Characterisation of Physico-Chemical Properties of Arachis Hypogaea L. Shells (Groundnut) as Environmental Remidation

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Abstract—The physico-chemical characteristics as well as chemical composition of Arachis hypogaea shell (AHS) ash were evaluated by different techniques such as X-Ray fluorescence, X-Ray diffraction and thermo-gravimetry. The material, which is considered a by-product obtained from Groundnut shelling, was investigated as a potential fertilizer, energy source and as animal feeds. And this will provide a reasonable economic means to this waste in an environmentally friendly manner. To achieve this objective, Arachis hypogaea shell ash was applied to radish crop in a greenhouse pot experiment having 11kg at33:1 ratio in Irish moss peat in each treated pot (T) compared to the control pot (C). Most of the yield and yield component of the radish crop in the treated pot experiment increased compared to the control.

Keywords—X-ray Defraction, X-ray Fluorescence, Thermo-gravimetric Analysis.

I. INTRODUCTION

Groundnut shells (Arachis hypogaea L) are an agricultural by-product from an oilseed leguminous crop groundnut. Scientifically Groundnut is known as Arachis hypogaea, its origin was traced to Bolivia at the end of the Andes (Krapovickas, 1968 cited in Singh and Oswalt, 1995) extending to north Argentina (RamanathaRao, 1988 cited in Singh and Oswalt, 1995). The cultivated groundnut belong to the section Arachis and series amphiploidies and family fabaceae (Gregory et al 1973 cited in Singh and Oswalt, 1995).The species A. hypogaea consist of two subspecies, ssp hypogaea and ssp fistigiata (Singh and Oswalt, 1995). Each of these two subspecies has two botanical varieties which give rise to four cultivated groundnut type according to Krapovickas and Rigoni (1960 cited in Sing and Oswalt, 1995) are as follows:

1. Arachis hypogaea hypogaea hypogaea Linn.
2. Arachis hypogaea hypogaea hirsute kohla.
3. Arachis hypogaea hypogaea fistigiata fistigiata Waldron.
4. Arachis hypogaea hypogaea fistigiata vulgaris Harz.

The other different names by which peanut is called includes groundnut, monkey nut, earthnut, gobber, gobber pea, peanut vine, potato bean, wild bean, earth-ball, truffle, Bambara, Chang Sheng Guo (Long-life nuts), pygmy nut and pig nut (Krapovickas and Gregory, 1994 cited in Singh and Oswalt, 1995).

Groundnut is the second most important leguminous crop the world over after soy beans as it provides food for human and livestock and form valuable dietary protein component in the absence of meat (Redden et al, 2005 cited in Sim, E. W., 2011). Groundnut kernel contains 47-53% oil and 25-36% protein (Pop and Colab., 1986; Prasad et al., 2011). Groundnut is the third most abundantly cultivated oilseed in the world and plays an important role in the economy of these West African countries, including the Gambia, Nigeria Ghana and Senegal (Folagbade and George, 2010, Nwanosike, 2011). In Africa, groundnut is grown mainly in these countries, Nigeria, Gambia, Sudan, Senegal, Chad, Ghana Congo and Niger (Prasad et al., 2010). In 2007, the total harvested area for groundnut in Africa was 9.04 ha with a total production of 8.7 million metric tonnes. The average productivity index for Nigeria was reported to be1720kg/ha, 500kg/ha was reported for Sudan and 700kg/ha was given for Senegal. Up till now Groundnut is the major export product for Senegal and the Gambia, it was the major export commodity for Nigeria before the discovery of petroleum in the Niger delta area (Adeeko and Ajibola, 1990 cited in Olajide and Igbeke, 2002; Nwanosika, 2011).

According to food and Agricultural report (2007 cited in Sim 2011), the World groundnut (Arachis hypogaea) in-shell total harvested area in 2007 was 23.4 million ha with a total production of 34.9 million metric tonnes (mt). The report has also indicated the increase in the total harvested area for groundnut production in 2007 by 3.7 million ha compared to 1990, this was also accompanied by an increase in groundnut production by 11.7 million mt. The world average productivity of groundnut in 2007 was about 1490kg/ha (FAO, 2007 cited in Sim, 2011). Groundnuts are predominately grown in the developing countries (Asia and Africa) which constitute 97% of the global area and 94% of the global production because the crops finds appropriate climate for optimum production in these parts of the world (Prasad, et al 2010). A recent study provides statistical evidence indicating the percentage of annual production of groundnut in Asia and Africa as (56%
and 40% of the global area and 68% and 25% of the global production, respectively. In 2007, Asia has been reported to have the largest area of groundnut cultivation by contributing 67% of the total world production (Prasad et al 2010). The total world production of peanut increased from 31.48 to 33.73 million metric tonnes of which groundnuts (Arachis hypogaea) increased by 7.13% in the year 2010 (Georgalos, 2010 in Sim, E. W., 2011). Global peanut production has increased to 35.88 million metric tonnes in 2011 (USDA, 2012, in Chang et al, 2012) which led to concern on agricultural waste management problem as this high production of peanut is accompanied by the generation of significant quantity of waste in countries such as China, which generates over 800 million tonnes of agricultural waste annually (Yue, et al, 2009 in Sim, E. W., 2011).

Groundnut is an important subsistence food crops throughout the tropics. In our contemporary societies it is mainly grown for the kernel and edible oil and the meal derived from them such as groundnut cake (Nwanosika, 2011) a very popular a popular in my African village perspective and the vegetative residue. Groundnut kernels, apart from oil and protein; they also contain about 10-15% carbohydrate and are rich in P; they are also a good source of vitamins B and E (Hashim et al 1999 in Chun., J., 2002; Nautiyal, 2002).

Groundnuts are used in various forms, the oil which is the cheapest of all types of vegetable oils and most extensively used oil in many countries as cooking oil, manufacture of margarine, preparation of salad (Weimer and Altes, 1998 in Olajide and Igbeka, 2002). The is used widely all over Africa as soup thickener (Atasie et al, 2009). The cake is used for animal feedstock and as a fertilizer. The shells are the dry pericarp of the mature pods contains chemical composition cellulose, carbohydrate, protein, minerals and lipids (Reddy, 1988 in Nautiyal, 2002). The shells have been utilized in a variety of application, such as source of activated carbon (Shukia and Pai, 2005; Wilson et al, 2006; Ramteke and Wate, 2007). Groundnut shells are used as fuel when pelletized and made as smokeless briquette (Blesa et al, 2001 cited in littlefiel, 2010; Harrel et al, 2010) as a soil conditioner, filler in fertilizer and feeds, or is processed as substitutes for cork and hardboard, or composting with the aid of lignin composting bacteria (Esaki et al, 1986 in Nautiyal, 2002). The foliage of groundnut crop is also serving as silage and forage in livestock production especially during the rainy season (Beuchat et al, 1992 in Nautiyal, 2002). Alabadan et al., 2006, in Falagbade and George, 2010) categorized Arachis hypogaea shell ash with about 8.66% calcium oxide (CaO), 1.93% Iron oxide (Fe2O3), 6.12% magnesium oxide(MgO), 15.92 silicon oxide (SiO2) and 6.73% Aluminium Oxide(Al2O3) under pozzolana. This composition makes it suitable for application in concrete as a partial replacement for cement with a measure of success achieved (Alabadan, 2005, in Falagbade and George, 2010).

Food and Agricultural Organization (FAO) of the United Nations reported fear of the creation of significant waste disposal problems around areas where agricultural waste, such as groundnuts shells, are grown and/ or where they are processed (FAO, 2005). The common methods of handling the disposal of oilseed harvest residue such as groundnut shell is mostly either by incineration, incorporation in soil on land dumping. However, incineration method will emit smoke and particulate matter, which causes air pollution. Incorporation of agricultural waste into soil influences physical, biological and chemical properties of soil (Osterli, 1972; Westendorf, 2000 in Sim, 2011). Therefore, it is necessary to develop improved methods of managing the huge amount of peanut shells, which poses a critical problem in waste management systems and subsequently causes environmental pollution (Westendorf, 2000 in Sim, 2011). Transforming groundnut (Arachis hypogea) shells into a valuable raw material, ingredient or product would be the better method to utilize them (Ebine, 1973; Crikenberger and Carawan, 1996 El-hagger, 2001; Lesdema, et al, 2004; Kyriazaki and Whitten more, 2006; Dongmezaet et al., 2009; Maheswari et al., 2010 in Sim, 2011).

II. AIMS AND OBJECTIVE OF THE STUDY

The aim and objective of this research work is to analyze Arachis hypogaea (groundnut) shell samples for their physico-chemical properties, in order to determine its suitability as a fertilizer as the best alternatives in curbing agricultural waste problems and reducing waste management costs.

III. LITERATURE REVIEW

A. Review of Plants Nutrients

All plants require inorganic elements or minerals for their life processes. Studies have indicated low organic matter content and imbalance in nutrient supply by depletion of essential micronutrient in an intensively cropped soil especially in tropical soils due to indiscriminate use of chemical fertilizer (Ronan, 2007). Arachis hypogoea shell ash or charcoal can replace synthetic fertilizer as it can supply macronutrients (C,H2,N2, P,K, Ca, Mg, and S) and micronutrient(Mn, Cu, Zn, Mo, B, Cl2 and Fe) to the soil to be used by crop (Ronan, 2007). Macro and micro elements are essential for plant growth (Fitzpatrick, 1974; Ronan, 2007). Minerals that are needed by plants in a relatively large amount are referred to as macro-elements, whereas minerals that are needed by the plant in very small amounts are denoted micro-elements or trace elements. Trace elements must be in correct proportions to avoid deficiency and excessive presence. Deficiency or excess of any one element affects plant growth. Plants develop symptoms indicating nutrient starvation or toxicity (Fitzpatrick, 1974; Ronan, 2007).

IV. REVIEW OF MACRO-NUTRIENT ELEMENTS FROM ASH

Although there have been many studies on the macro-element release from plant residues biomass ashes, the potential of Arachis hypogaea shell ash as macro-nutrient fertilizer has not been widely investigated. Novak et al. (2009) characterised Arachis hypogaea shell ash and suggested its use as a fertiliser to supply variety of both macro and micro elements to the soil. Multi-element release by
Arachis hypogaea shell ash could be an advantage when utilised as fertilizer. Ronan (2007) described (K, Ca, Mg, P, S, B, Cl, Cu, Fe, Mn, Mo, Ni, Zn, Co, Na and Si) as plant nutrient. Most trace elements exist in minerals as inclusions or foreign ions as opposed to main structural elements and are likely to be available in lesser quantities than macronutrients. Each macronutrient element plays the following specific function in plants: carbon (C), hydrogen (H), and oxygen (O) are macro elements where C is derived from the atmosphere, while the source H and O source is water (Fitzpatrick, 1974; Ronan 2007). These elements form major constituents of plant tissue. Nitrogen (N) is naturally derived from the atmosphere or dead tissues. N is transformed for plant utilization through nitrogen transformation, which includes ammonification, nitrification, and nitrogen fixation. Most plants absorb N in the form of ammonium or nitrate, the fertilizer source of N are ammonium, nitrates compounds or urea (Fitzpatrick, 1974). N deficiency in plants can lead to loss of colour and stunted growth (Fitzpatrick, 1974) Calcium, (Ca) a macronutrient, is necessary for the growth of meristem in plants. Meristem is a region of active cell division in plants. Ca deficiency results in malformation of the shoot tips, (i.e. the growing parts in plants) and excessive Ca presence can limit the availability of other nutrients. A major fertilizer source of Ca is gypsum (Fitzpatrick, 1974). Phosphorus (P) is also a macronutrient element which is a constituent of plant cell has a greater concentration in seeds. Phosphorus deficiency in plants causes a purplish coloration at the seedling stage, with yellowing of the plant leaves and stunted growth. The fertilizer sources of phosphorus (P) included any compound any compound containing phosphate, such as bones (Fitzpatrick, 1974) Potassium,(K) is a macronutrient essential in plant cell metabolic process. Its presence influences the absorption of other elements by plants and is also important in plants cell wall thickening by its ability to translocate carbohydrate. Symptoms of K deficiency in plants include yellowing of leaf tips and leaf margins. Fertilizer source of K is potash, such as plant ash. (Fitzpatrick, 1974). Magnesium (Mg) is a macronutrient which is active in enzyme systems and form part of the chlorophyll in plants. (Mg) is absorbed by plants in ionic form i.e.theMg+2 ion. Mg deficiency causes discolouration and premature defoliation in plants (Ranon,2007). Fertilizer sources of magnesium include any magnesium compound, such as Epsoms salts (magnesium sulphate (MgSO4). Sulphur S, is a macronutrient for the plants and is absorbed by plant in the sulphate (SO4) form. S can be a source of soil acidity. S deficiency causes younger leaves to turn yellow and stunted growth in plants. The source of fertilizer is any sulphate compound such as gypsum CaSO4 (Ranon, 2007)

V. REVIEW OF MICRONUTRIENTS

Iron (Fe), is a micronutrient absorbed by the plants in an ion form through plants foliage and roots systems. Manganese (Mn) also a micronutrient and plays a similar important function like iron in enzyme systems and are necessary for the synthesis of chlorophyll (Wild, 1993). These two elements have interrelated activity, for instance, Fe can be inactivated by an excess of Mn. Fe deficiency symptoms, known as Iron chlorosis, is only evident in old leaves which is observed as yellowing, particularly in the intervene area. Mn deficiency is similar to that of iron deficiency with the chlorosis more pronounced, marked with the whole of the intervene area where plant loses its green colour. The source of fertilizer for iron is chelated iron compounds and the fertilizer source for Mn is manganese compound i.e. where Fe is associated with organic compounds (Fitzpatrick, 1974; Ronan, 2007). Boron (B), is a micronutrient element and is absorbed by the plant in the form of borate. B is important in Ca utilization and the development of the various growing part of the plant. It is also essential in N fixation into nodules of leguminous crops such as beans. B deficiency leads to various conditions such as heart rote of beet and internal cork in apples. Deficiency symptoms include death of terminal buds of plants. The fertilizer source is borax compounds. Copper (Cu) and Zinc (Zn) are micronutrient elements. They are absorbed by plants in ionic as Cu+2 and Zn+2Cu and Zn are all necessary for the growth promoting substance in plants, as both form enzyme systems. Cu deficiency in plant causes leaves to become dark green. Plants have stunted growth and other symptoms include rapid wilting and weak stalks. Zn deficiency symptoms vary from plant to plant. Fertilizer source of Cu are Cu compounds and Zn compound for zinc. Molybdenum (Mo) is absorbed by plants in the form of the molybdate ion. It functions in the reduction of nitrate in the plant to avoid nitrate accumulation. Nitrate accumulation interferes with protein synthesis in plants. Mo deficiency causes general yellowing of older leaves at the bottom of plants and the rest of the plant appears light green in colour. The fertilizer source of Mo are any molybdate compounds (Fitzpatrick, 1974).Chlorine is important as a micronutrient because it regulates the osmotic pressure and cation balance in plants (Fitzpatrick, 1974)

VI. REVIEW ON ASH FERTILIZATION

Land use is optimized through technologies and management practices. The contemporary practice in agriculture is basically chemical based farming that can contribute considerable to degradation of natural resources, particularly soils. (Lopez et al, 2009). Therefore, various approaches have been tested on the use of available and renewable resources of plant nutrients for complementing and supplementing commercial fertilizers. As a result, efforts were made to systematically evaluate the feasibility and efficacy of organic residues, not only refurbishing soil productivity, but also in promoting the efficiency of chemical fertilizers (Lopez et al, 2009).

The combined use of organic and inorganic fertilizers in crop production has been widely recognised as a way of increasing yield and improving soil productivity. Agricultural activities produce billions of tonnes of other materials long regarded as waste. The main types of agricultural wastes are crop residues and farm animal wastes. Meaningful contributions to soil nutrient dynamic pool and beneficial effects on subsequent crops have been reported when such crop residues were returned to land and especially if the residues are of immediate utilisable form. With appropriate

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techniques, agricultural wastes can be recycled to produce an important source of energy and natural fertilizers for crops. Recycling agricultural wastes can help a developing country to reduce its dependence on foreign energy supplies and raise the standard of living in its rural areas.

Ash has been reported having good fertilisation characteristics, because it supplies the nutrient element with the exception of N to plants and can also functions as a liming agent in soil. Wood and peat ash was to raise soil pH and thereby enhancing microbial activity and N mineralization. Artificial fertilizer has a shorter lasting growth of about 15 years and even shorter response periods of 4-5 years of PK fertilizer compared to ash which has shown longer lasting effect of 30-40 years (Lopez et al, 2009).

VII. REVIEW ON ASH AS SOIL CONDITIONER

Biomass ash has been recommended to be used directly as a soil conditioner in different degraded soils, mainly for the purpose of forestry and floriculture (Gosh, 2004; Lopez et al, 2009; Pandey, and Singh, 2010). However, the recommendation for a large ash application to agricultural soils in a region cannot be made, unless extensive trials are conducted to establish a proper combination of ash with each type of soil to establish its quality and safety. Additionally, food-chain transfer studies for all potentially toxic elements present in ash are needed to evaluate the effect of heavy metals on human health. In future, attention should be given on some important aspects related to ash incorporation to soil including long-term studies on the impact of ash on soil quality, soil fertility, soil health and continuous monitoring on the properties of soil and ash.

A good understanding of how soil biota, especially earthworm, responds to amendment of agricultural soil with ash is required. Survival rate and function of soil micro-organisms and soil burrows such as earth worms are documented as valuable guides of soil health and fertility in agriculture. In ecological terms, structural features of burrows are known to have significant influences on hydrology, gas diffusion and nutrient distribution (Bouma, 1991; Bouche’ and Al-Addan 1997; Bastardy et al., 2002).

Complex branching of burrows in soil were found to be more efficient in conducting water into soil compared to a simple burrows. Siddiqui and Singh, 204) reported more branching and concentration of burrows near the soil surface in soil which is polluted with heavy metals, such as Cu, Cd, Pb, and Zn, than in non-polluted soil. However, the effect on the burrow characteristics of relatively low concentrations of heavy metals, such as those applied to soil through the ash addition has not been reported. Currently, Yunusa et al. (2009) cited in Siddiqui and Singh, 2004 determined basic structural features of burrows created by earthworms of native megascolecid and exotic Aporrectodea trapezoides and found that FA reduced the total volume of the burrow system (Vs) by ≤ 39% for native species and 29% for the exotic species. These reductions averaged 33% with addition of ash at 5 Mg ha-1 and 39% at 25 Mg ha-1. The native earthworms responded to treatment by burrowing deeper into the soil core and away from the ash-tainted surface soil. The exotic species reduced the depth of burrowing and remained close to the surface. FA addition did not have significant effect on tortuosity of the burrows for either earthworm species. A. trapezoides created predominantly vertical burrows, while the native megascolecid worms produced more horizontally oriented burrows in addition to vertical ones. These modifications of earthworm behaviour by FA addition to soil, along with previous experience with plant growth, suggest that an ash application rate of 5 Mg ha-1 is close to optimum for routine agronomic applications. Similarly, Maity et al. (2009) cited in Siddiqui and Singh, 2004 revealed that ≤ 50% of FA amendment does not apparently harm the earthworm L. mauritii respect of their survival and growth. A significant increase in tissue metallothionein level was recorded in L. mauritii without tissue metal accumulation, indicating that metallothionein is involved in scavenging free radicals and reactive oxygen species metabolites. It is concluded that this biochemical response observed in L. Mauritii exposed to FA amended soil could be used as a valuable tool for eco-toxicological field monitoring for other ash application such groundnut shell ash.

VIII. MATERIALS AND METHODS

Sample Collection and Treatment

The groundnut (Arachis hypogaea) samples were from the Clint Williams Texoma peanut company, Madill, Oklahoma73448USA. Company web site address: http://www.manta.com/c/mmfpj80/clint-williams-co. 5kg of the in shell groundnut samples were obtained from Starley Supermarket, Wolverhampton on 7/6/2012(Plate2.1a). The kernels were removed out of the shells by hand shelling. Approximately, 3.4kg of nut and 1.6kg of shells were obtained. The Arachis hypogaea shells (Plate 2. 1b) were brought to the Chemistry Laboratory, University of Wolverhampton on 6 July 2012 for analysis. The AHS laboratory samples were re-weighed using an electronic balance.

IX. DETERMINATION OF MOISTURE CONTENT OF ARACHIS HYPOGAEA SHELL SAMPLE

The moisture content of the Arachis hypogaea shells sample was determined by using the Thermodgravimetric method. 100g air dry weight of Arachis hypogaea shell sample was weighed using electronic balance (Model College B52) and placed in the oven in an aluminium tray containers of known weight at 105oC for 24hrs. Once dried, the samples were transferred from the oven after cooling and re-weighed to calculate the percentage moisture content. The following equation were applied in order to calculate the percentage moisture content:

\[
\text{Percentage moisture content} = \left( \frac{W_a - W_b}{W_a - W_c} \right) \times 100
\]

Where:
- \(W_a\) = Air dry weight of Arachis hypogaea shell (AHS) sample (g)
- \(W_b\) = Oven dry weight of Arachis hypogaea shell (AHS) sample (g)
- \(W_c\) = weight of aluminium foil (g)
The result is presented in Table I Ignition of the Arachis hypogaea shell sample in Muffle furnace.

The organic matter content in the Arachis hypogaea shell sample was burnt off by loss-on-ignition. 100g of oven dried (AHS) samples were used to perform the loss on ignition technique to obtain the inorganic ash content of the AHS sample. The dried samples were first burnt in the fume cupboard to reduce the mass to an ash. The pre-burn ash was placed in the weighed crucibles and were transferred into the Muffle furnace (Model, Carbolite, England). The sample was ignited in the furnace to 5000°C for 1 hour in order to burn off all organic matter in the sample to obtain inorganic ash. The ash sample was removed from the furnace and was placed in a desiccator for 30 mins to prevent re-absorption of moisture.

X. PROCEDURE FOR PREPARING THE POWDERED ARACHIS HYPOGAEA SHELL (AHS) SAMPLE
A known amount of the oven dried Arachis hypogaea shell samples were pulverized using a pulverizer (Model, Pulverisette6, Fritsch). The samples were crushed with pestle and mortar to reduce the particle size and were fed into the two metal steel cylinders of the pulveriser. Pulverization was carried at 5000 revolution per minute for 3 minutes.

XI. ANALYSIS OF WEIGHT LOSS OF ARACHIS HYPOGAEA SHELL (AHS) SAMPLE AT DIFFERENT TEMPERATURES BY THERMO-GRAVIMETRIC ANALYSIS (TGA)
Analysis was conducted to determine the moisture content and volatile matter by a Thermo-Gravimetric Analyser (Model, TGA7 Perkin Elmer). About 5-10 mg of the ignited AHS sample was approximately weighed to fit the small platinum microbalance pan on the TGA equipment. A set methodology was programmed into the TGA controller to ensure the results obtained aligned with the objective. The method was set as followed:

(i) Hold at 1 minute at 400°C
(ii) Heat for 400°C to 1000°C at 400°C/min with Nitrogen flow rate at 20 ml/min.

TGA procedure was followed to complete the analysis. Result of the analysis was displayed in terms of decomposition regime graph presented as (figure II).

XII. PREPARATION OF ARACHIS HYPOGAEA SHELL (AHS) SAMPLE PELLET FOR X-RAY FLUORESCENCE (XRF) ELEMENTAL ANALYSIS
8.5 g of AHS ash sample and 1.5g of wax binder was weighed using an electronic balance and was mixed. The mixture was compressed in a cylindrical mold at pressure (12 tonnes cm²) as described by Watson (1996) to form the ash pellet in (Plate 2.5). Elemental analysis was performed on Arachis hypogaea shell ash pellets using X-ray fluorescence spectrometer (Model, XEPOS FROM SOECTRO). Result of the analysis is presented in Table III.

XIII. PROCEDURE FOR X-RAY DIFFRACTION (RXD) ANALYSIS
X-ray diffraction analysis of the AHS ash sample was performed with an automated diffractometer (Model, Phillips PPW 1729 from pan analytical) equipped with graphite monochrometer using Cu-ka radiation. The ash sample was pressed into the sample holder, and then carefully placed in a goniometer and was rotated at a maintained angle. The data were collected on PC and was analyzed using a computerized search and match procedure. Result are presented in (Figure III).

XIV. POT EXPERIMENT
The aim of this experiment is to study the effect of Arachis hypogaea shell ash sample on yield and yield components of plants. The experiment was carried out in the green house unit and the associated laboratory that houses the growth chamber of the School of Applied Sciences, University of Wolverhampton. The radish seeds used in this experiment was provided by Dr. Malcolm Inman and was conducted under the advice of Dr. Inman from 31 July - 23 August 2012.

XV. MATERIAL
Irish moss Peat
10 plastic pots
Radish seed
Arachis hypogaea shell ash
Meter rule and maker
Laboratory record book

XVI. PROCEDURE FOR POT EXPERIMENT
Step 1. 435g of sieved air dry weight of Irish moss peat was mixed with 13g of Arachis hypogaea shell ash sample and weighed into 5 plastic pot labelled (T) treated. Each pot was filled with 89.6g mixture of Irish moss peat and Arachis hypogaea ash sample at the ratio of 33:1:2. Another 5 plastic pots was labelled control (U) untreated. Each pot was filled with 87g of peat.

Step 2. Equal numbers of radish seeds were 23 sown in the treated and the controlled pots by broadcasting followed by slightly stirring of the Irish moss peat mixture.

Step 3. The pots were covered and placed in the appropriate area in the greenhouse, arranged randomly. The plants were watered daily using a watering can.

Step 4. Measurement and observation of the following parameters were made daily:
   (i) Height of each plant in each pot
   (ii) Colour of plant
   (iii) Leaf number
XVII. STATISTICAL ANALYSIS
The data obtained were subjected to the analysis of variance. The means and standard deviation were compared by two sample t-tests (p<0.05).

XVIII. OBSERVATION OF GERMINATION RATE OF PLANTS
On germination, comparison between the controlled and the treated plants indicated the same rate of germination on 3 August 2012 day 6 (Plate 2.8).

XIX. VISUAL COMPARISON OF GROWTH DIFFERENCE IN PLANTS AFTER GERMINATION
Growth difference between the treated and the controlled plant was observed on 6 August 2012. Visual difference in growth is shown in plate 2.9. A daily record of shoot height, number of leaves and leaf colour of each plant was made.

XX. PLANT TRANSFER TO GROWTH CHAMBER
The plants were transferred from the greenhouse to growth chambers in the laboratory on the on 10 August 2012 Day 11. The Greenhouse did not provide consistency in environmental parameters due to seasonal variation in the month of August. The growth chamber provides precise control of environmental parameters involved in plant growth temperature of 220°C, humidity was less than 30%, photoperiod and light intensity of 16 hours light and dark.

XXI. HARVESTING OF PLANT
1. The plants were harvested on 23 August 2012 Day 21 by gently pulling them out of the peat.
2. The potting mix were washed off from the root of each plant.
3. The root of each plant, both the treated (T) and the controlled (C) was separated from the shoot with scissors and each root and shoot weights (both fresh and oven dried) were weighed separately using an electronic balance.

<table>
<thead>
<tr>
<th>Trial</th>
<th>Air dry weight of sample (g)</th>
<th>Oven dry weight of sample (g)</th>
<th>Difference (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100</td>
<td>88.30</td>
<td>11.70</td>
</tr>
<tr>
<td>2</td>
<td>100</td>
<td>88.20</td>
<td>11.80</td>
</tr>
<tr>
<td>3</td>
<td>100</td>
<td>88.30</td>
<td>11.70</td>
</tr>
</tbody>
</table>

Mean=11.73

Fig. 1 Thermo-Gravimetric Curve For Loss-On-Ignition For Determination Of Percentage Moisture Content, Organic Matter And Ash Content Of Ahs Sample At Different Temperatures.

<table>
<thead>
<tr>
<th>Sample</th>
<th>1st stage Temperature range</th>
<th>2nd stage Temperature range</th>
<th>3rd stage Temperature range</th>
</tr>
</thead>
<tbody>
<tr>
<td>AHS</td>
<td>30-100</td>
<td>200-500</td>
<td>500-700</td>
</tr>
</tbody>
</table>

Fig. 2 X-Ray diffraction pattern of Arachis hypogaea shells and ash

<table>
<thead>
<tr>
<th>Essential Elements</th>
<th>Macro-nutrient</th>
<th>Micro-nutrient</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>5.65</td>
<td>0.28</td>
</tr>
<tr>
<td>K</td>
<td>11.0</td>
<td>0.02</td>
</tr>
<tr>
<td>P</td>
<td>1.11</td>
<td>2.0</td>
</tr>
<tr>
<td>S</td>
<td>2.0</td>
<td>0.03</td>
</tr>
<tr>
<td>Mg</td>
<td>3.11</td>
<td>0.03</td>
</tr>
<tr>
<td>Na</td>
<td>1.84</td>
<td>0.09</td>
</tr>
<tr>
<td>Cl</td>
<td>0.18</td>
<td>1.15</td>
</tr>
<tr>
<td>Mn</td>
<td>0.18</td>
<td>0.28</td>
</tr>
<tr>
<td>Cu</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>B</td>
<td>2.0</td>
<td>0.03</td>
</tr>
<tr>
<td>Zn</td>
<td>0.03</td>
<td>0.03</td>
</tr>
<tr>
<td>Mo</td>
<td>0.09</td>
<td>0.09</td>
</tr>
<tr>
<td>Cr</td>
<td>0.18</td>
<td>1.15</td>
</tr>
</tbody>
</table>

The values are presented as means ±SD; Treated= plants which were applied Arachis hypogaea ash; Control(C)=Plants with no ash applied; p-value<0.005 (n=5)
Thermo-gravimetric Analysis

Control (C) = Plants without applied ash. (T) = Plant applied Arachis hypogaea shell ash. For each heating rate there was initial mass loss of about 9.7% of total weight recorded between 30°C and 150°C due to release of moisture (Chen et al., 2012; Hu et al., 2012). Thermal decomposition of AHS was determined to begin at 150°C and considered essentially finished at 700°C. Peak thermal degradation for hemicelluloses occur at 200, 292, 309, 318, for heating rate of 5, 10, 20, 30 and 40°C/min respectively. Moisture content for the samples were <12%, and this fits the theoretical range of moisture content for all low moisture food (Bradley, 1994; Crickenberger and Carawan, 1996) recommended the suitability of materials for swine foodstuff to have moisture content within the range found in Arachis hypogaea shell by this research work. Based on this finding therefore, Arachis hypogaea shell can be classified as low moisture agricultural by-product an indication that it is safe from microbiological spoilage and possible aflatoxin production by mould. Low moisture content material has the advantage as it does not require exhaustive drying processes which reduce cost of manufacturing animal feedstuff. Thus, moisture content of by-products is an important factor determining whether it is economical to be utilized as animal feedstuffs (Weiss, 2011).

The increasing ashing temperature >100°C leads to main carbonization reaction begins to dominate, resulting in declining content of ashes due to the sufficient combustion leading to degradation of hemicellulloses in the AHS at 100-337°C (figure 3.2). This agrees with Jankowski (2010) which reported the degradation temperature of hemicellulloses starts from 200-260 °C. Cellulose degradation occurs ~ 240-350°C as Jankowski (2010) reported high cellulose content in peanut shells, also in the literature, Lindsey and Turner (2019) reported the presence of lignin in peanut shell. Lignin degrades at 280-800 °C because it is thermally more stable than hemicellulloses and cellulose (Kyriazaki and Whittenmore, 2006; Singh et al., 2011). The ash content at 500°C was higher than those at 700°C because of the presence of few combustible substances in the incomplete combustion AHS at 500°C. It is evidence from this analysis that 500°C was too low to prepare AHS ash. The weight loss observed from degradation at 500-700°C was due to the inorganic constituents such as, oxides of potassium and calcium, as indicated in the XRD analysis. The inorganic constituents also have importance on the weight loss of Arachis hypogaea shell ash.

There was a significant weight loss between 200-700°C due to degradation of organic matter which constitutes a greater percentage of the biomass. At 700°C, the shell lost 89.58% its weight because all the organic matter has been volatized at the temperature beyond 500°C. The remain is the ash content of the AHS sample is completely inorganic, as shown by XRF analysis (Table III). Very low percentage of ash content obtained impliedly shows high percentage of organic matter content of Arachis hypogaea shells.

Any material with such significant percentage of organic matter and low ash content according to Jenkins et al., (1998) have higher heating values and therefore AHS can be suitable for fuel.

X-Ray Fluoreescence (XRF) Analysis

The level of concentration of essential elements from Arachis hypogaea shell ash obtained by X-Ray fluorescence analysis is represented in Table III. The analysis was carried out in duplicate. The data showed good reproducibility and the coefficient of variation of each test is very low. The result show high levels of both Macro and micro elements essential for plant growth. The level of concentrations of Ca, P, K, Mg, and S, which are classified as macronutrient according to Fitzpatrick (1974) agree with the typical concentration sufficient for plant growth listed by Epsin (1965; Campbell, 2000)

Phosphorus (P) Level in AHS Ash

The concentration level P found in AHS ash is 11mg/kg. This level is according to Epsin (1965; Campbell, 2000) sufficient for plants growth. Plant require P for the development of ATP (energy), sugar, and nucleic acid. Phosphorus also promotes rapid root development in seedlings planted in cool soils. It ensure vigorous early growth of seedling, promotes seed formation and reproduction in plants improves water use efficiency in plant and improves uniform crop maturity and quality (Fitzpatrick, 1974; Grandson, 1987 in McCauley et al., 2009).

Potassium (K) Level in AHS Ash

The level of concentration of K in the AHS ash was 11mg/kg which is sufficient for plant growth. K is utilized by plants in the activation of enzymes and co-enzymes and photosynthesis. K helps to regulate stomata opening in plants to prevent water loss during drought (ie it controls plant respiration, protein formation by rapid promotion and efficient conversion of nitrogen into protein and sugar transport, K builds disease resistance in plants) (Fitzpatrick, 1974; Mengel and Kirkby, 2001 in McCauley et al., 2009).

Magnesium (Mg) Level in AHS Ash

Mg concentration level in AHS ash was 3.11 mg/kg which is sufficient. Mg is the central molecule in chlorophyll and co-factors for the production of energy in the form of ATP in

| TABLE V | PLANT PARAMETERS FROM GREENHOUSE POT EXPERIMENT MEASURED AT 7 WEEKS POST TREATMENT |
|----------------|-------------------------------|----------------|----------------|
| Plant parameters | Control (C) | Treated (T) | p-value  |
| Height of fresh shoot(cm) | 1.26±0.012 | 4.26±0.128 | <0.0001 |
| Height of fresh root(cm) | 1.06±0.6 | 2.54±0.2 | <0.0001 |
| Fresh weight of shoot (g) | 6.03±0.024 | 16.71±6.32 | <0.0001 |
| Oven dry weight of shoot (g) | 0.63±0.04 | 1.36±0.090 | <0.0001 |
| Oven dry weight of root (g) | 0.32±0.008 | 0.45±0.03 | <0.0001 |

Note: These values are presented as mean± SD; Treated (T)= Plant applied Arachis hypogaea shell ash; Control (C)=Plants without applied ash.

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plants, Mg act as P carrier in plant and it also promotes the formation of fats and oil (Fitzpatrick, 1974; Jacobson and Jasper, 1991 in McCauley et al, 2009).

**Chlorine (Cl) Level in AHS Ash**

Cl concentration was 1.8mg/kg in the ash sample. This level agree with the level given as sufficient for plant growth. Cl is required by plants for leaf turgor and photosynthesis (Fitzpatrick, 1974; Engel et al. 2001 cited in McCauley et al 2001).

**Sulphur (S) Level in AHS Ash**

S concentration level was 2.0mg/kg which is sufficient because the level agreement with value for plant growth sufficiency level given by (Campbell,2002; Epsin, 2005).S is an essential constituents of certain amino acids and protein in plants. S help to maintain dark green colour in plants, promotes the nodule formation on legumes, stimulates seed production and encourages vigorous plant growth(Fitzpatrick, 1974; McCauley et al. 2009).

**Calcium (Ca) Level in AHS Ash**

Ca concentration level in the ash sample was 5.66mg/kg this level is sufficient for plant growth as stated by(Campbell,2002; Epsin, 2005).Ca is essential for cell wall formation for strong cells, translocation of sugars, root hair formation(i.e. feeder roots) Ca neutralized poisons produced in plants and encourages seed and fruit production.

**Micronutrient Element Concentration Level in AHS Ash**

Microelements are required in small amounts and must be present in correct proportions to prevent toxicity in plant. For many plants, the sufficiency range between deficiency and toxicity is narrow for micronutrient than macronutrient (Bady and Weil, 1999 cited in McCauley et al 2009).

**Manganese(Mn) Level in AHS Ash**

Mn is classified as a micronutrient. Its concentration level is 0.28mg/kg in the ash sample. This level agree with the sufficiency level 10-200ppm and lower than toxicity level which is 50-200ppm according to Jones (1998 cited in McCauley et al, 2009). The functions of Mn in plant are:
- Aiding oxidation and respiration processes in plants.
- Accelerates seed germination and plant maturity with high crop yields.
- Increase the availability of the macronutrient elements P, K, and Ca.
- Mn functions in photosynthesis, as it aids the formation of chlorophyll.

**Copper (Cu) Level in AHS Ash**

Cu concentration level in ash was 0.02mg/kg. It is classified as a micronutrient and required in small amounts by plant.(Fitzpatrick,1974). The level is in agreement with sufficiency and toxicity level stated by Jones (1998). Cu is essential for intercellular metabolism and acts as an oxidizer in plant processes.

**Zinc (Zn) Level in AHS Ash**

Zn concentration level was 0.03mg/kg and was also within the sufficiency range and below the toxicity range. Zn is need by plant for growth hormones, seed and grain production and is essential in protein synthesis rate of maturing of seed and plant height.

**Molybdenum (Mo) Level in AHS Ash**

Mo concentration level in ash was 0.002mg/kg. It is classified as a micronutrient and required in small amount, by plant. (Fitzpatrick,1974). The level agrees with sufficiency and toxicity levels stated by Jones (1998). Mo performs the following functions in plants:
- Helps in protein synthesis.
- Essential for legume nitrogen fixation.
- Helps enzyme systems.
- Aids the plant in N metabolism.

**Boron (B) Level in AHS Ash**

The concentration level is within the required sufficiency range of 10-200ppm and is <50 ppm,>50ppm is the toxicity range. B is essential to plants due to the following functions:
- Aids in nodule and seed production.
- Aids in calcium uptake and sugar production.
- Aids the plant in terminal bud production thereby enhancing growth and development.

**Chlorine (Cl) Level in AHS Ash**

Cl is classified as a micronutrient. Its concentration level was 1.8 mg/kg in the ash sample. This level agrees with the sufficiency level 10-200ppm and is lower than the toxicity level, which is 50-200ppm according to Jones (1998 cited in McCauley et al 2009). The functions of Cl in plant are:
- It helps the plant in photosynthesis.
- It controls water use efficiency in plant.
- Aids crop maturity.
- Helps the plant with disease control.
- Helps in sugar transportation.

**Iron (Fe) level in AHS ash.**

Fe concentration level in ash was 1.15mg/kg. It is classified as a micronutrient and required in small amounts by plants.(Fitzpatrick, 1974). The level agree with sufficiency and toxicity level stated by Jones (1998). Fe is needed by plants for chlorophyll synthesis (by acting as catalyst in chlorophyll formation), plant metabolism and oxidation.

**The X-Ray Diffraction (XRD) Analysis Result**

The XRD analysis result indicates the qualitative presence of crystalline minerals in AHS ash (figure 3.4).XRD analysis was conducted twice to ensure accuracy. XRD diffraction patterns detected at various peaks in Figure 3.4 indicate many crystalline phases. The oxide composition of the AHS ash is as follows:

Cao 10.91%, Si0 23.36%, Al2O3 6.73%, MgO 4.72%, SO3 6.40% k2O+N4O 25.28% and C03 6.40%

**Pot Experiment**

A pot experiment using radish plants was conducted to determine the suitability of *Arachis hypogaea* shell ash as applied to each treatment at the beginning of the experiment. After 21 days, the radish plants were harvested. Plants parameters, including average height, fresh and dry weight of shoot and roots of the control and the treated plants were
measured (Table IV and V). Table I shows significant differences in plant parameters between the control (C) plants and the treated (T) where the mean height of the control was 2.1cm after 21 days post germination. The treated (T) plants recorded mean height of 4.2cm. We can speculate that the significant growth difference between the control and the treated plant may be attributed to nutrient delivery by the AHS ash which show a sufficiency levels of macro and micro nutrient element in (Table II) There was significant difference between the weight of fresh shoot of control and the treated (Table V) The weight of shoot from the treated was greater than that of the control may be due to presence of high levels of Mg in the treated delivered by the AHS ash as Mg is one of the key element in chlorophyll structure (Fitzpatrick,1974)

XXIII. CONCLUSIONS

Arachis hypogaea shells are generally considered a waste product. However, the presented findings show it is rich in macro and micronutrients and contains high level of Ca, Mg, K, P, Na and the micro-nutrients Mn, Cu, Zn, Mo, B, Cl. and Fe. Utilization of AHS ash as organic fertilizer can also save the cost of chemical fertilizer, along with minimizing environmental pollution. The Thermo-gravimetric analysis of the AHS show low percentage moisture content indicating its suitability as an animal feedstuff. AHS contain high carbon content that is why there was significant weight loss during gravimetric analysis at high temperatures leaving a very low percentage of ash content which is purely inorganic, as shown by XRD analysis. This high percentage of organic matter and very low ash content shows that AHS can be utilised as fuel for heating.

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