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Variations in Chemical Composition, Functional Properties and Oil Quality of Groundnut (*Arachis Hypogaea*) as Influenced by Medium Dose Gamma Irradiation using Cobalt-60 Source

Victor N. Enujiugha[1*], Oladotun O. Oguntoyinbo[2], Ajobola M. Oyinloye[3], Oluwaseun A. Adesina[1], Mercy O. Olowolafe[1] and Funmilayo S. Adekanmbi[1]

[1]Department of Food Science and Technology, Federal University of Technology, Akure, Nigeria
[2]Department of Food Science and Technology, Lagos State University of Science and Technology, Ikorodu, Nigeria
[3]Department of Food Science and Technology, Federal University, Oye-Ekiti, Nigeria

*Corresponding author email: vnenujiugha@futa.edu.ng; Tel.:+2348034261870

Abstract

Groundnut samples were irradiated at 2.5 and 10 kGy, using cobalt-60 gamma source; non-irradiated nuts served as control. The parameters determined were the proximate and mineral composition, anti-nutritional factors and functional properties, as well as amino and fatty acids profiles, and oil quality of the samples. Irradiation did not have any significant effect on the proximate composition, except that fat content increased from 41.98 ± 0.03% dry wt. at 0 kGy to 42.06 ± 0.03% and 42.08 ± 0.05% at 2.5 and 10 kGy, respectively. The mean protein content of all the samples was 29.77%. Irradiation significantly ($P \leq 0.05$) increased the mineral contents of groundnut. Potassium being the most abundant in groundnut (28.56 ± 0.03 mg/100g) at 0 kGy was increased to 37.56 ± 0.01 mg/100g at 2.5 kGy and 36.31 ± 0.01 mg/100g at 10 kGy, respectively. Iron and sodium were low (2.05 ± 0.03 and 2.08 ± 0.03 mg/100g at 0 kGy, respectively; and 2.58 ± 0.02 and 2.82 ± 0.02 mg/100g, respectively). The oil absorption capacity for the groundnut flour samples increased significantly, with increased dose of irradiation (86 ± 0.58, 87 ± 0.58, and 94 ± 0.58% at 0, 2.5 and 10 kGy, respectively); while the foaming and emulsion capacities decreased. Interestingly, the water holding capacity of groundnut flour was not affected by irradiation. Peroxide and saponification values were not affected significantly ($P \leq 0.05$) by irradiation, while the iodine value decreased. Sulphur and aromatic amino acids were reduced significantly ($P \leq 0.05$) with increased dose of irradiation. There was reduction or elimination of unsaturated fatty acids at 2.5 and 10 kGy doses, with increase in saturation level due to irradiation. Anti-nutritional factors were reduced with increased dose of irradiation. The findings revealed that irradiation is still suitable as a method of preservation for groundnut, with minimal negative impact on overall nutritional quality.

Keywords: *γ-Irradiation, groundnut, chemical composition, amino acids, fatty acids*

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1. Introduction

The desire for higher quality, less severely processed, more natural, more nutritious and safer food by consumers is on the increase in various parts of the world (Enujiugha *et al*., 2012; 2023). This is especially applicable to oilseeds because of their innate postharvest deterioration through internal enzyme system (Enujiugha *et al*., 2004; Oguntoyinbo *et al*., 2023) and the external predisposition to microbial infestation and mycotoxicoses (Enujiugha *et al*., 2023). To this end, hurdle technology through combined irradiation and hydrothermal treatments are effective tools for the achievement of this objective. Food irradiation is an innovative method of preservation discovered several years ago but its commercial application has been slow, due to misconception and misunderstanding of terminologies and its operations (James 2000; Olotu *et al*., 2014a). Food irradiation as a technology for food safety was first recognised for inhibiting sprouting in potatoes, onions and for control of insect infestation; and with the increase in its acceptance, it is now used for many food products such as meat, poultry, fruits, spices, vegetables and fish with stated regulatory guidelines (Farkas, 1998). By definition, according to WHO (1991), food irradiation is the treatment of fresh or processed foods with ionizing radiation that inactivates biological contaminants (insects, moulds, bacteria) rendering foods safe to consume and extending their storage life time. Ionizing radiations used for food irradiation are such that have a high penetrating ability and do not cause irradiated foods to be radioactive. Gamma ray generated from

cobalt 60, is one of the most acceptable for food irradiation having a high penetrating ability and does not cause irradiated foods to be radioactive (Olotu *et al*., 2014a,b).

With the current research trend towards the use of lesser-known and unconventional oilseeds for commercial vegetable oil production (Talabi and Enujiugha, 2014), their storage prior to processing becomes ever more challenging because of the unsaturated nature of their oils (Enujiugha *et al*., 2023). Most of the underutilized oilseeds are reported to impact positively on organs of consumers (Talabi *et al*., 2023) owing to their high content of polyunsaturated fatty acids (PUFAs), and at the same time they can be processed into different products through nutritional and aesthetic value-addition (Enujiugha, 2000). Among the neglected and underutilized crop seeds and nuts is groundnut, which is noted for its high oil production and cultivated solely for that purpose. One major barrier to the full exploitation of groundnut is its predisposition to fungal spoilage and consequent occurrence of mycotoxins, especially aflatoxin B1. To take care of this microbiological hurdle, the use of gamma rays to disinfest and preserve this important oil crop has been explored by different researchers, but a comparative evaluation of the effect of high and low doses on the innate nutrients and bioactive components has not been fully carried out. Hence, the objective in this study was to compare two medium doses (higher and lower limits) and make recommendations for their application in a known food system (groundnut).

Groundnut (*Arachis hypogaea* L.) also known as peanut is an annual crop grown principally for its edible oil and protein rich kernels or seeds; it is now grown worldwide in the tropics and temperate zones primarily as an oil seed crop (Bansal *et al*., 1993). It is consumed fresh, roasted, dried, boiled and used in many recipes. Peanuts, like some other nuts, are rich in certain mono-unsaturated and polyunsaturated fatty acids. Irradiation of foods at a high dose can impact changes in the organoleptic properties which in most cases are unpleasant to consumers (Sanchez-Bel *et al*., 2005; Mexis and Kontominas, 2009). The unsaturated fatty acids subject nuts to lipid oxidation with the radiolytic effect of the irradiation resulting in the loss of essential fatty acids (such as linolenic acid and linoleic acid) and release of sulphur compounds, esters, ketones and aldehydes (off-flavour development) (Sajilata and Singhal, 2006). The aim of the present study was to determine the effect of irradiation on the chemical and functional properties of groundnut and the seed oil subjected to 2.5 kGy and 10 kGy, which represent the lower and upper limits of medium dose gamma irradiation.

Materials and Methods

2.1 Preparation of Samples

Shelled and dried groundnut seeds were purchased from a local farmer. The seeds were visually inspected and the defective ones were removed. The seeds were then transported to the laboratory and kept in airtight polyethylene containers in a dry and cool environment until ready for use. The seed oil was extracted, both from powdered raw unirradiated and irradiated nuts using Soxhlet apparatus with n-hexane as the extracting solvent (Enujiugha, 2000).

2.2 Irradiation of Nuts

Gamma-irradiation was done at Shedan Science and Technology Complex (SHESTCO), Abuja, Nigeria, under tropical ambient conditions (28±2 ºC). The irradiation of the nut samples was carried out (with the seeds contained in sealed polyethylene containers) using cobalt-60 gamma irradiation source (Model GS 1000, Category 4, Panorama Wet storage Source, Siemen, Germany) at an absorbed dose of 2.5 kGy and 10 kGy with an appropriate monitoring while the un-irradiated nut samples served as the control.

2.3 Proximate analysis

The proximate composition was determined on the samples by Standard Analytical methods. Moisture content according to method 964.22 (AOAC, 2012), protein content according to method 955.04 (AOAC, 2012); crude fat extracted overnight in a Soxhlet extractor with n-hexane and quantified gravimetrically, ash contents according to method 923.03 (AOAC, 2012); crude fibre determined after digesting a known weight of fat-free sample in refluxing 1.25 % sulphuric acid and 1.25 % sodium hydroxide; and carbohydrates determined by the difference method (subtracting the percent crude protein, crude fibre, crude fat, and ash from 100% dry matter).

2.4 Mineral analysis

The sodium (Na) and potassium (K) contents of the samples were determined using digital flame emission photometer (Sherwood Flame Photometer, model 410, Sherwood Scientific Ltd, cambridge, UK) as described by Dauda *et al*. (2022). The phosphorus was determined colorimetrically using phospho-vanadomolybdate (yellow) method and the absorbance was measured at 470 nm (AOAC, 2012). The other elemental concentrations were determined by using Atomic Absorption Spectrophotometer (AAS, Buck Model 20A, Buck Scientific, East Norwalk, CT06855, USA), after wet digestion of sample ash with a mixture of nitric and perchloric acids (1:1 v/v). All determinations were done in triplicates.

2.5 Determination of Anti-nutritional factors

The method of Wheeler and Ferrel (1971) as modified by Reddy *et al.* (1982) was used for phytic acid and phytate-phosphorus determinations. Phytic acid was extracted from each 3 g flour sample with 3% trichloroacetic acid by shaking at room temperature followed by high-speed centrifugation (30,000 x g for 5 min). The phytic acid in the supernatant was precipitated as ferric phytate, and iron in the sample was estimated. Phytate-phosphorus (phytate-P) was calculated from the iron results assuming a 4:6 iron : phosphorous molecular ratio according to Enujiugha and Olagundoye (2001).

Tannin contents were determined by the modified vanillin-HCl method (Burns, 1971; Price *et al.*, 1978). A 2 g sample was extracted with 50 ml 99.9% methanol for 20 min at room temperature with constant agitation. After centrifugation for 10 min at 653 x g, 5 ml of vanillin–HCl (2% vanillin, 1% HCl) reagent was added to 1 ml aliquots, and the colour developed after 20 min at room temperature was read at 500 nm. Correction for interference from natural pigments in the sample was achieved by subjecting the extract to the conditions of the reaction, but without vanillin reagent. A

standard curve was prepared using catechin (Sigma Chemical, St. Louis, MO) after correcting for blank.

Determination of oxalate was by the AOAC (2012) method. Exactly 1 g of finely ground sample was dissolved in 75 ml of 1.5 N H_2SO_4. The solution was carefully stirred intermittently with a magnetic stirrer for about 1 h and filtered using Whatman no. 1 filter paper. A 25 ml sample of the filtrate (extract) was collected and titrated hot (80 – 90 ºC) against 0.1 N $KMnO_4$ solution to the point when a faint pink colour appeared that persisted for at least 30 seconds.

2.6 Analysis of Functional Properties

The determination of water and oil absorption capacities followed a modification of the method of Prinyawiwatkul *et al.* (1997). Each flour sample (5.0 g) was thoroughly mixed, without pH adjustment with 25 ml of deionized water or oil in 50-ml centrifuge tubes. Suspensions were stirred intermittently over a 30 min period at room temperature (28 ± 2 ºC) and then centrifuged at 12,000 x g for 30 min at 25 ºC. The volume of decanted supernatant was measured, and the water and oil absorption capacities were then calculated.

For the least gelation concentration, triplicate suspensions of 1 - 20% seed flour sample (dry w/v, at 1% increment) were prepared in 10 ml of deionized water and mixed thoroughly without pH adjustment. The slurries were heated in 125 x 20 mm screw- capped test tubes in a water bath with in-built magnetic stirrer (Julabo Model SW22, Julabo Labortechnik GMBH, Seelbach, Germany) at 95 ± 2 ºC. After 1 h of heating, tubes were immediately cooled in tap water for 30 s and then in ice water for 5 min to accelerate gel formation. All tubes were then held at 4 ºC for 3 h. The least gelation concentration (percent) was determined as the concentration above which the sample remained in the bottom of the inverted tube (Enujiugha *et al*., 2003).

The foaming properties of the samples were determined using the procedure of Coffman and Garcia (1977). Exactly 2.0 g of sample was weighed into 60 ml distilled water in a 100 ml cylinder. Solid material was dispersed with spatula and the suspension was whipped for 5 min using ultra-Turax T25 mixer at a high speed. Volumes before and after whipping were noted and volume increase due to whipping was then calculated. The volume of foam in the standing cylinder was also recorded for foam stability studies at 1, 5, 10, 20, 30, 60, 90, 120 and 180 min after whipping. The results were expressed in percentages.

Emulsifying properties were determined using a modification of the method described by Ige *et al.* (1984). A known quantity (1.8 g) of sample was dispersed in 25 ml distilled water, and 25 ml vegetable oil (pure groundnut oil) was added. The 50 ml mixture was emulsified at high speed using ultra-Turax T25 mixer for 1 min. Emulsion was filled into centrifuge tubes and centrifuged for 5 min at 1,300 x g.

2.7 Fatty Acids Analysis

Fatty acids were determined using gas chromatographic analysis, as previously described (Olotu *et al*., 2014a), with some modifications. The fatty acid methyl esters were obtained quantitatively from the oil by direct transesterification with methanolic sodium hydroxide at room temperature, followed by subsequent methylation with 14% boron trifluoride (BF_3) – methanol. The component fatty acids were determined with a Johnson Q94 gas chromatograph with flame ionization detector. Exactly 1 µl of methylated sample was injected into gas liquid chromatograph using a micro syringe. The fatty acid methyl esters were analyzed by GLC using Q94 gas chromatograph with JCL 6000 For Windows 2.0 Chromatography Data System (Johnson Chromatography Ltd) under the following conditions: Column, glass; stationary phase, 10% bisethyleneglycol succinate polyester (DEGS); support, 60 - 80 mesh chromosorb W; carrier gas, nitrogen; inlet pressure, 20 psig; injection temperature, 200 ºC; detector, hydrogen flame ionization (FID); sensitivity, 1 x 10^{-9} A; chart speed, 5 mm / min; hydrogen pressure, 15 psig; oxygen pressure, 7 psig. The separated fatty acid methyl esters were identified by comparing their relative retention times with those of known standards and using the usual semi log plot of relative retention value versus equivalent chain length. The identified fatty acids were quantitated by multiplying peak areas by appropriate response factors. The fatty acids were expressed in percentages of the weight of total fatty acids in the oil, and all procedures were carried out in triplicates.

2.8 Determination of Amino Acids Profile

The amino acids profile in the groundnut sample was determined using the method of Olotu *et al*. (2014b), with slight modifications. The samples were dried to constant weight, defatted, hydrolyzed, evaporated in a rotatory evaporator and loaded into the technicon sequential multi sample amino acid analyzer (TSM). A known weight of sample was weighed into extraction thimble and the fat was extracted with chloroform/methanol (2:1) using Soxhlet extraction apparatus as described by AOAC (2012); the extraction lasted for 15 hours. A known weight of the defatted sample was then weighed into glass ampoule. 7 ml of 6N HCL was added and oxygen was expelled by passing nitrogen into the ampoule in order to avoid possible oxidation of some amino acids during hydrolysis e.g. methionine and cysteine. The glass ampoule was then sealed with Bunsen burner flame and put in an oven preset at 105 ± 5 ºC for 22 hours. The ampoule was allowed to cool before broken open at the tip arid the content was filtered to remove the remains. The filtrate was evaporated to dryness at 40 ºC under vacuum in a rotator evaporator. The residue was dissolved with 5 ml of acetate buffer (pH 2.0) and stored in plastic specimen bottles, which were kept in the freezer.

The amount of hydrolysate loaded into the TSM analyser was between 5 to 10 microliters. This was dispensed into the cartridge of the analyzer. The TSM analyser is designed to separate and analyze free acidic, neutral and basic amino acid of the hydrolysate. The period of an analysis lasted for 76 minutes. The total essential amino acids (TEAA), total acidic amino acids (TAAA), total sulphur amino acids (TSAA) and total aromatic amino acids (TArAA) were calculated and the predicted protein efficiency ratio (PER) was determined (i.e., PER = −0.468 + 0.454[Leu] − 0.105 [Tyr]). All determinations were carried out in triplicates.

2.9 Chemical Analysis of the seed oil

AOAC (2012) method was used for the determination of iodine value. Wij's solution was prepared by dissolving 8 g of

iodine trichloride in 200 ml of glacial acetic acid. About 0.2-0.5 g of sample was weighed into a glass stopper bottle of 250 ml capacity. Then 10 ml of carbon tetrachloride was added to the oil to dissolve and 20 ml of Wij's solution was added. A potassium iodide moistened stopper was used to clog the bottle. It was mixed and then allowed to stand in the dark for 30 min. After 30 min, 15 ml of KI solution and 100 ml was added. The solution was mixed and titrated with standard sodium thiosulphate after starch indicator has been added to it. Also titration was carried out simultaneously on blank by omitting oil.

Peroxide value was determined according to AOAC (2012) procedure. Two grams (2.0 g) oil samples were added into a stopper Erlenmeyer flask. 10 ml of glacial acetic acid and chloroform was mixed in the ratio of 3 to 2 and the solution was added and to dissolve the oil and this was followed by addition of potassium iodide (0.2 ml). The flask was stopped and hand shaken for 60 seconds using stop watch. 20 ml of glass distilled water was added followed by 0.5 ml stabilized starch solution (1%). The solution was titrated with 0.01M sodium thiosulphate solution and this was accompanied by vigorous shaking until the blue colour disappeared. A blank without oil solution without oil addition was also run under the same condition peroxide value (milligram /g oil).

In the determination of free fatty acids (FFAs), about 25 ml of diethyl ether was mixed with 25 ml of alcohol and 1 ml of phenolphthalein indicator was added and it was carefully neutralized with 0.1M NaOH. 1-10 g of oil was mixed with the neutral solvent and it was titrated with 0.1M NaOH until a pink coloration was obtained. FFA was calculated as oleic acid (1 ml 0.1M sodium hydroxide = equivalent to 0.282 g oleic acid) and acid value was calculated as 2 x FFA (Enujiugha *et al*., 2012).

For saponification value, about 50 ml of alcoholic KOH was added to 5 g of oil sample in a flask. A blank of 50 ml of alcoholic KOH was taken in another flask. Both of the flasks were connected to reflux condenser and boiled gently for an hour. The inside of condenser was rinsed down after cooling with little distilled water. Then, 1 ml of Phenolphthalein indicator was added and the titration was done against 0.5 M HCl until the pink colour just disappeared (AOAC, 2012).

2.10 Statistical Analysis

Data collected from the study (in triplicates) were subjected to analysis of variance (ANOVA). Differences among means were separated using Duncan's multiple range test; significances were accepted at 5% level ($P \leq 0.05$). The statistical software used was SPSS 10.0 for windows.

Results and Discussion

3.1 Proximate chemical composition of the samples

The results of the proximate chemical composition of irradiated and non-irradiated samples of groundnuts are presented in Table 1. The results showed that there was no significant difference in the proximate composition of all the samples. The insignificant difference in the proximate composition of the samples are in agreement with previous work of Inayatulah *et al*. (1987), which established that irradiation with 0.25, 0.5, 1.0, 2.5 and 5 kGy had no significant effect on the proximate composition of soybean, Al-Bachir (2004) for walnuts, Bela *et al*. (2008) for almonds and Siddhuraju *et al*. (2002) for sesbania. Seda *et al*. (2001) also reported that gamma irradiation did not induce any change in protein and oil content of soybean and groundnut.

Table 1: Proximate composition of irradiated and non-irradiated groundnut samples (%DM)

DOSES (kGy)	MC	Crude fibre	Ash	Fat	Protein	CHO	Energy value (kcal)
0	3.89±0.03a	2.60±0.03a	3.20±.003a	41.98±0.03b	29.82±0.11a	18.46±0.03a	569.32±0.10b
2. 5	3.90±0.05a	2.60±0.20a	3.25±0.50a	42.06±0.05a	29.71±0.01a	18.48±0.03a	571.30±0.50a
10	3.87±0.02a	2.59±0.04a	3.23±0.03a	42.08±0.01a	29.80±0.05a	18.46±0.05a	571.76±0.10a

Means in the same column with different letters are significantly different ($p \leq 0.05$), Mean ± S.D.

However, the increase in the fat contents of irradiated samples which is within the range stated for peanuts by Bansal, *et al* (1993) may be attributed to the breaking of bound fat as a result of irradiation leading to release of more fat. The energy value of irradiated samples at 2.5 kGy and 10 kGy are 571.30 ± 0.50 and 571.76 ± 0.10 kcal, respectively. The energy values of irradiated groundnut samples are more improved and significantly different from the non-irradiated sample. Although, overall, energy value did not increase with increased irradiation doses. The energy value of raw groundnut agrees with the findings of Ahmed and Young (1982), Asiedu (1992) and Gopalan (1971) who stated that 100 g of groundnut would provide about 570 kcal of dietary energy.

3.2 Mineral composition

The mineral compositions of irradiated and non-irradiated groundnut samples are presented in Table 2. The amounts of Na, K, Ca, Fe and P in the raw groundnuts were 2.08 ± 0.03, 28.56 ± 0.03, 8.17 ± 0.03 and 2.64 ± 0.04 mg/100g, respectively. Based on the obtained data in Table 2, the mineral content of groundnut was increased by irradiation. The Na, Ca, Fe and P increased with increased dose of irradiation. This may be attributed to the fact that irradiation destroys or reduces the anti-nutritional factors such as phytic acid and tannin which chelate certain mineral elements especially Ca, Mg, Fe and Zn.

The levels of K, Ca and P were relatively high in agreement with the findings of Enujiugha and Ayodele-Oni (2003). The same trend was observed by Balogun and Fatuga (1986), who linked the low sodium level of some legume seeds to the subnormal concentrations of sodium in tropical crops which were a reflection of the low sodium contents of the soils. The large amount of K relative to Na in all the samples could be an advantage to hypertensive patients because of reduced mineral imbalance (Enujiugha *et al*., 2003).

The Zn contents of all the samples were within the range of 3-4 mg/100g DM of zinc in the diet as recommended for humans (Enujiugha and Olagundoye, 2001); therefore, the non-irradiated and irradiated groundnuts may be considered as good sources of dietary zinc.

Table 2: Mineral composition of irradiated and non-irradiated groundnut (mg/100g)

DOSES (KGy)	K	Na	Ca	Mg	Zn	Fe	P
0	28.56±0.03c	2.08±0.03c	8.17±0.03c	3.91±0.01b	3.51±0.01c	2.05±0.03c	2.64±0.04c
2.5	37.56±0.01a	2.69±0.04b	11.86±0.04b	4.89±0.04a	3.88±0.03a	2.72±0.02b	3.27±0.05b
10	36.31±0.01b	2.82±0.02a	12.92±0.02a	4.50±0.48a	3.56±0.05b	2.85±0.02a	3.54±0.03a

Mean ± SD, values that have the same subscript in a column are not significantly different *($p \leq 0.05$).*

3.3 Functional properties

The water holding capacities of groundnut samples as presented in Table 3 is in agreement with the findings of Ihekoronye (1985), who studied the functional properties of red skin groundnuts. Gamma irradiation at dose levels of 2.5 and 10 kGy did not significantly affect the water absorption capacities (WAC) of groundnut. Our results are consistent with the findings of Abu *et al*. (2005), who found out that irradiation of cowpea seeds at dose levels up to 50 kGy had no effect on the water absorption capacity of cowpea flour. Similarly, Azim *et al*. (2009) reported that irradiation at 2 kGy of two cultivars of groundnut (*madani* and *sodari*) had no apparent effect on the water absorption capacity. Zayas (1997) also reported that water holding capacity was not affected by Gamma irradiation. The water holding capacity is an index of the amount of water retained within the protein matrix (Kinsella, 1976). The results of this study show that the functional capacity of the groundnut seed protein in thickening and food formulation is not reduced after irradiation.

Table 3 also shows an increase in the oil absorption capacity (OAC) with an increase in the irradiation dose. The groundnut irradiated at 10 kGy had the highest OAC of 94.00 ± 0.58%, followed by that irradiated at 2.5 kGy which had 87.00 ± 0.58% OAC and then the non-irradiated groundnut which had the lowest OAC of 86.00 ± 0.58%. These results conform to the previous findings of Abu *et al*. (2005), who reported that low dose of irradiation (2 kGy), had no effect on the OAC of cowpea. However, an increase in OAC of cowpea was observed at higher doses (10 and 50 kGy). The increase in OAC of irradiated groundnut may be attributed to the exposure of non-polar sites (Enujiugha *et al*, 2003).

It was observed that gamma irradiation decreased significantly ($P \leq 0.05$) the emulsion capacity of groundnut based on the data presented in Table 3. The non-irradiated groundnut had the highest value of 93.67 ± 0.04%, followed by irradiated groundnut at 2.5 kGy which had emulsion capacity of 80.67 ± 0.07%. Abu *et al*. (2005) reported a decrease in emulsion capacity of low dose irradiated (2 kGy) cowpea. The changes in emulsion properties may be attributed to protein aggregation as well as surface hydrophobicity which affect the emulsifying properties in different ways.

Non-irradiated groundnut flour gelled at 50% concentration, 2.5 kGy irradiated groundnut flour gelled at 60% concentration, while the one at 10 kGy gelled at 70% concentration, as shown in Table 3. Gamma irradiation brought about reduction in the gelation properties of groundnut flour as higher sample concentration (irrespective of sample size) was required to form a gel. Gel formation ability of flour is known to be influenced by the nature of the protein, starch and gums in the flour, as well as their interaction during heat treatment (Enujiugha *et al*, 2003). The reduction of gelling capacity may be attributed to protein denaturation that occurred during irradiation (Kinsella, 1976.)

According to the data in Table 3, the foaming capacity of non-irradiated groundnut was the highest (10.00 ± 0.06%) followed by the irradiated groundnut at 2.5 kGy (8.31 ± 0.09%) and then the irradiated groundnut at 10 kGy (5.00 ± 0.12%). Increase in the irradiation dose resulted in a significant decrease in the foaming capacity of groundnut. Our result is in agreement with the report of Abu *et al*. (2005). Functional properties such as foaming capacity, emulsification, oil and water absorption capacity have been reported to be protein dependent with no effect of irradiation at low dose (2 kGy) and significant effect has been shown at high irradiation (10 kGy and 50 kGy) on cowpea (Abu *et al*., 2005).

Table 3: Functional properties of irradiated and non-irradiated groundnut (%).

Dose (kGys)	FC (%)	EC (%)	LGC (%)	WAC (%)	OAC (%)
0	10.00±0.06a	93.67±0.04a	50.00±0.58a	80.00±0.58a	86.00±0.58bc
2.5	8.31±0.09b	91.00±0.58b	60.00±0.58b	80.00±0.58a	87.00±0.58b
10	5.00±0.12c	80.67±0.04c	70.00±0.58c	81.00±0.58a	94.00±0.58a

3.4 Oil quality parameters

The data in Table 4 indicate that, with regard to peroxide value (PV), there were no significant differences between the irradiated groundnuts at 2.5 and 10 kGy and non-irradiated groundnuts. PV values in the present study are in agreement with those of Al-Bashir (2004) who showed that there were no significant differences in peroxide values of irradiated and non-irradiated walnuts immediately after irradiation; and Sanchez-Bel *et al.* (2005) found that almonds irradiated at doses 3, 7 and 10 kGy did not affect lipid oxidation. Similarly Jan *et al*. (1988) reported no effect of irradiation on shelled walnut. In contrast, an increase in PV was reported in irradiated pine nut by Golge and Ova (2008). Chiou (1994) also reported that the peroxide content of peanut oils prepared from irradiated peanuts increased with irradiation dosage (2.5, 5.0, 7.5 and 10 kGy). Similarly, Mexis and Kontominas (2009) found a significant increase in PV of irradiated almonds. The mean peroxide value for all the samples in this study was 34.25

± 0.58, higher than the value reported by Onyeike and Acheru (2002) for groundnut which is 20.0 ± 2.10. It can be deduced that oil from irradiated groundnut at 2.5 and 10 kGy and non-irradiated groundnut would not store for longer period, because of the recorded higher peroxide values.

The iodine value of non-irradiated groundnut was 12.51 mg/100g as shown in Table 4, which is a little higher than the amount reported for African oil bean (10.13 mg/100g) and groundnut (9.7 mg/100g); and lower than the amount reported for conophor nut (20.4 mg/100g) by Enujiugha (2003). The results show that the iodine value decreased significantly with increased irradiation. At 2.5 kGy, it had the value of 10.43 ± 0.6 while at 10 kGy, it was 8.40 ± 0.44. The effects are in agreement with the result of Al-Bachir (2004) who showed that gamma irradiation at 0.5, 1.5 and 2.5 kGy significantly decreased the iodine value of oil extracted from irradiated walnuts. Decrease in iodine value after gamma irradiation may be attributed to the saturation of double bonds of unsaturated fatty acids by hydrogenation, which affects the quality of the oil. When water is irradiated, the ionization produces a cation radical including hydrogen atoms (H^+). Similar findings were obtained by Zeb and Ahmad (2004) who reported that the iodine value of sunflower and soybeans oil decreased significantly with high gamma irradiation (1, 5 and 20 kGy). Generally, iodine values of vegetable oils having double bonds are significantly affected by processing (Oyinloye and Enujiugha, 2017).

The data in Table 4 indicate that all doses of gamma irradiation significantly increased both the acid value and free fatty acids in groundnut. The increase in FFA may be attributed to the degradation of large lipid molecules producing smaller molecules including free fatty acids. The results agree with the findings of Al-Bachir (2004) who showed that free fatty acids in walnuts treated with 1.0, 1.5 and 2.0 KGy were significantly higher than in the control. Each of the oils had a free fatty acid concentration below the maximum limit of 5.0% reported for high-grade Nigeria palm oil (NIFOR, 1989). The nutritional value of a fat depends in some respect on the amount of free fatty acids. In the tropics, where vegetable oils are the most common dietary lipids, it has been shown that it is desirable to ensure that the free fatty acids content of cooking oil lies within limits of 0.0 -3.0% (Onyeike and Acheru,2002). The low levels of %FFA, in all the oils investigated, indicate that the oils are good edible oils that may be stored for a long time without spoilage via hydrolytic rancidity.

The data in Table 4 indicate that there was no significant difference in the saponification values of oils extracted from irradiated and non-irradiated groundnut. This finding agrees with that obtained by Azim *et al* (2009) and Zeb and Ahmed (2004). This shows no change in fatty acid chain length in the oil occurred after irradiation.

Table 4: Oil quality parameters of groundnut samples

Dose (KGy)	PV (mg/g oil)	IV(mg/100g)	AV (mg NaOH /g)	%FFA (oleic acid)	SV (mg KOH/g)
0	34.67±0.5a	12.51±0.09a	2.74±0.04a	1.38±0.04c	361±1.00a
2.5	34.67±0.5a	10.43±0.60b	4.65±0.02b	2.34±0.02b	359±1.73a
10	35.00±0.07a	8.40±0.44c	5.18±0.03a	2.61±0.03a	360±1.53a

3.5 Amino Acid profile of groundnut samples.

As shown in Table 5, lysine, histidine, arginine, aspartic acid, proline, cystine, valine, methionine, isoleucine, leucine, tyrosine and phenylalanine were noted to significantly decrease with irradiation, in a dose-dependent manner. On the other hand, increase or decrease in threonine, serine, glutamic acid, glycine and alanine were of no clear trend. The total essential amino acids (TEAA), total sulphur amino acids (TSAA) and total aromatic essential amino acids as presented in Table 6 reduced significantly as dose of irradiation increased. However, the percentage total acidic amino acids increased with increased irradiation dose (Table 6). The bioavailability of proteins in food was reported to be reduced by gamma irradiation (Gralic and Warchalewski, 2005). The observed decrease in amino acid content of the irradiated groundnut is in agreement with the findings of Olotu *et al*. (2014b) who reported a significant decrease in the acidic, basic, polar and non-polar amino acids in African oil bean seed as the irradiation dose increased; but, contradicts those of Sattar *et al*. (1990) who reported an increase in both essential and non-essential amino acids of Soya beans irradiated at a dose level of 0.1kGy. Siddharaju, *et al* (2002) expressed the impact of ionizing radiation on free amino acids to be dependent on the aqueous soaking after irradiation, the functional tissue and the sensitivity of the exposed system. In the irradiated groundnuts, cystine and methionine were the most limiting amino acids, having 1.39 ± 0.09 and 1.30 ± 0.03 g/100g protein, respectively. Matloubi *et al*. (2004) reported that Sulphur containing and aromatic amino acids are the most sensitive to irradiation while the simple (or common) amino acids could be formed by the destruction of complicated amino acids.

The predicted protein efficiency ratio (P-PER) was reduced with increased irradiation dose. These results could be related to the structure of amino acids, as simple (or common) amino acids due to irradiation undergo reductive deamination and decarboxylation. While the most abundant amino acid in the groundnut samples is glutamic acid which increases with irradiation doses.

Table 5: The amino acid composition of groundnut samples (mg/100g).

Amino acid	0 kGy	2.5 kGy	10 kGy
Lysine	3.28±0.08a	3.01±0.01b	2.52±0.02c
Histidine	2.35±0.05a	2.13±0.03b	1.88±0.03c
Arginine	10.98±0.05	9.87±0.07b	9.36±0.04c
Aspartic acid	11.90±0.05a	11.28±0.08b	10.78±0.03c
Threonine	2.77±0.08a	2.89±0.04a	2.52±0.02c
Serine	4.86±0.06a	4.34±0.04c	4.48±0.03b
Glutamic acid	17.21±0.01c	18.10±0.10a	17.88±0.02b
Proline	4.88±0.08a	4.35±0.05b	4.03±0.03c
Glycine	3.60±0.05a	3.23±0.03c	3.45±0.03b
Alanine	4.02±0.02b	4.21±0.01a	3.20±0.01c
Cystine	1.39±0.09a	1.19±0.03b	0.93±0.01c
Valine	4.53±0.03a	4.01±0.01b	3.89±0.04c
Methionine	1.30±0.03a	0.99±0.04b	0.81±0.01c
Isoleucine	3.64±0.04a	3.14±0.02b	2.64±0.04c
Leucine	6.70±0.05a	6.04±0.40b	5.16±0.03c
Tyrosine	4.33±0.55a	3.38±0.02b	3.06±0.03b
Pnylalanine	5.07±0.07a	4.65±0.03b	4.06±0.03c

Means that have the same alphabets in a row are not significantly different.

Table 6: The summary of amino acid composition of groundnut samples (mg/100g)

Amino acids	0 kGy	2.5 kGy	10 kGy
TAA	92.81	86.81	80.65
TEAA	46.34	41.30	36.83
TEAA/TAA (%)	49.96	47.58	45.67
TNEAA	46.47	45.51	43.82
TSAA	2.69	2.18	1.74
Cystine (%)	51.67	54.59	53.45
ArEAA	9.40	8.03	7.12
TAAA (%)	31.3	33.84	35.54
TBAA (%)	17.90	17.29	17.06
TNAA (%)	50.47	48.87	47.40
TESAA: TNEAA	1.00	0.91	0.84

TAA = Total amino acid
TEAA = total essential amino acid
TNEAA = total non-essential amino acid
TSAA = total sulphur amino acid
ArEAA = total aromatic essential amino acid
TAAA % = % total acidic amino acid
TBAA % =% total basic amino acid
TNAA % = % total neutral amino acid
TEAA: TNEAA = ratio of total essential amino acid

Table 7: The anti-nutritional factors in groundnut samples.

Dose	Oxalate mg/100g	Tannin mg/100g	Phytic acid mg/100g	Phytin-P mg/100g
0	0.13 ± 0.02a	0.05 ± 0.01a	1.68 ± 0.25a	0.46 ± 0.25a
2.5	0.07 ± 0.01b	0.04 ± 0.01ab	1.40 ± 0.00b	0.38 ± 0.01b
10	0.05 ± 0.01b	0.03 ± 0.00b	1.24 ± 0.01c	0.34 ± 0.01c

Mean ± SD

3.6 Antinutritional factors in groundnut samples.

From the results presented in Table 7, the oxalate level in groundnut and the phytate content were reduced significantly as the irradiation dose increased. The tannin content of groundnut at 10 kGy was significantly different from the control but not significantly different from that of 2.5 kGy dose level. The Phytic acid decreased significantly with increase in irradiation. These obtained results for tannin and phytic acid are in-line with Hassan *et al*. (2009) who reported the decrease in tannin and phytic acid to be dose-dependent. The reduction in the phytic acid of the irradiated groundnut may be due to structural cleavages of the phytic acid (Duodu *et al*., 1999)

The reduction in the phytate level after irradiation may be attributed to phosphorylation which occurred during irradiation. Generally, processing techniques reduce the level of antinutritional factors in oil seeds and legumes, as reported by Enujiugha *et al*. (2003) and Enujiugha and Akanbi (2005). The reduction in antinutritional factors in oil seeds and

legumes by irradiation will be an advantage by increasing the bioavailability of certain minerals and proteins as reported by Hurrell *et al*. (2003).

3.7 Fatty acid composition in the samples.

The fatty acid profiles of groundnut samples as presented in Table 8 indicate that linoleic acids (C18:2 trans-9, 12 and cis-9, 12) are the most abundant fatty acids in the non-irradiated sample and later absent in the irradiated samples. The oleic acid is only present as (C18:1 trans -9) and was 3.17 ± 0.02% of total fatty acid; this was greatly reduced by irradiation at 2.5 kGy and 10 kGy to 0.04 ± 0.01, and 0.07 ± 0.01, respectively. Also butyric acid was eliminated totally by irradiation, while formations of some fatty acids were induced during irradiation. The trans fatty acid of oleic acid was significantly reduced as the irradiation increased whereas the trans fatty acid of linoleic was completely eliminated at 2.5 kGy and 10 kGy. Trans-fatty acids have been implicated in cancer (Tsuzuki et al., 2010). The changes in the fatty acid profiles may be attributed to transformation and changes in configuration of the fatty acids which occurred during irradiation.

Table 8: Fatty acid composition of groundnut samples (% fatty acids)

Fatty Acid (%)	0 kGy	2.5 kGy	10 kGy
Butyric acid (C4:0)	3.38 ± 0.02	ND	ND
C6:0	ND	0.11 ± 0.03	ND
Lauric acid (C12:0)	0.23 ± 0.01	0.02 ± 0.01	ND
C13:0	ND	ND	0.07 ± 0.02
Myristic acid (C14:0)	ND	ND	0.07 ± 0.02
Palmitic acid (C16:0)	7.91 ± 0.02	ND	0.35 ± 0.03
Palmitoleic acid (C16:1)	ND	3.66 ± 0.03	9.57 ± 0.02
Heptadecanoic acid (C17:0)	ND	2.77 ± 0.01	ND
Stearic acid (C18:0)	ND	ND	0.09 ± 0.03
Oleic acid (C18:1, trans)	3.17 ± 0.02	0.04 ± 0.01	0.07 ± 0.01
Linoleic acid (C18:2, trans)	52.27 ± 0.12	ND	ND
Linoleic acid (C18:2, cis)	17.00 ± 0.02	ND	ND
Linolenic acid (C18:3, cis-6,9,12)	ND	29.13 ± 0.20	38.63 ± 0.03
Arachidic acid (C20:0)	0.23 ± 0.02	7.91 ± 0.05	ND
Eicosenoic acid (20:1, cis-11)	2.05 ± 0.04	16.72 ± 0.60	27.86 ± 0.05
C20:2, cis-11,14	ND	1.76 ± 0.05	4.08 ± 0.50
EPA (C20:5, cis-5,8,11,14,17)	ND	0.04 ± 0.01	ND
C21:0	ND	15.11 ± 0.43	ND
Behenic acid (C22:0)	ND	2.04 ± 0.06	0.06 ± 0.01
C22:1 (cis-13)	7.80 ± 0.05	0.66 ± 0.05	ND
Lignoceric acid (C23:0)	ND	ND	6.35 ± 0.72
C24:0	0.18 ± 0.08	ND	0.32 ± 0.07
C24:1 (cis-15)	6.02 ± 0.02	0.03 ± 0.01	ND
TUFA	88.31	68.37	80.21
TSFA	11.93	25.92	17.79

Mean ± SD ND = Not detected

However, linolenic acid, C18:3 (cis-6, 9, 12) which was not present in the non-irradiated sample, was later formed in the irradiated samples. The amount formed increased with irradiation doses as shown in Table 8. Arachidonic acid was not found in any of the samples studied. The total unsaturated fatty acids reduced significantly with increased dose of irradiation while the total saturated fatty acids increased. The increase in the level of saturation may be due to partial hydrogenation after hydrolysis of water (James, 2000). Oil extract of irradiated nuts is therefore suitable for margarine making owing to the level of hydrogenation.

4. Conclusion

This study has revealed that gamma-irradiation applied to groundnuts at two doses (2.5 and 10 kGy) did not affect the proximate chemical composition of the seeds, but reduced the biological value of the seed protein and exposed the seed oil to both oxidative and hydrolytic rancidity, with a higher level of saturation. However, gamma-irradiation eliminated or reduced the levels of oxalates, tannins, and phytic acids, and consequently improved the mineral bioavailability of groundnuts and potentially capable of preventing micronutrient deficiencies in vulnerable populations. Also, irradiation of groundnut at 2.5 and 10 kGy would reduce the risks of certain cancer by eliminating trans-fatty acids. Conclusively, irradiation up to 10 kGy dose is recommended for the de-infestation and preservation of groundnuts as it does not change the overall nutrient composition and availability.

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