manual instructions and the extracts conductivities were determined.

Oil blend preparation and characterization

Four hundred gram (400 g) of palm oil and 100 g of palm kernel oil purchased from the retail market at Oroki, Ile-Ife, Osun State, Nigeria, were blended to give a ratio of 4:1 by weight (Onyegbado et al., 2002). Forty gram (40 g) of the blended oil was heated to 70°C and poured into a cell in a Tri-stimulus Colorimeter (Model:

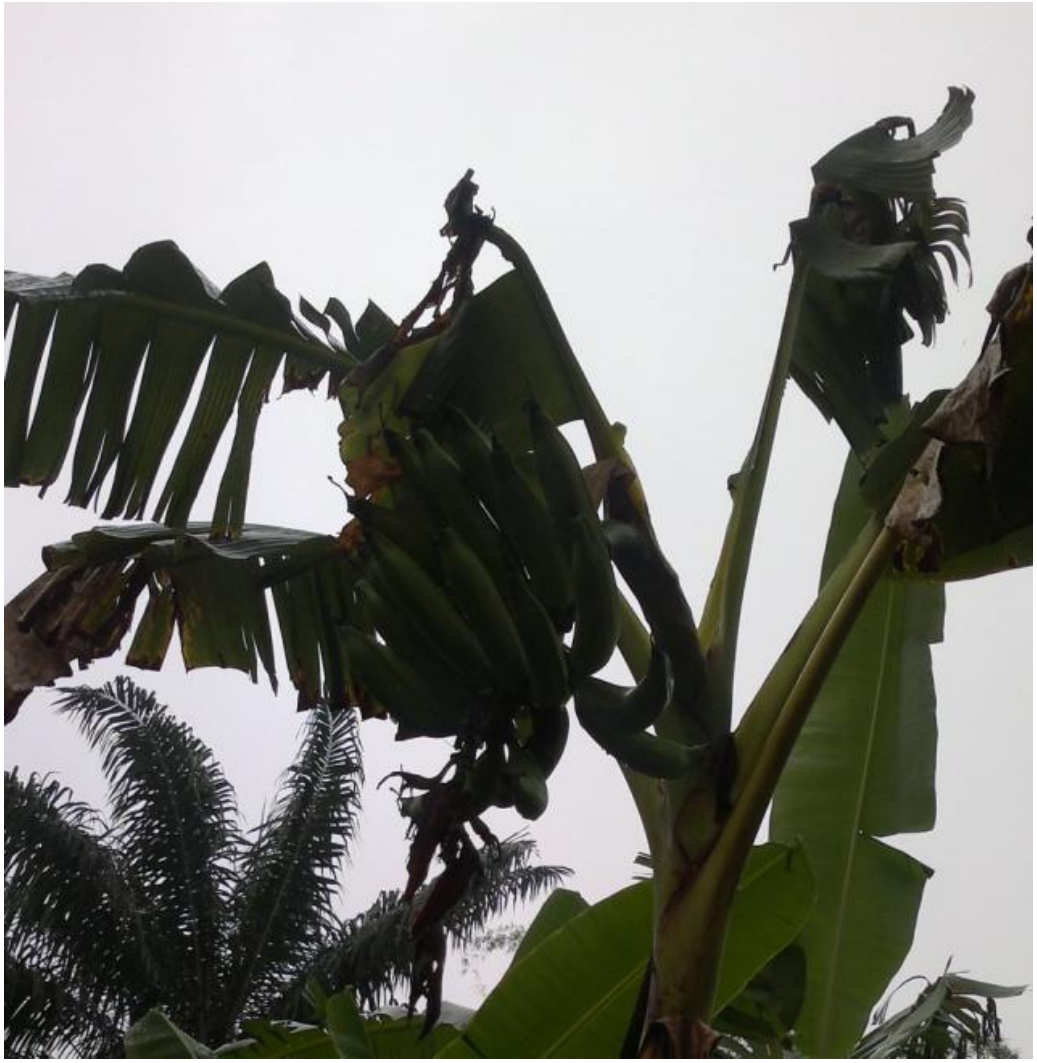

Figure 1. Plantain (*Musa balbisiana*).

Macbeth-Munsell disk colorimeter) at the Chemical Engineering Department, Obafemi Awolowo University, Ile-Ife, Osun State, Nigeria. The readings were taken when the meter colour matched the blended sample colour. Forty gram (40 g) each of the unbleached palm oil, unbleached palm kernel oil, bleached palm oil, bleached palm kernel oil, and unbleached oil blend were also poured into the Tri-stimulus Colorimeter at intervals, and the colours units were recorded to ascertain the actual colour of the blended oil.

Determination of saponification value of blended oil

Five gram (5 g) of blended oil sample was accurately weighed into a 250 mL flask, 50 mL of alcoholic KOH solution was added and the content was refluxed. Test for complete saponification was carried out by dropping the mixture in water at interval; whenever the traces of oil are seen, it shows incomplete saponification. Reflux was continued until saponification was completed at 80°C. The mixture was cooled and 10 cm^3 of the mixture was pipette into a conical flask, two drops of phenolphthalein indicator was added. 0.5 M HCl was put in the burette and titrated against the mixture. This was done in triplicates and the average value was recorded.

Saponification reaction using the ash-extracts

One hundred and ten milliliter (110 mL) of the ashed peel (Banana and plantain separately) extract was heated to half of the original volume (concentrated to 50% alkali) by heating and evaporating in a beaker (saponification pot) (Babayemi et al., 2011). This is because in soap making, a slight excess of alkali is usually recommended in order to ensure that all the fat is saponified and also because of the antibacterial effect of the alkalis (Kirk et al., 1954). The concentrated extract was heated to 80°C and 7.0 g of bleached oil blend was gradually charged into the pot. The temperature was maintained at 80°C and 5 mL of distilled water was added intermittently while the mixture was continuously stirred. Saponification continued until the solution became creamy. This took approximately 40 min. About 10 mL of sodium chloride brine was charged into the beaker content (saponification pot) and the soap was completely homogenized and maintained at the temperature of 70°C for 30 min. The crude soap was separated by allowing the beaker and its content to cool. The soap formed a layer

Figure 2. Banana (*Musa acuminate*).

on the surface of the beaker while lye (a solution of glycerol and brine) was below. The lye was removed by scooping the surface into another container. The neat soap was then cooled.

RESULTS AND DISCUSSION

Analytical validation

The pH of banana and plantain peels ash derived solutions are 12.05 and 12.88, respectively which confirmed alkali production from banana and plantain peels, the molarities of the banana and plantain ash extract were 0.45 and 0.49, respectively and the metal analysis (Table 1) showed metals of varying concentrations.

Thorsten et al. (2002) stated that soaps are key components of most lubricating greases, which are usually emulsions of calcium soap or lithium soaps and mineral oil. These calcium- and lithium-based greases are widely used. Other metallic soaps are also useful, including those of aluminium, sodium, and mixtures of them. Such soaps are also used as thickeners to increase the viscosity of oils. The ash derived alkali contains varying concentrations of different metals (as shown by conductivity values of 61.7 µS/cm in banana peels and 64.2 µS/cm in plantain peels). Since emulsion of Ca, Li and many other metal soaps and their mixtures are used in most lubricating greases and are often called thickener (Cavitch and Miller, 1995; Thorsten et al., 2002), the soap made from these ash derived alkali of banana and plantain could be useful as a thickener in lubricating greases and will be more economical than those from inorganic sources.

Although the soaps produced from the ash-derived alkalis were not solid, they were soft and jelly-like, this is expected as the percentage concentration of K in banana and plantain were 41.45 and 32.54% and that of sodium were 0.72 and 0.37%, respectively (Table 1) of the total metal ions analyzed in each sample. Almost as a rule, the

Table 1. Concentrations and percentage compositions of ash derived alkali from banana and plantain peels.

Element	Concentration in PP (mg/kg) ± SD	Composition of elements (%)	Concentration of BP (mg/kg) ± SD	Composition of elements (%)
Ca	106.78±0.00	14.98	76.86±0.00	17.50
Mg	66.48±0.00	9.33	32.33±0.01	7.36
K	231.93±0.00	32.54	181.99±0.0	41.45
Na	2.66±0.00	0.37	3.18±0.00	0.72
Mn	29.64±0.00	4.16	23.74±0.00	5.41
Fe	241.63±0.00	33.9	99.18±0.02	22.58
Cu	2.45±0.00	0.34	1.67±0.00	0.38
Zn	30.70±0.00	4.31	19.74±0.00	4.50
Pb	0.02±0.00	0.003	0.02±0.00	0.005
Cr	0.02±0.00	0.003	0.04±0.00	0.009
Cd	0.003±0.00	0.000	0± 0.00	0.00
Pd	0.07±0.03	0.01	0.05±0.02	0.01
Ni	0.06±0.02	0.0084	0.05±0.02	0.011
Ag	0.02±0.01	0.0028	0.02±0.00	0.005
B	0.23±0.02	0.03	0.19±0.01	0.04
Al	0.03±0.01	0.004	0.019±0.01	0.044
	712.72	99.99	439.08	100.03

PP- Plantain peel, BP- banana peel.

solubility of soap in water increased in the size of the monovalent cation (base); an increase in the size of a divalent cation, (Mg, Ca) results in a decrease in the foamability (Gupta and Wiese, 1997). Potassium soaps are more soluble in water than sodium soaps; in concentrated form they are called soft soap. Also, sodium soaps prepared from sodium hydroxide are firm, whereas potassium soaps, derived from potassium hydroxide are soft. Because of their softness and greater solubility, potassium soaps require less water to liquefy and thus can contain more cleaning agent than liquefied sodium soap and can be used as shampoos, shaving creams, cleaning of dirty floors and cooking utensils, in emulsion polymerization processes used in rubber and plastic industries and in such other similar uses (http://en.wikipedia.org/wiki/Potassium_hydroxide). The presence of Ca and Mg ions limit its foam ability.

The palm oil/palm kernel oil had a saponification value of 177.61. According to the study of Bailey et al. (2000), fats and oils can be characterized by their saponification numbers; one mole of fat requires three moles of KOH for complete saponification. If a fat contains fatty acids of relatively high molecular weights, then one gram of the fat will consist of fewer moles. Thus, fats having greater percentages of high molecular weight fatty acids will have lower saponification numbers than fats having greater percentages of lower molecular weight fatty acids. Therefore, the palm oil/palm kernel oil was supposed to have lower molecular weight fatty acid and high saponification value (Palm oil 196 to 205 and Palm Kernel oil 242 to 250, when free from moistures and unsaponifiable matter (Lewkowitsch, 1922). Other unsaponifiable matters present in the oil may be responsible for lower saponification number.

Lewkowitsch (1922) said fats of different species of animals and plants vary widely. Indeed, the fat, from a given natural source, say a given species of animal or plant, may contain the same triglycerides in slightly different proportions, depending upon the conditions of the environment prevailing while the fat was being formed. It was pointed out that the properties of the fat of an animal vary somewhat with the diet and also with the tissue from which it is obtained. Fruit may yield two fats of different properties, one from the pulp and one from the kernel. In the case of plants, the fat may also vary with the cultural variety of the plant and with the climatic and soil conditions under which the plant was grown. Soaps made from fatty acid of longer chain C16 to C18 contribute to the cleansing properties of soap (Gupta and Wiese, 1997), thus the soaps made with palm kernel and palm oil (with chain length C16 to C18) in this work will have good cleansing properties.

The redness of the oil was considerably reduced by bleaching, in which yellowness increased giving the oil a light colour. The redness of the oil is as a result of high carotenoid pigments which contribute to the colour of the resulting soap. Onyekwere (1996) had shown that bleaching of the oil removed carotenoid pigment and odour of palm oil in resulting soap.

Spectrophotometry analysis of the metallic ions present in ashed samples solution (Table 1) showed that the alkali consist of ions that are essential diet components by contributing iron, calcium, potassium and other elements, which are usually in short supply in human in some cases. It had been stated that plantains and banana are good sources of vitamins and minerals, particularly iron (24 mg/kg), potassium (9.5 mg/kg), calcium (715 mg/kg), vitamin A, ascorbic acid, thiamin, riboflavin and niacin. The sodium content (351 mg/kg) is low in dietary terms, hence recommended for low sodium diets (Stover and Simmonds, 1987; Welford et al., 1988).

The essential elements in the banana and the plantain alkali in this study were in the order K > Fe > Ca > Mg > Mn > Zn > Na and Fe > K > Ca > Mg > Zn > Mn > Na. The element with the least concentration in these series was Na, which supported the claim in previous findings (Stover and Simmonds, 1987; Welford et al., 1988) and also showed that the unripe banana and plantain pulp may contain metals in similar order, and a slight difference may be due to the type of soil they are grown and the type of agricultural practices at different places. Elements such as Fe, Ca, Mg and Zn are essential for building red blood cells, bone formation, growth and development; Zn and Mn are key components of metallo-enzyme or are involved in crucial biological functions, such as oxygen transport, free radical scavenging or hormonal activity also required for metabolism (Parsons and Barosa, 2007).

In this study Zn was found in banana and plantain alkali in concentration of 30.90 and 19.74 mg/kg, respectively. Zinc is an essential trace metal for plants, animals and human as it is associated with many enzymes and with certain proteins. The major health concern for zinc in general is marginal or deficient zinc intake rather than toxicity. Zinc is considered as being of low toxicity due to the wide margin between usual environmental concentrations and toxic levels. However, high levels of zinc are undesirable as it may lead to copper deficiency by inhibiting copper absorption (Iwegbu et al., 2011). All these elements could enrich/nourish the skin when soaps, through the ash derived alkali, are used for bathing. Other metals such as Pd and Ni were less than 0.1 mg/kg, Pb, Cr, Ag, B and Al were less than 0.05 mg/kg and Cd less than 0.01 mg/kg. The Commission of European Communities (2008) stated 0.3 and 0.05 mg/kg for Pb and Cd as the maximum contaminants level in foodstuff, as contained in food supplement as sold.

In this study, the values for banana and plantain peels were (Pb 0.02 mg/kg in both peels and Cd 0.00, 0.03 mg/kg in banana and plantain, respectively). These values are lower compared with the CEC recommended maximum levels. Cadmium had been associated with hypertension, liver disease and kidney damage while Pb causes brain damage (Asaolu et al., 2002); but the levels in this work were far below the level that could cause damage to humans. Chromium was relatively low in the samples. The levels of chromium observed in these samples do not pose any contamination hazard to users. Since it is essential to keep contaminants at levels which do not cause health concerns in order to protect public health (CEC, 2008), any contact made by the soap produced with banana and plantain ash derived alkali with humans through absorption by skin when in use may not likely pose health risk.

Conclusion

Neat soap, having physical properties as pure potassium hydroxide soap is derivable from the water extract of ashes of plantain and banana peels. The concentrations of elements with health risks are within the allowable range of CEC (2008) limit of elements concentration in food stuff. Efforts need to be made to reduce the level of other macro and micro elements that constitute impurities in the alkali. This will make agricultural wastes more useful, thereby cutting down on, and eventually eliminating the need for importation of inorganic raw materials for production of thickeners and cleaning agents.

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