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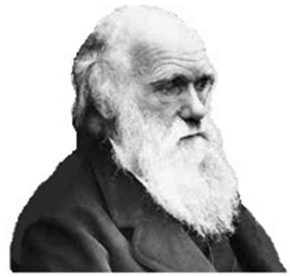

World News of Natural Sciences

An International Scientific Journal

WNOFNS 49 (2023) 156-164 EISSN 2543-5426

Distribution of selected metals and phytochemicals in seeds and peels extract of watermelon (*Citrullus lanatus* (Thunb.) Mansf.) in Bayelsa State, Nigeria

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ABSTRACT

The nutritional benefits of agricultural trash and the therapeutic properties of leftover agricultural product parts are still being thoroughly researched in Africa. This investigation looked at the distribution of specific metals and phytochemicals in Bayelsa state, Nigeria, watermelon (*Citrullus lanatus*) seed and peel samples. Watermelons (*Citrullus lanatus*) were picked for their seeds and peel samples after being brought from several gardens in Nigeria's Bayelsa state. Ether acetate was used to extract the samples. The extracts were evaluated at various concentrations, including 10 mg/ml, 5 mg/ml, 2.5 mg/ml, 1.25 mg/ml, 0.625 mg/ml, and 0.3125 mg/ml, for phytochemicals. The phytochemical screening of the ethyl acetate extracts of seed and peel samples, revealed the presence of flavonoids, terpenoids, tannins and cardiac glycosides in seed extracts while flavonoids, phenols, terpernoids, cardiac glycosides, carboxylic acids, quinine and xanthoproteins were detected in peel sample. The samples were digested with an aqua regia and analyzed for metals using atomic absorption spectrometry (AAS). The total concentrations of the metals analyzed varied from 51.05 to 58.40 mg/kg,((5.20±54.73),mean concentrations of the individual metals from result showed iron Fe (28.70-32.60 mg/kg), Mn (11.67-14.14 mg/kg), K (0.24-0.25 mg/kg), Zn (7.89 -9.11 mg/kg), Ni (0.01 -0.03 mg/kg), Cu (0.42 -0.48 mg/kg), Mg (1.29 -1.47 mg/kg), Ca (0.56 -0.57 mg/kg) and Pb (0.00-0.01 mg/kg). Iron Fe concentrations were predominant in both seed and peel samples of (*Citrullus lanatus*). The concentrations of metal in seed and peel samples followed this order Fe>Mn > Zn > Mg >Ca>Cu > K > Ni >Pb and the concentrations of Fe and Mn were relatively higher than WHO daily intake permissible limits in *Citrullus lanatus*.

***Keywords*:** Watermelon, Citrullus lanatus, metalsand flavonoids, phenols, terpernoids, cardiac glycosides, carboxylic acids, quinine and xanthoproteins

(Received 12 May 2023; Accepted 05 June 2023; Date of Publication 06 June 2023)

1. INTRODUCTION

Watermelon (*Citrullus lanatus*) is an edible part of flower plant, it is consist of about 6 % sugar and 91 % water hence the name water melon, it is of the family cucurbitaceae, originated from the vine of Southern Africa, this berries are wildly consumed by both adult and children in Nigeria. Though the peels andseeds of the *Citrullus lanatus* are disposed as waste, water melon is composed of cellulose, hemi-cellulose and pectin that support its texture and firmness, its interior can be of different colors (red, pink, yellow or water) (Sobukola *et al.*, 2010). Watermelons, on the other hand, have a high vitamin C content, are low in fat and sodium, and can be used for juice and other types of drinks, stir-fries, stews, pickles, and occasionally as vegetables. However, when berries are processed, 30–40% of the parts (peels, seeds, and pulp) are discarded, despite the fact that these parts are excellent sources of valuable bioactive compounds or nutrients (Zuchowski *et al.*, 2011)

Citrullus lanatus are rich in vitamin C and beta-carotene, which makes them antioxidant and antibacterial. They also aid in the prevention of certain malignant cells. Because antibiotic resistance is a global public health concern in terms of food borne illness and nosocomial infections, the antibacterial chemicals produced by this plant are of utmost importance (Aderson, 2001). The phytochemicals found in plants' leaves, roots, stems, seeds, and peels make up the antibiotic. These phytochemicals include phenols, tannins, saponins, alkaloids, flavonoids, steroids, carotenoids, and glycosides, all of which are necessary for both humans and animals to survive (Ajayi*et al.,* 2010).

While some metals, such as cadmium, lead, and mercury, are food contaminants at any concentration levels, while others, such as iron, zinc, copper, and so on, are necessary for biochemical processes, the berries (*Citrullus lanatus*) contain both essential and toxic metals bearing the activities in the environment and agricultural practices surrounding the cultivation of the flower plant. The present of these metals in plants are attributed to the characteristics of the soil, the ability of plants to selectively accumulate these metals, in addition, the other sources of trace metals to plants are rainfall in atmospheric polluted areas, plant protection agents and fertilizers.

The exposure of trace metals from *Citrullus lanatus* through consumption ofthis flower plant and products made from it could have severe health consequences and to the ecosystem safety and also, the essential contributions of phytochemicals in the watermelon peels and seedsto humans healh development (Anang *et al*., 2018). Given to this background, there is a need to assess the concentration levels of metals and phytochemicals in watermelon seeds and peel samples sold Bayelsa State, Nigeria.

Toascertain ifthe concentrationlevels meet the international requirement set by WHO. Serious research has been done on watermelon's nutrient contents, phytochemical analysis, and naturally occurring products (Tarbiri*et al.,* 2016). Profile of phenolic and other polar components from watermelon (*Citrillus lanatus*) hydro-methanolic extract (Abu Reidah *et al.*, 2013), and Sorokina*et al.,* 2021). The aforementioned research were primarily concerned with the phytochemicals and nutrient makeup of watermelon, however they omitted data on the metal distribution in watermelon in Bayelsa State, Nigeria.

In Bayelsa State, Nigeria, there are few or no data on the distribution of metals and phytochemicals in watermelon (*Citrillus lanatus*) peel and seed samples. As a result, this study will detail the distribution of specific metals as well as the phytochemical profile of watermelons sold in Nigeria's Bayelsa State.

2. MATERIALS AND METHODS

The sample location is Bayelsa State, Nigeria. This area experience a typical climate with distinct rainy (May to October) and dry season (November to April). The monthly atmospheric temperature ranged from 23 °C to 34 °C while the rainfall ranged from 12.16 – 554 mm respectively.

2. 1. Sample collection

The samples (watermelon) were brought from different gardens in Bayelsa state, Nigeria. The samples were identified and authenticated by a taxonomist in the Biological sciences in University of Africa, Toru-Orua., Bayelsa state, Nigeria.

2. 2. Sample preparation

The samples were thoroughly washed and the peels and seeds samples were carefully removed respectively and dried in a SMO 5E laboratory oven at 150 °C for a day to avoid contamination. The samples were grounded with blender and subjected to elemental and phytochemical analysis

2. 3. Sample extraction and phytochemical analysis

The watermelon (*Citrullus lanatus*) seed and peel samples were weighed into two different extractors (15.87 g and 50.04 g) respectively 250 ml of ethyl acetate was measured into a flask coupled with extractor in ratio (1:3). Ethyl acetate extract was filter and placed in a water bath to dry. The extract obtained were transferred into a pre weighed sample container and stored at a room temperature.

Phytochemical analysis: detection of various active phytochemical analysis was carried out on the extracts of peel and seed samples of watermelon (*Citrullus lanatus*) using a standard method as described by Sofowora (1993). Phytochemicals screened in peel and seed extract were flavonoids, terpenoids, tannins, cardiac glycosides, phenols, carboxylic acids, quinine and xanthoproteins.

Flavonoids: NaOH was added to 4 ml of the extract and few drops of concentrated H_2SO_4, Phenol: 1 ml of extract added 2 ml of distilled water and then iron (ii) chloride, Terpenoids: some ml of extract, 2 ml of chloroform and 3 ml of iron (iii) chloride, Tannins: to extract, few drops of iron (iii) chloride, Cardiac glycosides: 5 ml of the extract added glacial acetic acid and then few drops of iron (iii) chloride, Carboxylic acid: few drops of sodium bicarbonate to the extract, Quinones: a solution (KOH) was added to 1 ml of the extract and Xanthoproteins: few drops of HNO_3 was added to 1 ml of the extract and observed color change. (Sofowora 1993).

2. 4. Sample extraction and chemical analysis for metals

0.5g of the peel and seed samples of *Citrullus lanatus* will be placed in digestion tube respectively. 10 mL of aqua regia (3:1 HCl : HNO_3) (Sigma-Aldrich) will be added and swirled to wet the sample and will be allowed to stand overnight. The next day, the tube will be heated in a heating block of 50 °C for 30 min and raised to temperature of 120 °C for 2 hr. The digest will be filtered through Whatman No. 1 filter paper and will be diluted to 25 mL with 0.25 mol/L HNO_3 (Zhang *et al.*, 2010). The sample solutions will be analysed Fe, Mn, Zn, Mg, Ca, Cu, K, Ni andPb using atomic adsorption spectrometry (Perkin Elmer Analyst 200 Shelton CT, USA).

2. 5. Phytochemical screening.

The crude extracts were evalated for flavonoids, terpenoids, tannins, cardiac glycosides, phenols, carboxylic acids, quinine and xanthoproteins, using standard procedure Sofowora (1993).

3. RESULT AND DISCUSSIONS

3. 1. Concentrations of metal in watermelon (*Citrullus lanatus*) peel and seed samples

The total concentrations of metals in peel and seed samples of watermelon (*Citrullus lanatus)* in Bayelsa state, Nigeria varied significantly from 51.05 to 58.40 mg/kg with standard deviation and mean concentration of (5.20±54.73) (Table 1, 2).

Table 1. Metal concentrations in seed and peel samples in water melon (*Citrullus lanatus*) in Bayelsa state, Nigeria (mg/kg).

	Seed (S1)	Peel (P1)
Manganese	11.67	14.14
Potassium	0.25	0.24
Zinc	7.89	9.11
Magnesium	1.47	1.29
Iron	28.70	32.60
Nickel	0.01	0.03
Lead	0.00	0.01
Calcium	0.56	0.57
Total	51.05	58.40

Although the total concentrations of metal in the peel sample were marginally higher than those in the seed sample, P1>S1, this may be due to the fact that watermelon peels have a higher retention capacity, a larger surface area, and are more exposed to anthropogenic activity contamination than flower plant seeds are. The individual metal concentrations in the seed and peel samples were Mn, with concentrations ranging from 0.1 to 0.3 ppm. from 11.67 to 14.14

mg/kg with (SD± Mean) concentration of (1.75±12.91), K varied from 0.24 to 0.25 mg/kg (0.01±0.25), Zn ranged from 7.89 to 9.11 mg/kg (0.86±8.50) while Mg varied from 1.29 to 1.47 mg/kg (0.13±1.38), Fe showeda variation from 28.7 to 32.6 mg/kg (2.76±30.65) but Ni varied from 0.01 to 0.03 (0.01±0.02), though Cu concentrations ranged significantly from 0.42 to 0.48 mg/kg (0.04± 0.45), Pb varied 0.0 to 0.01 mg/kg (0.01± 0.01) and Ca concentration ranged from 0.56 to 0.57 mg/kg (0.01± 0.57) respectively, the concentrations ofiron (Fe) were more abundant in peel and seed sample of *Citrullus lanatus*.

But more dominant in peel sample with concentration 32.6 mg/kg this may be as result of thenature of geological, topographical feature of the area, different authors have reported a high Fe concentration in soils of Bayelsa State, Nigeria though it was observed that Mg and Cu were relatively more abundant in seed compared to the peel sample of water melon. In the average the concentrations of metal followed this pattern Fe > Mn > Zn > Mg > Ca > Cu > K > Ni > Pb. (Fig. 1).

However, the metal concentrations in water melon (Citrulluslanatus) peel and seed samples from Bayelsa state, Nigeria are comparable to the results of a study that was published in Lagos state, Nigeria that examined the metal levels in various fruits and vegetables (Sobukola, *et al.,* 2010). However, this study's water melon peel sample had a higher content of iron than the research on Citrulluslanatus that was conducted in Edo state, Nigeria (Okunrobo*et al.,* 2012). From (Fig. 1): Fe, Mn, Zn, Ca, Ni and Pb concentrations were more frequent in peel sample, however, the K, Mg, and Cuconcentrations were slightly higher in seed sample of water melon (*Citrullus lanatus*).

Table 2. Summary of statistics of metal concentrations in seed and peel of watermelon (*Citrullus lanatus*) Bayelsa state, Nigeria (mg/kg)

	Mean	SD	Median	MIN	MAX
Manganese	12.91	1.75	12.91	11.67	14.14
Potassium	0.25	0.01	0.25	0.24	0.25
Zinc	8.50	0.86	8.50	7.89	9.11
Magnesium	1.38	0.13	1.38	1.29	1.47
Iron	30.65	2.76	30.65	28.70	32.60
Nickel	0.02	0.01	0.02	0.01	0.03
Copper	0.45	0.04	0.45	0.42	0.48
Calcium	0.57	0.01	0.57	0.56	0.57
Total	54.73	5.20	54.73	51.05	58.40

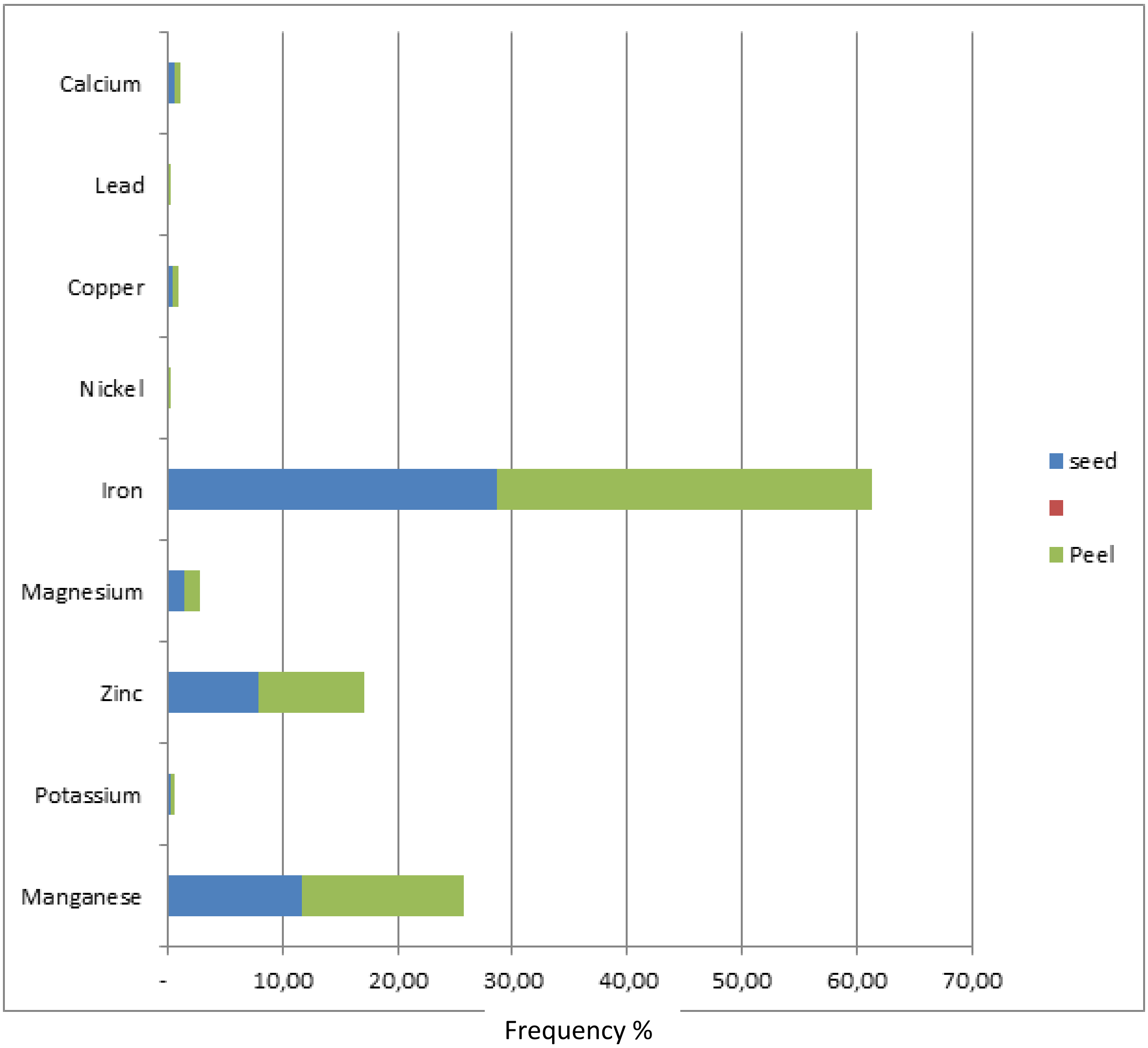

Figure 1. Metal concentrations in seed and peel samples in watermelon (*Citrutus lanatus*) in Bayelsa State

3. 2. Phytochemical constituents

Ethyl acetate extraction yield 15.87 g and 50.04 g for seed and peel samples respectively. Phytochemicals are compounds that occur naturally in plant, they are very active anti -parasitic agents in plant, in this study phytochemical screening of the ethyl acetate extracts of seed and peel samples of watermelon (*Citrillus lanatus*) showed the presence of flavonoids, terpenoids and cardiac glycosides in both samples (seeds and peels) of water melon (Table 3), though, tannins was only detected in the seed sample. However, this study's observation is comparable to that of Okunrobobo et al., (2012) and Suman et al. (2013), which showed the presence of tannins, saponins, alkaloids, terpenoids, glycosides, flavonoids, and phenols in water melon seeds. In contrast, this study found flavonoids, terpenoids, and cardiac glycosides among the selected phytochemicals found in the water melon seed sample.

Alkaloids, quinines, flavonoids, saponins, and tannins were present in the seeds of distinct types of home-grown watermelon (*Citrillus lanatus*) that Gwana et al. (2014) observed in Borno state, Nigeria.

Although, these studies only looked at the phytochemicals in water melon seeds, the current study concentrated on the seeds and peels of water melon. The peel sample in this study found the presence of flavonoids, terpenoids, cardiac glycosides, phenols, quinine, carboxylic acid, and xanthoprotein in the peels of C*itrullus lanatus.* Therefore, the observations from this study, can be used to inference that the nutritional and medicinal values present in seeds and peels of water melon cannot be overemphasized, so it should serve both as food, medicine to humans and therefore stand as an alternative to orthodox medicine if well processed, because phytochemicals are secondary metabolites and also play an important role in diseases prevention and natural antioxidant activity (Tabiri et al., 2016).

Tannins have been found to form irreversible complexes with proline- rich protein (Shimada, 2006) also Parekh and Chanda (2007) reported that tannins reacts effectively with proteins to cause tanning effect which plays an important function in the treatment of inflamed or ulcerated tissue, anticancer activity, so the presence of tannins in the seed of watermelon (*Citrullus lanatus*) support medicinal use of this seed for treatment of different ailments, also the peels of watermelon was observed to contain 80 % of phytochemicals, its use as medicine for treatment of ailments should be encouraged.

Table 3. Phytochemical constituents in seed and peel samples of watermelon (*Citrillus lanatus*)

Phytochemical component	Seeds S1	Peels P1
Flavonoids	+	+
Phenols	-	+
Terpenoids	+	+
Tannins	+	-
Cardiac glycosides	+	+
Carboxylic acid	-	+
Quinone	-	+
Xanthoprotoeins	-	+

4. CONCLUSIONS

This study revealed that the concentrations and profile of £9 metal in peel and seed samples of watermelon (*Citrullus lanatus*) varied significantly. Metal profile showed that the Fe concentration was most abundant in peel and seed samples of *Citrullus lanatus*. The metal concentrations in peel sample was more elevated, though the metal concentrations were below the recommended permissible limits. Except of iron (Fe) and Mn which are above the recommended limit by WHO. The phytochemical screening revealed the presence of flavonoids, terpenoids, tannins and cardiac glycosides in seed extracts while flavonoids, phenols, terpernoids, cardiac glycosides, carboxylic acids, quinine and xanthoproteins were detected in peel sample. Therefore the seed and peel from watermelon (*Citrullus lanatus*) should be recommended healthy for human consumption and medicinal purposes.

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