ANALYSES OF COPPER CONCENTRATIONS IN PALM KERNEL CAKE FROM THREE INDUSTRIAL PALM KERNEL OIL MILLS.

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ABSTRACT

Palm kernel cake, a by-product of palm kernel seed oil processing was analysed for its metallic contamination as livestock feed without modification or Zinc supplementation. Metalloid analysis of cake from industrial output revealed Copper II ion (Cu^{2+}) concentration in quantities dangerous to livestock. Samples of Palm kernel cake, De-oxidised cake and Palm kernel oil products from industrial lines were analysed to determine sources of contamination in the cake using flame photometry, flame emission spectroscopy and Atomic Absorption Spectrometry. The sources of contamination were traced to the feed quality, materials of construction of the expeller section and degree of purification of bye-product and waste discharged. Preliminary investigation in fresh fruit showed that copper was a component, in the range of 14.43±0.4 and 17.03±0.6 (µg/g) but higher copper content was later found associated with by–products at higher concentrations along the process lines, especially at the crushing and solvent extraction stages. To take care of high copper concentrations and obtain less contaminated cake from industrial practices with a good inventory mechanism with free and dried kernel with concerns to the materials of construction to enhance continuous usage of cake as livestock feed supplement was proposed.

Keywords: Contamination, Metalloid, Cake, Expression, Extraction, Purification, Supplement

1.0 INTRODUCTION

Oil Palm (*Elaeis guineansis*) abundantly produces a number of useful by-products as a plant. It is the source of Oil palm fronds (OPF), oil palm trunks (OPT), palm press fibre (PPF), empty fruit bunches (EFB), palm kernel cake (PKC), palm oil mill effluent (POME; also called sludge and decanter cake) and palm kernel shells (PKS) throughout the year and this guarantees their supply and availability as major ingredients for livestock feeding [1].The oil palm fruit consists of three different layers of shell known as pericarp which comprises of exocarp (outer shell), mesocarp (fibrous material) and the inner-shell comprising the endocarp and kernel or endosperm. The demand for crude palm kernel oil (CPKO), palm-kernel cake (PKC) and Palm Kernel Sludge (PKS) in the market is very huge, and as a matter of fact, the demand for it is all year round plus the profit in this business is amazingly good [2].The oil palm fruits generate two types of oils: crude palm oil (CPO) from the outer mesocarp and crude palm kernel oil (CPKO).

Three methods of palm kernel oil extraction methods reported includes; mechanical extraction (screw-pressing), solvent extraction and pre-pressing followed by solvent extraction [3]. Other form of extraction in the Southern part of Nigeria is by frying the kernels to extract the oil called 'Adin' which most often is black or dark brown in colour because of its processing at high temperature. The product serves both domestic and medicinal purposes, while the burnt cake is discarded.

The chemical composition of PKC depends essentially on the oil extraction method. In industrial processing of palm kernel, mechanical expression and solvent extraction are most popular. Breaker roll or a swinging hammer grinder or a combination of both then breaks the kernel into small fragments. This increases the surface area of the kernels, thus facilitating flaking. In direct screw pressing, kernels must undergo seed preparation operations such as size reduction, flaking and steam conditioning prior to mechanical extraction. The last one involves a chemical influence of the solvent which help extract as much oil as possible from its sources. The direct solvent extraction process is used in larger plants. However, oil recovery is more complete than in screw pressing. Solvent extraction had been found to be more efficient; it involved the use of more volatile oils to extract the needed oil and later separated more often by distillation. Strict quality control right from fruit processing to kernel extraction is necessary to ensure production of good quality oil and by-products. However, residual oil in the cake can influence the composition and characteristics with time, thus making the cake bad and hindering further use of this cake.

The extraction of oil from Palm kernel is an important product for human diet from nut or kernel of oil palm which generate the cake, oil, and the shell as a by-product. Crushed palm kernels seeds generally results in the production of PKC and palm kernel shell as by-products [4]. They constitute about 45%-48% by weight of palm nut and on a wet basis; the kernels contain about 47%-50% by weight of the oil whose properties and characteristics are quite different from palm fruit oil but rather resembles coconut oil [5]. Palm kernel cake (PKC) is a by-product of palm kernel oil extraction provides moderate nutrition with approximately 16-18% of crude protein (CP) and 13-20% crude fiber (CF) hence, usage of PKC is common in ruminant diets, but limited in the non-ruminant diets especially in poultry diets due to the high fibre content [6]. PKC is one alternative feed resource that can be used in livestock feeds as by-product of oil extraction and it is abundant in the tropical areas of the world [7].

Palm kernel cake inclusion into monogastric animals' meal such as poultry and pig has been greeted with different modifications and formulations to make PKC valuable in improved feed for livestock. For instance, replacing maize with palm kernel cake (PKC) on the performance and economy of production of growing pigs recoded efficient utilization of the diet [8]. Other studies have shown that Enzyme-supplemented PKC with mannanase activity could break down the non-starch polysaccharides (mannans) of PKC, to improving its nutritive quality [9,10]. Reported proximate analysis of PKC is shown in Table 1:

Table 1: Proximate Analtsis of PKC content

Nutrient composition of	Alimon Report PKC Ingredients (%)	Dairo & Fasuyi Report PKC Ingredients (%)	Onwudike report PKC Ingredients (%)
Dry matter	88.0-94.5	91.8	-
Crude protein (CP)	14.5-19.6	20.0	17-21
Crude fiber (CF)	13.0-20.0	-	10-17
Ether extract	5.0-8.0	15.47	0.7-0.9
Ash	3.0-12.0	8.6	4-5
Calcium	0.2-0.3	-	-
Phosphorus	0.48-0.7	-	-
Metabolizable energy, MJ/Kg			
Chicken	6.50-7.50	-	-
Amino acid, g/16 g N			
Lysine	2.68	-	-
Methionine	1.75	-	-

Sources: Alimon (2004); Dairo and Fasuyi (2007) and Onwudike 1988
Sharmila et al., 2014

Palm kernel cake PKC becomes an important feed ingredient, with its world production figure and the formulation of a supplementary feed. Using PKC can effectively and efficiently replace maize, weight for weight, in diets of growing pigs as an energy source [8]. Studies on the utilisation of PKC as substitute to corn and soy meals as the main source of protein in supplementary livestock feed production has been researched and the results obtained are subjected to modifications and formulations because of high copper content broadcast in PKC. Deadly effects of copper content in PKC supplementary feed was reported and addition of zinc either with or without ammonium molybdate in PKC diet was reported to inhibit the copper content in the organs of treated livestock [11]. It had hitherto been reported to be used as a filler to increase the bulkiness of feed while providing some protein, energy, minerals and vitamins [12]. The mineral content of PKC is presented in Table 2;

TABLE 2: MINERAL CONTENTS OF PALM KERNEL CAKE

Mineral content	**Available Quantity**
Calcium (%)	0.21 – 0.34
Phosphorus (%)	0.48 – 0.71
Magnesium(%)	0.16 – 0.33
Potassium (%)	0.76 – 0.93
Sulphur (%)	0.19 – 0.23
Copper (ppm)	20.5 – 28.9
Zinc (ppm)	40.5 – 50.0
Iron (ppm)	835 – 6130
Manganese (ppm)	132 – 340
Molybdenum (ppm)	0.70 – 0.79
Selenium (ppm)	0.23 – 0.30

Source: Alimon, A.R.(2004)

Usage of excess PKC in sheep was reported to cause chronic toxicity [13]. Death of sampled animals was associated mainly with hepatic necrosis, whilst jaundice and haemoglobinuria were the most remarkable clinical signs [14]. These changes are quite consistent to those of chronic copper toxicity [15,16]. The level of copper in PKC was found to be relatively high which was about 11 to 55 ug/g dry weight [13, 17]and supplementation with either sodium molybdate or ferous sulphate was reported to reduce the incidence of the disease [13, 14]. The copper content of 21-28 ppm is higher than that required by ruminants. In fact, sheep fed diets containing PKC above 50% may suffer high accumulation of copper in the liver if fed too long and develop copper toxicity symptoms [18, 19, 20]. These investigations on the usage of PKC and effects of the copper ions contaminations in the meal did not explore possible sources of the copper contaminant.

This research project is aimed at investigating sources of the copper content in palm kernel cake (PKC) from solvent extracted and mechanical expression processes so as to circumvent chronic toxicity caused by high copper content which are reportedly hazardous when palm kernel cake from Industrial sources are used to feed livestock. The process lines of industrial palm oil processing were therefore investigated as case study for this purpose

2.0 Materials and Methods

Palm Kernel seeds that have suffered no environmental and processing damages were selected suitable as control samples. Raw palm kernel materials and extracted cake recipes were sourced from three (3) industrial Oil mills at Soka, Ibadan. Samples from solvent extraction plant and Deoxidized cake (DOC) from desolventiser toaster section of the plants were obtained. Copper contents in the PKC, DOC, materials of construction of press compartment of the plant and oil produced were obtained as recipes for analyses.

2.1 Preliminary Experiment

The moisture content of the palm seeds or endocarp was determined by weighing, 100g of forage lightly packed in Petri-dish. The sample was then placed in the oven and operated at 50^{o}C to be dried. At intervals of about two to three minutes, the dish was removed, weighed and recorded until constant weight was attained. This process is repeated thrice and the average weight was recorded. The metalloid ions of the samples were also tested using characteristic flame colour test, over a Bunsen burner. The characteristic emission spectrum was used to differentiate suspected elements and analytical method was adopted to determine the copper content in materials [21].

2.2 Testing for Copper Contaminant in processed Cake.

About 0.2g dry weight of the pkc samples prepared were weighed and digested in a pyrex glass tube with 70% nitric acid and 30% zinc nitrate solutions. All tubes were covered with glass marbles and left overnight. The tubes were heated in a heating block at 140^{o}C until all the samples were completely digested and the colour changed from dark brown to colourless. The digested samples were diluted in distilled water for further analysis in spectrophotometer.

Copper contents of each sample were analyzed in an atomic absorption spectrophotometer at wavelengths of 324.7mm and 213.9mm, respectively. The spectrophotometer was standardized with a solution containing 2.0, 4.0, 6.0, 8.0, and 10.0 µg/ml of copper prepared from cupric nitrate (1mg/ml) in 0.1m Nitric Acid respectively. The performance of the spectrophotometer were frequently monitored and re-standardized when necessary [22]. All measurements on the respective analysis were expressed as the mean values of repeated samples measurement.

3.0 Results and Discussions

The moisture content MC of samples from the respective industrial supplies was in the range of 15 to 19% on dry basis with average moisture estimated at 18.35%. Higher moisture content was reported to promote microbial growth, kernel fruit with MC of 15% as obtained from 'Coy A' which was closer to the recommended MC in the range of 12 to 15% for save and longer storage. Therefore, fresh kernels should undergo some level of dehydration before storage. The quality control of the kernel stocking should therefore start from reducing level of impurity and the moisture content of kernel or seed practically by drying to reduce the possibilities of degradation. Respiration during storage produces CO_2 and heat, which can affect the quality of the palm kernel fruit; good aeration and low temperatures in a controlled atmosphere prevent damage from the by-products of respiration. This implied, storage methods adopted by farmers and suppliers should be monitored. Once obtained, palm kernel seed should be stored in controlled environment to retard respiration.

It is evident that there was copper content in the fresh fruits kernel, evaluated to be in the range of 14 to 17µg/g on dry weight basis is admissible without jeopardy. These values are lower than the reported hazardous or dangerous quantity of 21-28 ppm for direct livestock diet. Therefore, further investigation of other sources of the copper along the process plant was imperative. Copper concentrations in the respective pulverized Palm Kernel seed (PKS), Palm Kernel Cake (PKC) and De-Oxidised Cake (DOC), is presented in Table 3.

TABLE 3: Results Of Analysis Of Copper In Cakes From Industrial Samples

Sources of Samples	**Coy A**	**Coy B**	**Coy C**
Cake Analysis	(µg/g)	(µg/g)	(µg/g)
Fresh Palm Kernel Fruit (PKF)	16.78±0.5	14.43±0.4	17.03±0.6
Palm Kernel Cake (PKC)	1689.98±186.98	1856.66±274.07	1873.38±305.77
Deoxidized Cake (DOC)	1086.46±76.98	992.06±75.38	999.82±75.29
Oil Analysis			
Solvent extracted PKO	1027.62±153.01	955.06±152.82	1135.48±153.54
Mechanically Pressed PKO	2594.48±65.59	0	0

N.B: Coy A,B,C represent Oil Mill Company Sudit, Lina and Shasu respectively

The magnitudes of Copper in the respective samples were found to be minimal from the fresh kernels seed analysis, implying that this quantity may not be sufficient for the controversial toxicity of the cake as lethargic. The gradual accumulation of the copper content along the process line is displayed in Figure 1:

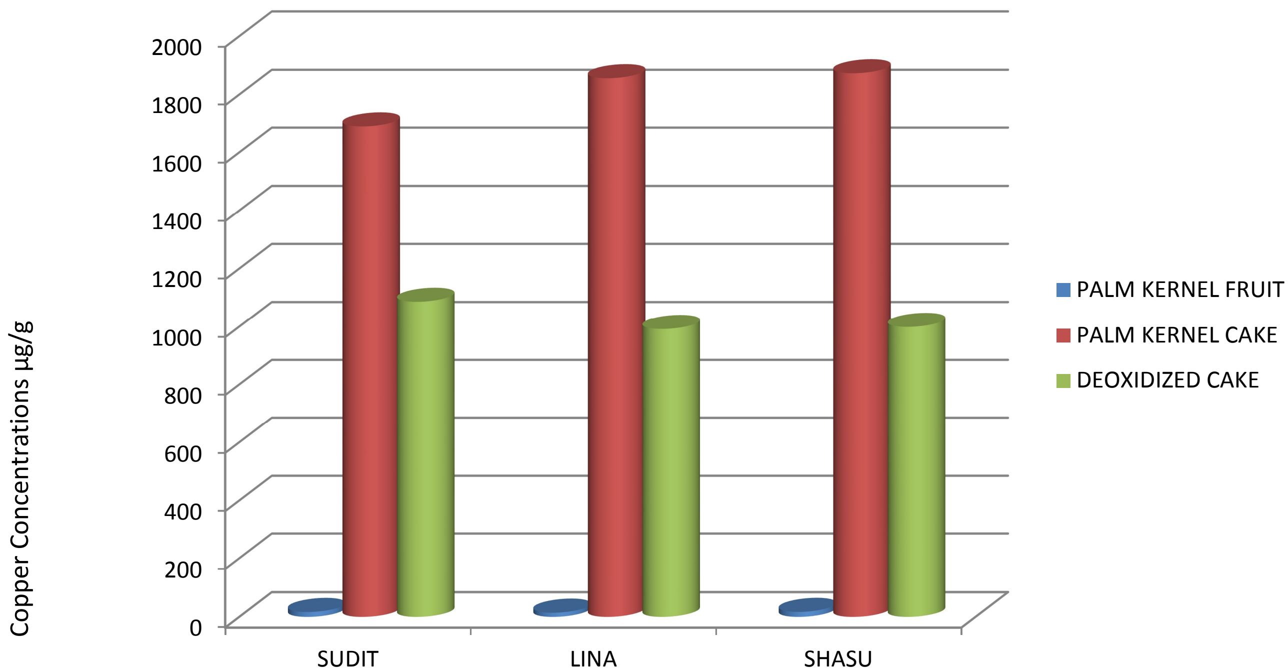

FIG 1: Copper Concentrations of Respective Cake Samples

Measured concentrations of copper in the DOC attained a higher concentration up to about 1000 ug/g from the respective process plants Coy A (Sudit), Coy B (Lina), and Coy C (Shasu). Further increase was also observed when the Palm kernel cake was analysed. This marked increase could not be traced except to the materials of constructions as there were no alternative input of material of any sought along the process lines.

The flame emission spectroscopy investigation carried out on the other compartments revealed the presence of Copper metal mainly at the stripping column, crusher and hexane pipe as alloy components of the structures. Result of test is shown in Table 4.

TABLE 4: Flame Emission Spectroscopy of Compartments

Source Of Sample	Observation	Inference
Stripping Column	Green Flame	Copper Present
Crusher	Green Flame	Copper Present
Seize Wire	Glowing Yellow Flame	Sodium Metal Present
Wet dust catcher	Glowing Red Flame	Calcium Metal Present
Hexane Pipe	Green Flame	Copper Present

Copper concentration was observed higher in PKC and DOC than in the fresh fruit, this could be associated with copper contamination during processing of the by-products. It could be seen that the copper content in DOC was high for each company but higher in PKC that was processed in the solvent extraction plant. These variations depends considerably on chemical composition of the source of feed, the efficiency of oil extraction process from the Therefore, the material of construction in the crushing plant had significant copper content asserted by the characteristic colour test of strip metals from crushing plant. This suggests that contamination had infusion from material of construction in the crushing plant since PKC was derived after removal of larger percentage of oil present in the kernel seed.

The sources of copper contamination were traced to the crushing plant and solvent extraction plant as observed in flame emission spectroscopy carried out. The percentage increase of copper contamination was higher in the crushing plant than the concentration of copper content found in the DOC from solvent extraction plant evaluated at about 53%. Meanwhile similar test on materials from solvent plant indicates the presence of other metals which are non toxic to the body of animals (especially Calcium and Sodium) except for the stripping column which also contributes to the contamination of the oil in the final process of miscella in the solvent extraction plant. Thus copper content in the palm kernel oil increases to an average value of (1027.62± 153.01 μg/g). The significant concentration in mechanically pressed PKO (2594.48± 65.59 μg/g) shows that the copper concentration in solvent extracted PKO reduces by about 40%. During the period of investigation the crushing plant of Lina Oil Mill and Shasu Oil Mill were not in operation and the PKO sample was not available.

CONCLUSIONS

Copper was detected as component of the fresh palm kernel fruit but higher copper content was detected to be associated with the processing of PKC. Source of further metallic ion contamination was traced to the shells remnant in palm kernel seed as raw material fed into the plant. Some palm kernel seeds that were not properly de-shelled thus added more copper content to the resulting cake. In view of the materials of construction, the hexane pipe corrosion may have added more copper ion as contaminant to the analyzed by-products. Hence, flooding in the extractor and flow pressure during processing should be avoided or minimized to prevent wear of internal part of the pipe. Therefore, it is recommended that material of construction should made of stainless steel while clean and uncontaminated kernels should be used, this would improve profit margins of productivity as cake generated will enjoy secondary usage with ease.

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