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Assessment of alkaline content and heavy metals in some agro-waste obtained from Pauta farmlands, Kaduna State, Nigeria

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Abstract

The study was carried out to assess the level of heavy metals (Cd, Cr Mn, Fe, Zn,), alkali metals (K, Na, Ca) and potash (KOH, K2CO3) contents in Agro waste products produced in Pauta area of Igabi Local Government Area Kaduna north using Atomic Absorption Spectrophotometer (AAS), Flame photometer and titrimetric methods. The mean concentrations determined across the samples were given as follows: For the beans Husk, groundnut husk, guinea corn husk, rice husk and millet husk, Mn (5.013-26.345 mg/kg), Fe (3.548-8.757 mg/kg), Zn (1.459-2.118 mg/kg), Cd (0.005-0.013 mg/kg), Pb (0.092-0.181 mg/kg), Cr (0.108-0.400 mg/kg). The mean concentrations of Mn, Fe and Cr obtained in the Agro waste samples were higher compared to the safety limits recommended by Food and Agricultural Organization/World Health Organization, (2006) with the exception of Zn and Cd which showed a lower level. The results for the concentration of trace elements in the samples varied between ranged Ca (40.711-80.265 mg/kg), K (1.3-8.9 mg/kg), and Na (2.5-5.3 mg/kg). It has been observed that groundnut husk (GHS) has higher concentration of calcium than its counterparts. All the Agro waste samples analysed for trace metals were below the limit recommended by Health Canada, (2006). The calculated percentage yield of KOH (43.62%) and K_2CO_3 (79.62%) in all the Agro waste products of were significant. Therefore, the results above obtained for all the parameters suggest that these Agro wastes products are safe for potash production and for related agricultural, domestic and industrial uses since the heavy metal and trace metal contents of most of the samples analysed are within acceptable or safe limit while the alkaline content is also rich enough.

Keywords: Agricultural waste, Alkali, Potash, heavy metal, spectroscopy.

Introduction

Agricultural wastes are waste derived from plant or animal material that are considered impractical either because they are considered to be of no positive economic position or because they are not cultivated for any specific purpose[1]. It comprises mainly of livestock and poultry manure, residual materials in solid liquid form produced during the production and marketing of livestock, poultry or fur-bearing animals; it also includes grain, vegetable, and fruit harvest residues[2]. In Nigeria, large quantities of these wastes are generated annually and are mostly underutilized. The concept of waste to wealth is an emerging and effective waste management strategy which is fast receiving attention in the twenty first century. With agricultural wastes vastly available abundantly at almost no costs, it has the potential to provide a low cost adsorbent for cleaning of our environment.

ALKALI: Alkali isa soluble base, typically the hydroxide or carbonate of alkali metals (potassium or sodium). It could be obtained locally, from ashes by extraction with water. When made by the extraction method, it is usually mentioned to as potash[3]. The main soluble metal in organic matter matrixes is potassium, while this depends on the classes of the plant material and the kind of soil where the plant grows. Alkalis are carbonates of sodium and potassium. It is commonly believed that the soluble mineral in ashes is not primarily or largely alkali: some potash content may produce very low alkali, depending on the sources of the ashes[4]. The word soda ash in place of potash may be used if the main alkali metal measured is sodium. Potash is defined as a white crystalline residue that is left over after aqueous extract from ashes is subjected to evaporation[5]. The manufacture and procedure of potash date back to ancient times in several countries of the world was first used as a crude agent for domestic cleansing by using ashes mixed with water to clean oil-stained materials. Potash has a substantial use in Africa and Nigeria in particular, from the ancient times till date[6,7]. There has been development of skills in potash used as active component in the production of local soap and as a useful raw material for some local potash-based industries[8].

There has been a significant improvement in its production in recent times; this has given rise to extraction with water, which sometimes is concentrated by evaporation. If the prepared solution is leftward for some days, some crystals usually grow on the wall of the container, or as a film on the solution, or settling at the bottom of the container.

Materials and methods

Sample location and collection of sample: Kaduna state is an ancient town located in north-western part of Nigeria, on the Kaduna River. Kaduna is a commercial Centre and a major transportation hub for the surrounding farming areas which has rail and road junction. The population of Kaduna was at 4,760,084 as of the 2006 Nigerian census, and this is believed to have grown to over 5.8 million as at 2013. The symbol of Kaduna state is the crocodile, called Kada in the native Hausa language[9].

Sample Preparation: The Husks of various samples collected were pretreated by washing with distilled water to remove impurities and combusted at temperature of 250°C for 8 hours using muffle furnace. The temperature of the furnace was allowed to cool to 175°C before it was opened slightly. Samples were removed after internal temperature was dropped to 30°C and procedure was repeated for each of the prepared sample[10].

Sample analysis sample extraction: The ash extract was prepared by weighing 10g of the ash with the aid of analytical balance, from already prepared plant sample and then dissolved in conical flasks containing 100 cm^3 of water (10g/100 cm^3). The mixture in each flask was allowed for 2 hours before it was filtered with the aid of whatman No. 1 filter paper to obtain the ash extract solution. The pH of the different extract was determined using the pH meter[10].

$$2H_2SO_4(aq) + K_2CO_3(aq) \longrightarrow 2KSO_4(aq) + CO_2(g) + H_2O$$

Determination of Carbonate and Hydroxide Content in sample: Double-indicator method was employed in the acid-base titrimetric analysis of the mixture of alkali hydroxide and carbonate[11]. A portion (10 cm^3) of the extract was pipetted into an Erlenmeyer flask, 2 drops of phenolphthalein indicator added, and the mixture titrated against a 0.1M H2S04 until a colorless solution was obtained. At that point, the whole of the hydroxide and half of the carbonates have reacted, giving a burette reading *V*1. The equation of the reaction is as shown below:

$$H_2SO_4(aq) + KOH(aq)K_2SO_4(aq) + H_2O \longrightarrow$$
$$H_2SO_4(aq) + K_2CO_3(aq)K_2SO_4(aq) + KHCO_{3(aq)} \longrightarrow$$

Methyl orange was added to the resulting colourless solution and titrated until the colour changed from yellow to orange. At that point, the remaining bicarbonate was neutralized by the acid; the burette reading now becomes *V*2. The equation of the reaction is as follows:

$$H_2SO_4(aq) + KHSO_4(aq) \longrightarrow K_2SO_4(aq) + H_2O\ (l) + CO_2(g)$$

Calculations: Titre for neutralization of KHCO3 = *V*2-*V*1, Titre for neutralization of KOH = *V*1 – (*V*2-*V*1), Titre for neutralization of K2CO3 = 2(*V*2-*V*1).

Determination of potash content: A portion (3.45g) of each sample was weighed and completely combusted to ashes in an oven at 450°C. The ash was leached with 100 $cm^3$of distilled water. The leachate containing the impure (crude) potash was evaporated to dryness to obtained the potash. The residue was dry to a constant weight at 105°C in an oven. The weight W_1 of ash is extracted with water of volume V, and by evaporating the water of volume V to complete dryness, constant weight W_2 of residue was obtained. The Potash Content (PCa) (% of ash) is derived as:

V_1 yield W_2

$$V\ yield = \frac{W2}{V1} * V(unit\ weight)$$

$$PC = \left(\frac{W2}{V1}\right) * \frac{1}{W1} * 100$$

Non-Potash Content (NPC_a) (% of ash) is given by:

$$NPCa = 100 - \left(\frac{W2}{V1} * V\right) * \frac{1}{W1} * 100$$

If sample of weight w has yielded the ash w_1, the potash content (PCS) (% of sample) is given by:

$$PCa = \left(\frac{W2}{V1} * V\right) * \frac{1}{V1} * 100$$

Non-potash content (NPC_a) (% of sample) is given by:

$$NPCa = 100 - \left(\frac{W2}{V1} * V\right) * \frac{1}{W1} * 100$$

Analysis of heavy metals: A portion (5g) of the sample was weighed and 100 cm^3 Concentrated Nitric acid was measured and both transferred to a 250 cm^3beaker, It was swirled and allowed to stand for 10 min, then evaporated on a hot plate and allowed to cool, 50 $cm^3$of concentrated nitric acid and 10 $cm^3$of perchloric acid (HClO4) were further added and evaporation continued till the sample was completely ashed (grey in colour). The digest was quantitatively filtered using whatman filter paper and transferred to 100 cm^3volumetric flask and made up to the mark with distilled water. A blank was also prepared in the same way using same procedure. Atomic Absorption Spectrometer available at Ahmadu Bello University Chemistry Department was used to analyzed Cd, Pb, Zn and Fe. The concentrations of the metals were then determined from calibration curves of the various metals[12].

The metals, calcium (Ca), potassium (K) and sodium (Na) were determined from the digested sample using flame photometry. The instrument (flame photometer) monochromator was set to 589.0 nm, the dial was turned to the calcium (Ca), potassium (K) and sodium (Na) Position using a filter-based instrument. The flame was lighted and 0.5% Sulphuric acid (the blank) was aspirated for calibration of the nebulizer. A calibration curve was determined for sodium ion using the direct-intensity method. First, the instrument was set to read 0% Transmittance while aspirating 0.5% Sulphuric acid, and the instrument reset to read 0 % Transmittance, and to read 100% Transmittance.

Analysis of Alkali and Alkaline Earth Metals using Flame Photometer: The % Transmittance for prepared solution of 5, 10, 20 ppm sodium solutions were determination and used for the calibration curve. The best straight line that passes through these data by at least squares regression analysis was determined, 25 cm^3 portion of the unknown solution was diluted into 100 cm^3 flask with 0.5% (v/v) Sulphuric acid, and the emission of this diluted sample at the same time that the direct intensity calibration curve mentioned above at the same instrument conditions was measured. The concentration of the unknown solution prepared in ppm was determined from the calibration curve and the result in terms of 95% confidence limits[13]. Standard addition method for the determination of calcium (Ca), potassium (K), sodium (Na), and unknown was performed[13], the emission of solutions and calibration curve was measured and performed respectively, and the best straight line that passes through these data by a least squares regression analysis was calculated accordingly. The concentration of the metals in the unknown in ppm and the result in terms of 95 % confidence limits was estimated[13].

Statistical analysis: Data Analysis: Data obtained was subjected to Statistical analysis using Microsoft Office Excel and Minitab software. The data were expressed in terms of descriptive statistics were presented with Mean values as (Mean ± SD). A p-value less than 0.05 were considered as Significant. Fischer Least Significant Differences (LSD) was used to group the means.

Results and discussion

Table-1 shows the various mean concentrations (mg/kg) of (Mn, Fe, Zn Cd, Pb, Cr) determined in the five (5) Agro wastes (Beans husk, Groundnut husk, Guinea corn husk, Rice husk, Millet husk) using atomic absorption spectrophotometry (AAS). The minimum and maximum mean concentrations varied between the ranged of Mn (5.013-26.345 mg/kg), Fe (3.548-8.757 mg/kg), Zn (1.459-2.118 mg/kg), Cd (0.005-0.013 mg/kg), Pb (0.092-0.181 mg/kg) and Cr (0.108-0.400 mg/kg) respectively.

The highest mean concentrations of Mn, Fe, Zn, Cd, Pb and Cr were recorded in BHS (26.345mg/kg), BHS (8.757 mg/kg), GCHS (2.118 mg/kg), MHS (0.013 mg/kg), RHS (0.181 mg/kg) and GCHS (0.400 mg/kg) respectively.

Manganese is a salient trace element considered to be higher in concentration in BHS (26.345 mg/kg) than the other crop samples. Manganese is a micro element with significant health benefit which includes its contribution to development healthy bone structure, bone metabolism, and the creation of essential enzymes for building bones. It also acts as a co-enzyme which help metabolic activities in the human body. Apart from these, there are other health benefits of manganese including the formation of connective tissues, absorption of calcium, proper functioning of the thyroid gland and sex hormones, regulation of blood sugar level, and fats and carbohydrates metabolism. The highest mean concentration of Mn (26.345 mg/kg) as indicated in Table-1 in the studied Agro wastes is greater than the values reported by Ying in China (3.016 mg/g)[14] and higher than the permissible limit (0.300 mg/kg) recommended by health Canada[15]. These values are also too low to provide for the Recommended Daily allowance for Fe in both adult male (10 mg/day) and female (15 mg/day) from a nutritional point of view.

The values obtained in Table-1 for Fe ranged from (3.548-8.757 mg/kg) in the various agro-wastes. These values are higher than the range reported by Edem in Calabar (0.002 to 0.004 mg/kg)[16] but much lower than those reported by Okoye in South East Nigeria (59.00 to 102.40)[17] and far below the joint FAO/WHO permissible limit (0.300 mg/kg) for Fe in Cereals[18]. These values are also too low to provide for the Recommended Daily allowance for Fe in both adult male (10mg/day) and female (15mg/day) from a nutritional point of view.

Table-1: Concentrations (mg/kg) of Heavy Metals (Mn, Fe, Zn Cd, Pb, Cr) in Agro-Waste products.

SAMPLES					
Heavy Metals	BHS	GHS	GCHS	RHS	MHS
Mn	26.345±2.43	5.013±0.16	18.965±1.68	12.03±0.45	9.110±0.75
Fe	8.751±1.29	5.369±0.53	3.548±1.03	3.637±0.46	7.921±1.52
Zn	1.937±0.67	1.459±0.18	2.118±1.58	1.483±0.54	1.565±0.25
Cd	0.03±0.02	0.008±0.01	0.005±0.01	0.010±0.00	0.013±0.01
Pb	0.092±0.05	0.096±0.05	0.127±0.03	0.181±0.10	0.143±0.05
Cr	0.271±0.08	0.108±0.01	0.400±0.10	0.272±0.26	0.268±0.26

Keys: BHS (Beans husk), GHS (Groundnut husk), GCHS (Guinea corn husk), RHS (Rice husk), MHS (Millet husk).

Table-1 also depicts the variation existing in the concentration of Zinc in the five samples. It shows that the concentration of Zinc is considerably higher in Guinea corn husk (2.118 mg/kg) than its corresponding crop samples. The presence of high concentration of Zinc in a work area or farm can affect its workers and inhabitants such that it can cause loss of appetite, slow wound recovery, decreased sense of taste and smell and so on[19]. The values of zinc obtained range from (1.459 - 2.118 mg/kg) in these agro wastes samples. These values are higher than the range (0.04 - 0.19mg/kg) reported by Edem in 2009[16] but far below the range reported by Ahmed and Mohammed (4.893 to 15.450 mg/kg)[20]. The result of zinc obtained from these analyses has no negative effect on human because it is below permissible limit of 11 mg/day for men and 8 mg/day for women.

Not only that, another element discovered in the five agro waste samples is cadmium which the mean concentration ranged from (0.005- 0.013 mg/kg) which might consequently expose the dwellers of Pauta farm to its environmental effects such as development of benign pneumocomos and retinitis respectively through the food chain[19]. These values are higher than the range (0.002 to 0.004mg/kg) reported by Edem found in Wheat flours[16]. Also, Okoye studied cereals in South eastern Nigeria and found that the amount of cadmium as (0.007 to 0.23mg/kg)[17], and less than Ahmed and Mohammed in Cereal products (0.091-0.143mg/kg)[20]. These differences could be due to differences in the concentration of the metal in the soils where these plants were grown. These values are however, below the safety limit (0.05 mg/kg) recommended by FAO/WHO[21].

Lead another element considered is said to be harmful to the ecosystem in that it tends to wipe out the population of micro-organisms in soil which consequently slows down decomposition of organic matter. It also affects the central nervous system of animals in habiting an environment where its concentration is high. Lead Concentrations obtained for these agro-wastes was within the range (0.092 to 0.181 mg/kg) which is less than the range reported by Ahmed and Mohammed in Egypt (0.116 to 0.390 mg/kg)[21] but higher than the range (0.007 to 0.032 mg/kg) reported by Okoye *et al.,* in the South east Nigeria[17]. This could be due to differences in anthropogenic activities that introduce metals into the soil in the areas where these Cereals were grown or even deposition of Pb on surfaces during production, transport and Marketing or by emissions from Vehicles and industries[22]. These values are also below the WHO safe limit for Pb in cereals as reported by Ahmed and Mohammed[20].

In Table-1 highest Cr concentration (0.400 mg/kg) was found in GCHS and the lowest (0.108 mg/kg) in GHS. All the remaining studied samples showed minor variations amongst each other. Cr which is considered as an essential trace element in the regulation of some metabolic chemical activities in the body such as regulation of sugar, and fat in living organisms[23]. An estimated safe and adequate daily intake of Cr for adults ranges from 50 to 200 µg[24]. Cr is also harmful when its consumption exceeds the permissible level. It interferes with essential body metabolism, acts as a gastric irritant and causes skin ulcers, bronchitis and dermatitis[25]. The WHO permissible limit for Cr in food is 0.5 ppm[26]. The concentrations of Cr in all the analyzed samples were below the permissible limit.

The result presented in Table-2 revealed that the lowest and the highest alkali metal concentrations in all the Agro Waste analysed ranged between Ca (40.711-80.265 mg/kg), K (1.3-8.9 mg/kg) and Na (2.5-5.3 mg/kg) samples. The highest alkali metal concentrations were observed in GHS (80.265 mg/kg), RHS (8.9 mg/kg), GCHS (5.3 mg/kg) respectively.

Out of all the metals found in Table-2 for Agro wastes samples from all the farmlands calcium with the highest concentration (80.265 mg/kg) can be said to be said the most important element which are utilized in strengthening of bones and other body materials in the body. However, as important as calcium is, it deficiency causes some adverse effects to the body system such as kidney stones, sclerosis of kidney and blood vessel[19]. The value recorded for Ca(80.265 mg/kg) is lower (200 mg/kg) than the limit recommended by FAO/WHO[21].

Comparatively, potassium and sodium are having highest concentrations of (8.9 mg/kg) and (5.3 mg/kg) both elements are known to be of importance to human health. Potassium is a macro element which is essential for normal cell function together with sodium; potassium plays a vital role in fluid homeostasis, with broad health effects. Potassium plays a significant role in lowering elevated blood pressure, foods that are rich in potassium (especially fruits, vegetables, dairy products, and seafood) include many other nutrients that may be beneficial for cardiovascular and general health[27]. The concentrations of both K and Na recorded were lower than the limit recommended by FAO/WHO[21].

Table-2: Concentrations (mg/kg) of Alkali Metals (Ca, K, Na) in Agro-Waste products.

	SAMPLE				
Metals	BHS	GHS	GCHS	RHS	MHS
Ca	57.169±1.48	80.265±0.32	40.711±4.30	44.768±0.48	77.251±0.24
K	8.4±0.20	1.3±0.20	4.2±0.087	8.9±0.63	1.4±0.28
Na	4.9±0.76	2.5±0.23	5.3±0.17	4.3±0.31	3.2±0.046

Keys: BHS (Beans husk), GHS (Groundnut husk), GCHS (Guinea corn husk), RHS (Rice husk), MHS (Millet husk).

Table-3: Percentage (%) of Hydroxide (KOH) and K2CO3(Carbonate)in Agro-waste products.

SAMPLE					
POTASH	BHS	GHS	GCHS	RHS	MHS
KOH (%)	23.99±0.429	21.03±0.783	43.62±0.926	1.90±0.957	19.66±0.1511
K2CO3 (%)	61.69±0.302	64.09±1.282	45.76±4.04	79.62±0.198	65.20±1.647

Keys: BHS (Beans husk), GHS (Groundnut husk), GCHS (Guinea corn husk), RHS (Rice husk), MHS (Millet husk).

Table-3 shows the results for both the carbonate and hydroxide contents in the Agro waste products in Puata area. The lowest and the highest percentage yield of KOH (1.90-43.62%) and K2CO3 (45.76-79.62%) analysed in the five (5) different Agro waste products are stated above. The highest percentage was observed in GCHS (43.62%) and RHS (79.62%) samples. The percentage yield of both hydroxide (KOH) and the carbonate (K2CO3) were significant in all samples analysed.

Conclusion

The finding of the work identified that; concentrations of heavy metals (Mn, Fe, Pb, Cr) determined in the five (5) Agro wastes (Beans husk, Groundnut husk, Guinea corn husk, Rice husk, Millet husk) using atomic absorption spectrophotometry (AAS) were lower than the safety limits recommended by FAO/WHO with the exception of cadmium and zinc which showed a little concentration far above the recommended threshold limit. The concentrations of all (Ca, Na, K) determined were below the recommended therefore the Agro-waste products will serve as a good source of these essential trace metals. The percentage yield of the potash has proved the feasibility of producing alkali from agricultural waste product s and investigating the effectiveness of such alkali is significant.

Conclusively, it's affirmed that the concentration of the mentioned heavy metals and trace elements in the samples can be traced to its formation processes as discussed. Consequently, their availability in the environment is considerably moderate or rather said within permissible limits. Hence, they might not pose any serious health challenges to the farmers, dwellers, plants, aquatic organisms and inhabitant of the areas where the five samples were obtained.

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