ASSESSMENT OF MINERAL ELEMENTS AND HEAVY METALS PRESENT IN THE LEAVES, STEM BARK AND PODS EXTRACT OF VACHELLIA NILOTICA

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Abstract: According to the World Health Organization (WHO) about 80% of the world population still depend directly on medicinal plants for their basic health care needs. Vachellia nilotica has a long history of 'ethno' uses due to its versatility and availability, it has been reported that different parts of the plant has been used to treat various ailments ranging from diarrhea, internal bleeding and skin diseases among others. However, there has been widespread consumption of medicinal plants in recent years, because of this it's essential to check for their efficacy and safety. So, it's against this backdrop that this current study aims at assessing the mineral elements and heavy metals present in the leaves, pods and stem bark extract of Vachellia nilotica. The plant parts were collected fresh, healthy and free from any organic substance, they were extracted using acetone as a solvent and were evaluated for mineral elements and heavy metals using an X-ray Fluorescence analyzer. The result obtained revealed that all plant parts tested were rich in both macro (Ca, Mg, Fe, S etc.) and micro elements/nutrients (Mn, Ni, Cu, Zn etc.). However, the leaves recorded to have the highest values with most exceeding the permissible limit set by WHO/FAO, while moderate in the pods extract and the least values were mostly obtained in the stem bark extract. Potential carcinogenic heavy metals like cadmium, chromium, arsenic, cobalt and vanadium were not detected. However, mercury was found to be slightly below the WHO limit in leaves (0.88ppm) but exceeding the limit with 2.43ppm in pods and 1.37ppm in stem bark. So also nickel which was found only in pods (2.47ppm) and stem bark (2.15ppm), other heavy metal like lead was detected but recorded a value below the WHO limit. In addition to that other rare earth metals like rubidium, cesium, and strontium among others were detected. This study has concluded that the stem bark, pods and leaves of the plant may not be safe for consumption due to presence of toxic heavy metals like mercury which can pose a serious health hazard to human and other rare earth metals who have no any permissible limit established by WHO.

Keywords: Vachellia nilotica, pods, stem bark, leaves, macro elements, micro elements, heavy metals, rare earth metals, permissible limit.

INTRODUCTION

One of the earliest recognized traditional forms of medical practice to mankind is the consumption of medicinal plants for therapeutic purposes. These plants are used in the treatment and management of different ailments or diseases such as infections, diarrhea, rheumatism, cough, asthma, impotency, cold and malaria among others. Sustainability of health was another important use of medicinal plants as they were utilized as nutritional supplements due to their rich elemental constituents (Leonid et al., 2017). Over the years, the uses of these medicinal plants grew in both developed and developing countries and today according to the World health organization, over 80% of the world population still depend directly on medicinal plants for their medicinal purposes (Sarkar et al., 2015).

Vachellia species, commonly known as thorn trees in Africa are very important economic plants as sources of tannins, gums, timber, fuel, fodder and traditional medicines (Bargali and Bargali, 2009). Vachellia species have been used as traditional medicinal plants since the early days of civilizations. Different parts of the Vachellia species like the roots, stem bark, pods, leaves and seeds have been used traditionally for the treatments of various ailments by many cultures (Lassak and McCarthy, 2011). They are roughly 1,350 species worldwide (Ogunwade et al., 2010). But Vachellia nilotica is the most traditionally used as it has a wide distribution in Africa and Asia, it is a plant that belongs to the family Fabaceae commonly known as "Bagaruwa" among the "Hausa" speaking people of northern Nigeria. it is also invasive and able to thrive in varying environmental conditions and many of its parts are used for treatment of ailments.(Nusrat et al., 2016).

Although medicinal plants are known for their efficiency in their curing abilities which may be attributed to the presence of organic constituents like vitamins, essential oils, secondary metabolites etc. over dose or prolonged usage of medicinal plants lead to accumulation of

Different elements which causes various health problems (Jabeen et al., 2010; Abdelhafeez et al., 2013). Because heavy metals are ubiquitous in trace concentrations in soil, medicinal plants grown in these soils face the heavy metal stress and cause changes in the production of secondary metabolites (Karayil et al., 2014). The essential metals the plants bioaccumulate from the soil can produce toxic effects when taken in high concentrations while the non-essential metals are toxic even in low concentrations for human health (Karayil et al., 2014). Therefore it is essential to maintain safety, quality of the plants to avoid serious health problems. Hence, this present study has made an attempt to determine the elemental composition of the stem bark, pods and leaves of Vachellia nilotica.

MATERIALS AND METHOD

Study Area

The study was conducted in Katsina State, a large city situated in the Northern part of Nigeria. Katsina state which covers an area of 24,192 km² is located between latitude 11º08'N and 13º22'N and longitude 6º5'E and 9º2'E. The state is located some 260 kilometers east of the city of Sokoto and 135 kilometers northwest of Kano and about 7 miles south of the border between Nigeria and Niger.

The city is the centre of an Agricultural region producing groundnuts; cotton, hides, millet and guinea corn and also has mills for producing peanut oil and steel. However, people in the study area engage in additional activities such as pottery, herbal medicine practitioning and local crafts etc. The city's estimated population in 2016 was 7,831,300 and the population of the city is mainly from Fulani and Hausa ethnic groups.

Collection and Identification of Plant Material

The leaves, pods and bark of Vachellia nilotica were collected from the Katsina Local Government Area of Katsina State, Nigeria.. A ladder was used to climb on the above-named

tree plant in which few branches containing both leaves and pods of the plant were cut off using a sharp knife and a pair of scissors, where as a scraper was used to scrape off the stem bark of the Vachellia nilotica plant. All the plant parts mentioned above were collected fresh, healthy and free from organic contaminants that may interfere with the substances of interest by washing them with clean water. The plant materials collected were identified in the herbarium, with voucher number UMYUH 1991 in the Department of Biological sciences, Umaru Musa Yar'adua University, Katsina.

Preparation for Plant Material Extraction

The pods, leaves and bark of Vachellia nilotica obtained were washed thoroughly with tap water followed with sterilized distilled water, the leaves were air dried at room temperature for a week, the pods for three weeks and the stem bark for four weeks. After all plant materials were completely dried out, they were ground into fine powder using mortar and pestle. The crude extracts were then weighed, labelled and saved in a dark well tighten container and kept until used. (Mukhtar and Tukur, 1999).

Plant Extraction

The powdered material of Vachellia nilotica leaves, pods and bark, 50g for each were extracted exhaustively using continuous extraction with (200ml) of acetone in a Soxhlet extractor (Harborne 1973) (Idris et al., 2009). The extracts were further placed in a rotary evaporator at 40ºC to remove the solvents and obtain the extracts in a dried form.

X-Ray Fluorescence Analysis (XRF)

A thermo fisher with model number ARL QUANT'X EDXRF Analyzer was used to determine the elemental composition of the Vachellia nilotica leaves, stem bark and pods extract. About 2g of Acetone extract of leaves, pods and stem bark were analyzed using the x-ray fluorescence (XRF) machine. The machine was run according to the manufacturer's instruction.

RESULT

X-Ray Fluorescence Analysis

Table 3.1 shows the x-ray fluorescence analysis done on the acetone extracts of Vachellia nilotica. The XRF determined the elemental composition present in the acetone extracts of stem bark, pods and leaves of Vachellia nilotica. One of the most abundant mineral elements found were: Iron, calcium, zinc, aluminium, magnesium, potassium, sodium, chlorine and manganese among others.

The percentage concentration of Iron found in leaves was 0.0905% which was the highest among pods and stem bark, superseded by stem bark with 0.002042% and pods with 0.00173%. The zinc content of the acetone leaves extract was 0.02672%, 0.002486% in stem bark and 0.00547% in pods. The highest zinc concentration was also obtained in the leaf extract of V. nilotica. Aluminium was another element obtained from the XRF analysis, which was only present in the leaves with 0.05378% and the pods with 0.00852% while none was found in the stem bark.

Magnesium content differed among the plant parts, highest magnesium concentration showed in leaves (0.2850%) followed by pods (0.0639%) and the least concentration was obtained in the stem bark (0.0288%). Other minerals like Sulphur, phosphorus, calcium, potassium and manganese all had the highest concentration in the leaves while for most of these minerals the least concentration was obtained in the stem bark of Vachellia nilotica. Other heavy metals like lead, nickel, molybdenum and selenium were also obtained.

Table 3.1 X-ray Fluorescence (XRF) Test of Acetone Extracts of Vachellia nilotica Concentration.

Elements	Acetone leaves(%)	Acetone pods(%)	Acetone bark(%)
Fe	0.09054	0.00173	0.002042
Cu	0.000529	0.001213	0.000485
Hg	0.000088	0.000243	0.000137
Ni	----------	0.0002476	0.000215
Eu	0.000024	----------	--------
Zn	0.02672	0.000547	0.002486
Al	0.05378	0.00852	--------
Mg	0.2850	0.0639	0.0288
Na	0.0910	0.0033	0.00898
S	0.17199	0.03806	0.02910
P	0.26686	0.01170	0.01785
Ca	3.7122	----------	0.03123
K	1.0236	0.4030	0.04799
Mn	0.02450	0.000186	0.00038
Ba	---------	0.005	---------
Pb	0.000385	----------	0.000013
Rb	0.002254	0.000784	0.000210
Sr	0.04165	0.000168	0.000379
Th	0.000009	0.000002	0.000001
Br	0.00268	0.00500	0.00082
Mo	-----------	0.000009	0.00016
Cs	0.000003	----------	0.000014
Cl	2.963	1.462	0.761

DISCUSSION

4.1 X-Ray Fluorescence Analysis

The results of XRF analysis showed the presence of several mineral elements like Mg, K, Mn, Fe, Ni, Cu, Zn, Cd, Pb etc. all analyzed in the acetone extracts of the stem bark, leaves and pods of the Vachellia nilotica. It can be observed a variation in the concentration of the quantified elements both essential and non-essential or heavy minerals, that is to say each mineral element differs in concentration in each plant part.

Mineral elements not only serve as nutritional sources for both plants and animals but also play other important roles in the environment. Inorganic chemical elements have been shown to be essential in nutrition and are important structural components in cellular processes (Mohammed et al., 2014). On the other hand, there has been increased use of herbal drugs in recent years. Heavy metals are ubiquitous in trace concentrations in nature. Plants grown on heavy metal rich soils and waters undergo stress and show changes in production of secondary metabolites. High levels of heavy metal contamination in medicinal or other plants may suppress secondary metabolite production. WHO (1998) recommended that medicinal plants which form the raw material for the finished product must be checked for the presence of heavy metal and pesticide residues etc. The traditional medicines cater about 85% of the world population for their health needs. It is essential to maintain safety, quality and efficacy of the plant and their products to avoid serious health problems (Sudha et al., 2014).

The percentage concentration of the mineral elements was converted to part per million (ppm) which is equivalent to milligram per kilogram (mg/kg) i.e. (1ppm= 1mg/kg).

IRON: The Iron (Fe) content in the acetone extracts was found different in all different plant parts. The highest was found in the leaves (905.4ppm) followed by the stem bark (20.43ppm) and the least was in the pods (17.3ppm). The stem bark and the pods were found to be within the safe limits (0.50-50ppm) (Mohammed et al., 2014) while the leaves exceeded the acceptable levels. According to WHO/FAO the permissible limit for Iron (Fe) in herbal medicine/ plants is 48mg/kg (WHO/FAO, 2009). Where both the stem bark and the pods were below the permissible limit and the leaves exceeded the permissible limit. This finding is in line with the study of Verma et al. (2014) who reported that the Iron content in Acacia catechu was highest in the leaves (62.94ppm), followed by the bark (60.52ppm) and the least in the pods (10.71ppm) and moderate in the stem and root. In another research by Mohammed et al. (2014) who worked on the elemental analysis of aqueous and fractionated

Pod extracts of Vachellia nilotica concluded that the Iron content of the pods were within the acceptable range limit (0.54ppm). Iron is a component of the respiratory pigments (hemoglobin and myoglobin) and enzymes e.g. cytochromes, catalases, peroxidases, aldehyde oxidase, and succinic dehydrogenase etc. concerned in tissue oxidation.

Iron is essential for oxygen and electron transport within the body (Fraga and Otaza, 2002) The ingestion of large quantities of iron salts may lead to severe necrotizing gastritis with vomiting, hemorrhage and diarrhea followed by circulatory shock, also diseases of aging such as Alzheimer's disease, other neurodegenerative disease, arteriosclerosis, diabetes may all be contributed to excess Iron and Copper (Brewer, 2010). Individuals demonstrate signs of gastro intestinal toxicity after ingestion of more than 20mg/kg iron while moderate intoxication occurs when ingestion of elemental iron exceeds 40mg/kg and ingestion exceeding 60mg/kg can cause severe toxicity and may be lethal also (Spanierman, 2011). In plants, Iron plays many biological roles in the processes as diverse as photosynthesis, chloroplast development and chlorophyll biosynthesis. Iron is a major constituent of the cell systems (Shinde et al., 2015).

COPPER AND ZINC: Copper and Zinc act as essential micronutrients up to certain concentration, Copper plays an important role in the oxidative defense system. Copper is a constituent of the blood pigment hemocyanin which is replaced by the iron complexed haemoglobin. Though copper is an essential element necessary for proper functioning of organs and systems in the body in minute quantities, high levels of copper leads to toxic conditions like nausea, diarrhea, liver and kidney damage (Fry et al., 2012). Copper compounds are used as bacteriostatic substances, fungicides and wood preservatives (Fry et al., 2012). A human being can have a dietary deficiency but very rarely because of other plants consumed that are rich in copper like legumes, copper deficiency symptoms can

Produce anemia bone abnormalities, impaired growth abnormalities in glucose and cholesterol metabolism (Bola et al., 2017).

Chronic toxicity does not normally occur in humans because of transport systems that regulate absorption and excretion. Copper helps the body to use iron, It is also important for nerve function, bone growth, enhanced body use of sugar and protection of cell membranes from destruction by free radicals. A wide range of cardiovascular and blood disorders may be contributed to copper deficiency (Liang and Zhou et al., 2007).

In plants, copper plays a role in carbon dioxide absorption and its increase leads to plant growth retardation and leaf chlorosis (Lewis et al., 2001; Shinde et al., 2015). The copper concentration varied in the plant parts, the least was in the stem bark (4.85ppm), then the leaves (5.29ppm) and the highest was in the pods (12.13ppm). WHO permissible limits in Cu for medicinal plants is 10 mg/kg, while its intake in food is 2-3 mg/day (WHO, 2005). While the WHO/FAO guideline for safe limits of copper in plants is 40mg/kg (WHO/FOA, 2007) Also, the permissible limit set by FAO/WHO in edible plants is 3 mg/kg. This finding contradicts the findings of Shinde et al., 2015 who worked on the polluted and non-polluted stem bark of Vachellia nilotica and found the copper concentration of the non-polluted stem bark to be 43.57ppm which is higher than the value of stem bark in this study likewise in the study reported by Mohammed et al., 2014 who reported the copper value in pods of same plant to be 0.04ppm.

Zinc is an essential element, and cellular zinc promotes homeostatic control to avoid accumulation of surplus zinc. It is also a powerful guardian against viral infections and protects the β- cells from destruction (Abdirahman et al., 2015). Exposure to excessive zinc results in copper deficiency and cell apoptosis. In addition, zinc deficiency has been linked to a suppressed immune response (Plum et al., 2010). Zinc and copper are considered important

For metabolizing glucose and lowering cholesterol (Krupanidihi et al., 2008). The highest concentration was in leaves (267.2ppm), then the stem bark (24.86ppm) and the least in the pods (5.47ppm). The pods and stem bark fall within the WHO/FAO set for permissible limits of Zinc in medicinal plants 50mg/kg except for the leaves whose value was above the limit. In the study of Verma et al., 2014, they reported the zinc value of A. catechu to be the highest in the roots, followed by the bark, stem, leaves and the least was in the pods similar to this present study. Zinc also plays a role in sexual development, puberty, pregnancy and menopause. Higher zinc intake protects people from cadmium poisoning while the symptoms of zinc overdose (10- 15 times higher than recommended daily allowance (RDI) may cause vomiting, dizziness, fever and diarrhea (Verma, 2014).

MAGNESIUM: Magnesium is required in the plasma and extracellular fluid, where it helps in maintaining osmotic equilibrium. It is required in many enzyme catalyzed reactions, especially those in which nucleotides participate where the reactive species is the magnesium salt, e.g. MgATP2-. Lack of Magnesium is associated with abnormal irritability of muscle and convulsions and excess Mg with depression of the central nervous system. The permissible limit of Magnesium set by WHO in plants was 2000 mg/kg, while its daily intake is set to be 350 mg/day for men and 300 mg/kg for women (FA0/WHO, 1984). The leaves recorded the highest with 2850ppm, then pods with 639ppm and the least was the bark with 288ppm. Leonid et al2017 also reported a high magnesium value in Moringa oleifera leaves and roots and Hibiscus sabdariffa ranging from 3232.76 – 4450.26mg/kg.

POTASSIUM: Potassium is important for its diuretic nature and helps in the proper function of the brain as well as nerves, thereby preventing stroke. It plays part in acid-base and water regulation in the blood and tissues. It has been reported that a high potassium diet lowers blood pressure in individuals with raised blood pressure (MacGregor et al., 2008). In addition to its contribution to the electrolytes and function of the nerves in the human body, Potassium

has been linked to bone health and osteoporosis prevention according to studies of intake of 2500 mg/day done in the United Kingdom (Susan et al., 2008). The highest value was observed in the leaves (10236ppm), then pods (4030ppm) and the least in the stem bark (479.9ppm). Similar values were reported in the study of Leonid et al. (2017) who observed the potassium value of his herbal plants to range between 12095.5 – 17234.11 mg/kg which is above the value obtained in this study.

SODIUM: The sodium content in V. nilotica was highest in the leaves 910 parts per million (ppm), moderate in the stem bark (89.8ppm) and the least was in the pods with a value of 33ppm. The regulation of Potassium is intimately involved with that of Sodium in the human body and the two are largely interdependent. Sodium and Potassium take part in ionic balance of the human body and maintain tissue excitability, carry normal muscle contraction, help in formation of gastric juice in the stomach (Brody, 1998). A K/Na ratio in diet is an important factor in prevention of hypertension and atherosclerosis since K (Potassium) depresses and Na (Sodium) enhances blood pressure (Yoshimura et al., 1991; Shivani et al., 2013). This present study contradicts a study done in Kenya by Abdirahman et al. (2015) who analyzed the mineral composition of the aqueous stem bark of V. nilotica and recorded a value (2448.2 ug/g) less than the one obtained in this study.

While another study conducted in Maiduguri on the aqueous pod extract of the same plant by Mohammed et al. (2015) recorded a lesser value (0.23ppm) compared to the value obtained in this present study. It also disagrees with the study done in Abuja carried out by Sunday et al. (2010) who reported the absence of sodium in the pods of the same plant. Hassan and Omaima, 2010 worked on the fresh and old leaves of V. nilotica in Saudi Arabia and recorded values of 0.70% and 0.85% respectively which also contradicts this present study. The difference in the values of the sodium content can be due to the difference in environmental conditions found in the different regions. Furthermore, the regulatory/

Permissible limits of the WHO/FAO have not been established yet for the sodium in medicinal plants. However, the recommended daily allowance of sodium is 0.12-0.37g/d for infants,1.5-1.7g/d for children and 1.2-1.5g/d for adults (Crook, 2006) and there is no data established for the permissible limit of sodium in medicinal plants by WHO.

CALCIUM: The calcium content in the leaves was 37122ppm and the bark was 312.3ppm while none was detected in the pods. Calcium is an essential nutrient that plays a vital role in neuromuscular function, absorption of dietary vitamin B, many enzyme-mediated processes like activation of pancreatic lipase, blood clotting, metabolic processes as well as providing rigidity to the skeleton. Calcium fluxes are also important mediators of hormonal effects on target organs through several intracellular signaling pathways (WHO/FAO, 2004). The recommended daily allowance for taking calcium is 800mg for adults and for children 500- 1000mg while the permissible limit for calcium in medicinal herbs is 614ppm (Moabe et al., 2012; Omokehide et al., 2013).

In another research, the permissible limit for calcium is ranged between 360-800ppm, therefore the bark falls below the permissible limit while the leaves exceeded the permissible limits. The absence of calcium in the pods of this present study coincides with the study of Sunday et al. (2010) who also reported the absence of calcium in the aqueous pod extract of the same plant in Abuja but disagrees with the study done in Maiduguri by Mohammed et al. (2014) who detected the presence of calcium in his aqueous pod extract of the same plant which was 0.40ppm. Meanwhile for the stem bark, the study of Abdirahman et al. (2015) in Kenya reported the presence of calcium but a lesser value (675.5ug/g) obtained from the one obtained in this present study. Hassan and Omaima, (2011) also reported a lesser percentage value of fresh and old leaves of Vachellia nilotica in Saudi Arabia to be 1.50 and 2.00% respectively which disagrees with this study.

PHOSPHORUS: Phosphorus is one of the primary macronutrients based on plant requirements. Phosphorus has many important functions in plants and medicinal plants, the primary one being the storage and transfer of energy through the plant. Adenosine diphosphate (ADP) and adenosine triphosphate (ATP) are high-energy phosphate compounds that control most processes in plants including photosynthesis, respiration, protein and nucleic acid synthesis, and nutrient transport through the plant's cells (Sharpley et al., 1996; Naser and Muhammad, 2012). It also plays a great role in medicinal plants, part of which includes plant height like increase in number of leaves and leaf length and observed reduction in shoot growth due to deficiency of phosphorus (Boroomond et al., 2011b). Secondly, it plays a role in the oil content of medicinal plants. A study reported by Boroomond et al. (2011a) recorded a significant higher gel content of Aloe vera due to phosphorus application. Phosphorus is also tied to calcium in bone structure and plays a significant role in CNS (Central nervous system) function. Many enzymes contain a base phosphoprotein and Phospholipids are involved in nerve conduction. Phosphate is the primary ion in extra and intracellular fluid; It aids absorption of dietary constituents, helps to maintain the blood at a slightly alkaline level, regulates enzyme activity and is involved in the transmission of nerve impulses (Karade et al., 2004; Gupta et al., 2014).

Phosphorus content were 2668.6ppm, 178.5ppm and 117ppm for Vachellia nilotica leaves, stem bark and pods respectively. The highest content was obtained in the leaves and the least in the pods. However, WHO permissible limit for phosphorus in medicinal plants has not yet been established. The studies of Hassan and Omaima, (2011), Mohammed et al. (2015) and Godghate et al. (2014) contradicts the findings of this present study with respect to their findings on the leaves, pods and stem bark of the same plant whose values were much less than the ones obtained in the present study except for the stem bark which was higher.

MANGANESE: Manganese is known as an essential trace element which acts as cofactor for many enzymes. It is less toxic than any other metal, however, can cause neurological disorders if its concentration exceeds 5mg/m3 due to continuous exposure to manganese dust and fumes (Alpana et al., 2013) in plants excessive manganese causes reduction in photosynthetic rate in leaves and is also associated with chlorosis (Kitao et al., 1997; Shinde et al., 2015). However, the deficiency of manganese in humans may lead to immunodeficiency disorder, rheumatic arthritis in adults, disorder of bony cartilaginous growth in infants, as well as myocardial infarction and other cardiovascular diseases (Dey et al., 2009). On the other hand, manganese plays an important role in oxidation reduction processes in plants, such as the electron transport in photosynthesis.

Manganese is an important antioxidant structure that protects plant cells by deactivating free radicals which can destroy plant tissue (Sayed et al., 2011). Manganese can be correlated with therapeutic properties against diabetic and cardiovascular diseases (Prasad, 2008). In addition, it is reported to have a role in neurodegenerative diseases (Aaron et al., 2011).

The concentration of manganese in the leaves of Vachellia nilotica was 245ppm while the pods and stem bark had 1.86 and 3.8ppm respectively. The permissible level set by FAO/WHO in medicinal plants is 200 mg/kg, and a daily intake is 11 mg/day (WHO, 1998). On another report by Mohammed et al., 2014 who reported the standard concentration for manganese is between 10-20 ppm. Nevertheless, in this present study, except for Manganese level in the leaves, all other parts were below the permissible limit. However, this study disagrees with the study of Alpana et al. (2013) India, who reported the concentration of manganese in the leaves and stem bark of the same plant to be 3.16 and 5.22ppm respectively. It also contradicts the study carried out in Maiduguri by Mohammed et al. (2014) reported the concentration of manganese in the pods to be 0.50ppm and another study

reported by Sunday et al. (2010) in Abuja, who recorded the absence of manganese in the pods of Vachellia nilotica.

ALUMINIUM: Aluminium is not an essential nutrient, it is used by some plants, but it is toxic to many plants. High levels of aluminium has so many effects on plants, some of which include a decrease in number of roots produced, which prevents the plant from being able to uptake phosphorus, calcium, magnesium and Sulphur. Sulphur on the other hand is a macronutrient; it is a component of some plant amino acids and is required for good protein content. Sulphur is required for the production of chlorophyll and a number of enzymes and it also helps legume form associations with nitrogen fixing bacteria (Wade, 2019). The highest concentration of aluminium and Sulphur was found in the leaves with values 537.8ppm and 1719.9 ppm respectively. The pods aluminium content was 85.2 ppm and for Sulphur was 380.6ppm. For the stem bark, aluminium was absent while it recorded a value of 291ppm for Sulphur.

A study reported by Sarma et al. who worked on the accumulation of heavy metals in some medicinal plants analyzed the aluminium contents in some medicinal plants which is similar to this present study, some of the medicinal plants analyzed among others were Azadirachta indica (leave) was 960ug/g, Garcinia pedunculata (bark) had non-detected, Andrographis paniculate (fruits) 2470ug/g.

In another study by Zengin et al., 2008 also reported that occasionally, very high levels of aluminium was reported in some plants reaching an aluminium level up to 1772 mg/kg in Sage and 1446 mg/kg in coriander. However, there is no data on the establishment of the permissible limits for Aluminium and Sulphur by European Pharmacopeia (2009) and/or the WHO/FDA (Sarma et al., 2011).

NICKEL: Nickel is a plant micronutrient. It contributes to nitrogen fixation and the metabolism of urea (a nitrogen containing compound) and is important for seed germination. Nickel is also important for bacteria and fungi, which are both important for good plant growth. Deficiency of nickel can cause leaf chlorosis and its toxicity in plants can impede the uptake of other essential nutrients especially iron. It also inhibits seed germination, shoot and root growth (Wade, 2019).

The observed concentration level of nickel in the analyzed plant pods was 2.476ppm which was the highest value obtained among the plant parts, it was succeeded by the bark with a value of 2.15ppm while non-was detected in the leaves of the plant. The permissible limit for nickel established by WHO, 1984 for edible plants was 1.63mg/kg and WHO, 2005 for medicinal plants was 1.53mg/kg. Nickel concentrations in the bark and pods of Vachellia nilotica in the present study were above the permissible limit set for both medicinal and edible plants. Therefore, the results show that except for the leaves, both the bark and the pods contain unsafe levels of nickel and this might cause toxic effects to human health.

The Nickel toxicity in humans is not a very common occurrence because its absorption in the body is very low (Pendias, 1992; Leonid et al., 2017). The most common ailment arising from Nickel is an allergic dermatitis known as nickel itch, which usually occurs when the skin is moisture state (Moabe et al., 2012) Nickel has been also identified as carcinogen and adversely affects lungs and nasal cavities (Moabe et al., 2012).

Nickel is required in minute quantities for the body as mostly in the pancrease and hence plays an important role in the production of insulin. Its deficiency results in liver disorder (Leonid et al., 2017). The daily intake of Nickel is recommended to be less than 1 mg/day, beyond this it's toxic (Leonid et al., 2017). The result in this work is below that obtained by Odoh and Ajiboye, (2019) in some herbal medicinal products consumed in Taraba state used

in the management of some ailments. Two other studies reported by Hassan and Omaima, (2011) in Saudi and Sunday et al. (2010) in Abuja who analyzed same plant parts obtained lower values than the values obtained in this present study.

MOLYBDENUM: Molybdenum is a plant micronutrient which is only required in very small amounts, but it is important for nitrogen metabolism; without molybdenum, plants may be able to take up nitrogen but if in form of nitrate they can't process it and make amino acids and proteins. Molybdenum also plays an essential role in the use of phosphorus within plants, without it; plants will struggle to convert inorganic phosphorus to organic. Deficiency of this element causes stunted plant growth, nitrogen deficiency, leaves exhibit spots of chlorosis, reduced grain and fruit production etc. Molybdenum toxicity is rare, and it is of greater concern to ruminants than it is to plants. However, high levels of this element can reduce the absorption of other nutrients (Wade, 2019).

Molybdenum content in the pods and stem bark of Vachellia nilotica were 0.09 and 1.6ppm respectively while it was not detected in the leaves. There is no limit for molybdenum concentration in medicinal plants by World Health Organization, but a study done in Brazil reported by Nayara et al. (2017) stated that the Representative diets of various countries showed an average concentration of molybdenum in diet should be 0.23 mg/kg; this corresponds to a daily intake of 100 μg of molybdenum per day for adults.

CHLORINE: Chlorine is classed as a plant micronutrient meaning its essential for the proper growth of plants. It is important for plant photosynthesis as it is involved in the opening and closing of stomata. It also helps ensure leaves are firm. The deficiency of chlorine in plants results in blotchy leaf chlorosis and necrosis and severe cases of its deficiency may result in bronzing and/or wilting of leaves, while its toxicity in plants may result in necrosis along leaf margins and smaller than usual leaves and plants (Wade, 2019).

Chlorine was found in all the plant parts, the highest concentration was obtained in the leaves with a value of 2.963ppm, a moderate value was obtained in the pods (1.462ppm) and the least concentration was obtained in the stem bark (0.761ppm). As far as chlorine is concerned, there is no data available on establishment of the regulatory or permissible limit for chlorine in medicinal plants by WHO/FAO, FDA and European Pharmacopeia (Sarma et al., 2011).

LEAD: The lead concentration was only detected in the leaves (3.85ppm) and the stem bark (0.13ppm). According to the World Health Organization (WHO, 2007) the permissible limit for lead in medicinal plants is 10ppm or 10mg/kg. Fortunately, the lead concentration in the observed plant parts is not a matter of concern from the toxicity point of view as far as permissible limit in medicinal plant is concerned. Lead is non-essential and a potential toxic trace element having functions neither in human's body nor in plants. Lead is associated with impairment of childhood cognitive function (Canfield, 2003; Odoh and Raphael, 2019). A high lead level during pregnancy is directly related to several outcomes such as spontaneous abortion, low birth weight and impaired neurodevelopment (Rabinowitz et al., 1987; Odoh and Raphael, 2019). Lead poisoning occurs when the concentration reaches between 100.00 -

140.00 μg/L (Goldfrank, 1998; Odoh and Raphael, 2019). According to the International Agency for Research on Cancer (IARC), inorganic lead is carcinogenic to humans.

MERCURY: Mercury is the most toxic heavy metal in the environment. It is added into the environment by man from farming industry (fungicides, seed stabilizers), by drugs industry, paper industry and batteries (Zhang and Wong, 2007). Exposure to it can damage central nervous system and other health hazards are brought to it by humans (Khushnoodur rehman et al., 2019) Terrestrial plants are generally insensitive to the harmful effects of mercury compounds; however, mercury is known to affect photosynthesis and oxidative metabolism by interfering with electron transport in chloroplasts and mitochondria. Mercury also inhibits the activity of aquaporins and reduces plant water uptake. (Bieby et al., 2011)

Mercury and its compounds are cumulative toxins and in small quantities are hazardous to human health. The major effects of mercury poisoning manifest as neurological and renal disturbances and has effects on the brain (Resaee et al., 2005; Bieby et al., 2011).

The mercury concentration in Vachellia nilotica plant parts was highest in the pods (2.43ppm), moderate in the stem bark (1.37ppm) and the least was obtained in the leaves (0.88ppm). The regulatory /permissible limits values for mercury established by the WHO/FDA, European pharmacopeia and FAO/ WHO PTWI are 1ppm, 0.1ppm and 5ug/kg / body weight (Sarma et al., 2011). However, In Canada 0.2ppm has been prescribed as the limit for mercury in raw herbal material. In China and Singapore however, 0.5ppm limit has been proposed by (WHO 2007) (Alpana et al., 2013). All the plant parts analyzed were beyond the permissible limit except for the limit set unfortunately. The study of Alpana et al. (2013) who analyzed the stem bark and the leaves of the same plant reported that mercury was not detected in the plant parts which contradicts this present study.

EUROPIUM: Europium was another heavy metal detected but only in the leaves with a value of 0.24 ppm while it wasn't detected in the pods and the stem bark.

BARIUM: Barium was only found in the pods with a value of 50ppm. Barium is an alkaline earth metal which occurs as a trace metal in igneous and sedimentary rocks. It is a non-essential element to terrestrial organisms and known to be toxic at elevated concentrations (Dane et al., 2013). In nature it occurs mainly as low soluble minerals such as barite ($BaSO_4$) and Witherite ($BaCO_3$). Even though, there is no data available for the permissible limit for barium in medicinal plants, Paris and Jones,1998; Cleide et al., 2012 reported in their study that most of the plants analyzed had a concentration of Barium between 4 to 50mg/kg and concentrations of 200- 500mg/kg which was slightly toxic or toxic respectively. Another study of Remegius, 2012 reported levels of Barium concentration of 25, 55 and 72.6mg/kg which is in line with the values obtained in this study.

RUBIDIUM: Rubidium was found highest in leaves (22.54ppm), followed by pods (7.84ppm) and the least was in the stem bark (2.1ppm). Rubidium belongs to the ultra-trace element essential for plants and animals. Based on some literature and studies undergone, it was reported that rubidium content in soil is inversely correlated with the pH of the soil i.e. the highest amount of this element is found in sour soil. So also, the intake of it by plants increases with decrease in soil pH and its absorption by plants is inhibited by high amounts of high potassium, and the level of this element decreases with age in plants (Kosla et al., 2002). A study conducted in Brazil by Paulo et al. (2016), analyzed the concentration of some medicinal plants which fell within the range of the values obtained in this study for Rubidium.

STRONTIUM: The highest concentration of strontium was obtained in the leaves (416.5ppm), moderate in the stem bark (3.79ppm) and pods had the least concentration (1.68ppm). Naturally occurring strontium is abundant in the Earth's crust ranking 15th at 340ppm, very close to barium. Strontium is a minor component of other mineral deposits and may occur in near sedimentary rocks etc. (Anna and Irene, 2018).

THORIUM: The concentrations of Thorium in all plant parts were negligible, the leaves had 0.09ppm, the pods 0.02ppm and the least was in the stem bark with a value of 0.01ppm. Thorium is surprisingly abundant in the earth's crust, it is found in small amounts in most rocks and soils. It also occurs in several minerals, the most common being the rare earth thorium phosphate mineral, monazite, which contains up to 12% of thorium oxide. There is little information about the uptake and accumulation or storage of thorium by different plant species but the factors affecting plant uptake depends on the soil type, climate relief, vegetation season and parent rocks etc. (Irina, 2008).

BROMINE: Bromine on the other hand had its highest value in pods (50ppm), followed by leaves (26.8ppm) and the least was obtained in stem bark (8.6ppm). Bromine is not an essential element for animals or plants and since it compensates for chlorine in case of chlorine deficiency in plants and not as toxic as iodine in plants, no damage due to excessive absorption of bromine has been reported except for the damage due to agricultural chemicals containing bromine such as methyl bromides. However, since excessive intake by humans is harmful to health, a maximum permissible limit of bromine in food for inorganic bromide residues has been established by WHO/FAO and the content of bromine in crops has been evaluated in connection with this limit (Kouchi and Yumiko, 1982).

CESIUM: Cesium concentration in the parts of the plant was not significant, as the leaves had a value of 0.03ppm and the stem bark had 0.14ppm while non-was detected in the pods of Vachellia nilotica. Cesium is a trace element in the soil. It is toxic to plants when absorbed at high concentrations, although this rarely occurs under normal environment conditions (Paulo et al., 2016). Cesium is predominantly present in solution as the free hydrated cation Cs+ with little or no tendency to form soluble complexes. Cesium is taken up by plant roots and translocated to the above ground parts but the mechanism behind the transportation is not completely understood (Zhu and Smolders, 2000). This present study is in line with the study of Paulo et al. (2016) who analyzed Cesium in some medicinal plants in Brazil. The medicinal plants among others included A. millefolium, A. sativum, A. lappa and A. montana etc.

The result of the analysis showed that the Vachellia nilotica parts (stem bark, leaves and pods) are rich in mineral elements especially magnesium, Sulphur, phosphorus, calcium,

Chlorine and Potassium, this becomes so important when the usefulness of this elements to the human body is considered. These elements are very important in human nutrition. They are required for repair of worn out cells, strong bone and teeth, building of red blood cells, maintaining osmotic balance and for body mechanisms (WHO, 2008) likewise the trace elements or micronutrients like manganese, molybdenum, nickel, copper, zinc etc. which have been stated to play a great role in treatment of diseases (Singh et al., 2010). It was also observed that the leaves had the highest concentration in almost all the mineral elements except for few like copper, nickel etc.

In Iron, the highest concentration was obtained in the leaves this may be due to the Iron's association with photosynthesis as it is involved in chloroplast development (Luttge et al., 2010) and because of this leaves display higher Iron content than any other plant part. In leaves, 50-100mg/kg of Iron may be critical but on the other hand leaves may reach up to 2000mg/kg of Iron due to its low toxicity, and the high levels are not of concern to human health (Remegius, 2012).

Magnesium was also highest in leaves, this element/mineral is a constituent of chlorophyll and is involved in the activation of many ATP dependent enzymes and carbohydrate portioning, so is no surprise if the leaves bear the highest concentration.

Calcium was the highest concentration among other minerals/ macronutrients and like others this was also obtained in the leaves. This mineral function as a second messenger in signal transduction and is immobile in the phloem, therefore it accumulates in older plant parts, while in fruits it's generally lower than the leaves (Remigius, 2012). This might explain why it was found absent in the pods. Calcium ranges from 0.1 to 2.5% in plant dry matter but can reach more than 10% in old leaves without showing serious symptoms of growth inhibition (Remigius, 2012) and this might explain why leaves had the highest concentration among other plant parts in this study. Other medicinal plants like poppy (Papaver somniferum) are also known to have a high calcium content (Chizzola and Dodos, 2007).

According to Luttge, (2010) and Remigius, (2012), Potassium is another mineral found in high concentrations in plant tissues, this is applicable to this study as potassium is the third mineral with highest concentration after calcium and chlorine. This might be because potassium is easily mobile in the phloem and may be distributed within the plant, and this is due to one of its many roles like phloem transportation, osmoregulation, photosynthesis and protein synthesis.

In leaves, manganese ranges from 20-300mg/kg (Pendias, 2011) this broad range is also valid in medicinal plants. Manganese is important for redox processes, and the oxygen evolution in photosynthesis is manganese dependent (Luttge et al., 2010). As observed in this study, other literatures have also reported that some species of plants have manganese rich leaves.

For copper, the normal or sufficient range for normal growth in plants is 5- 20mg/kg, which all the plant parts in this study fell within the range. Ordinarily, the amount of concentration for zinc and nickel in leaves is 25-150mg/kg and 0.1-5mg/kg respectively. Zinc toxicity symptoms may develop when it exceeds 400mg/mg while the concentration in this study for leaves was below this concentration.

Nickel on the other hand was absent in the leaves but according to Marschner, 1995 and Remigius, 2012, nickel was said to accumulate in seeds of some Fabaceae members, which might explain the reason why pods had the highest concentration of nickel in this study.

Other medicinal plants like Alstona boonei, Pycnanthus angolensis, magnifera indica, Khaya iroresis, Nauclea diderichii, Morinda lucida among others were evaluated for mineral elements (macro elements and micro elements) and have been reported by Richard and

Ayomadewa, 2014 to be rich in calcium, magnesium, zinc, iron, copper, manganese, lead and phosphorus among others. They are also known for their different biological activities like antimicrobial, antibacterial and antifungal activities and to be used for management of different illnesses.

The result of the toxic heavy metal content in the plant parts (stem bark, leaves and pods) indicated that in all three samples the lead content was below the permissible limit but unfortunately, mercury content was slightly above the permissible limit established by WHO. However, in this study other toxic heavy metals identified as potentially carcinogenic and mutagenic by International Agency for Research on Cancer (IARC) like cadmium, chromium, arsenic, vanadium, beryllium, cobalt and antimony were not detected in the plant parts. The last trace element which was also obtained slightly above the permissible limit is nickel. Concentrations of other analyzed trace elements and rare earth elements reported had no data available on their permissible limit established by WHO which might be due to their unknown biological importance or non-hazardous nature, however, the concentrations of these elements were not alarming.

The uptake and bioaccumulation of heavy metals in herbs and other plants materials are influenced by a number of factors such as climate, atmospheric deposition, concentration in the soil, the nature of the soil on which the herbs are grown and the degree of maturity of the plant at the time of harvest, Long-term uses of treated or untreated wastewater, heavy traffic ways, and organic manures waste sludge, fertilizers and pesticides which may affect the physicochemical properties of the soil such as pH, organic matter and polluted aerosols which can be deposited on soil and are absorbed by plants leaves, barks and fruits (Nwachukwu et al., 2010; Liu et al., 2007; Sharma et al., 2006; Remon et al., 2005; Samali et al., 2017).

Lastly, the mineral and heavy metal concentrations reported herein that was not par with some literatures that reported on the same plant, might be due to different growth conditions, genetic factors, geographical variation in the level of soil fertility, mineral uptake efficiency and the analytical procedure employed.

CONCLUSION

This study demonstrated that the Vachellia nilotica stem bark, pods and leaves extracts were rich in mineral elements especially magnesium, Sulphur, phosphorus, chlorine and potassium among others, this becomes important when viewed at the role these elements play in combating illnesses and of course at a nutritional perspective. So also, other micro and macro elements were found to be present in the plant extracts, likewise rare earth metals and some heavy metals.

Overall, it was observed that the leaves extract had the highest concentration of mineral elements, followed by the pods extract and the least was in stem bark extracts except in some few heavy metals. Fortunately, potential carcinogenic heavy metals like cadmium, chromium, arsenic etc. were not detected in the extracts but mercury and lead were detected. The lead concentration in leaves and stem bark were below the permissible limit while it was totally absent in the pods extract. The only concern is in the mercury concentration which was slightly high in the pods and stem bark extracts and lower than the WHO limit in the leaves extract. Chlorine and other rare earth metals like europium, cesium, rubidium etc. were found at varying concentrations among the extracts but no data was obtained pertaining their biological importance, hazardous nature or WHO's limit in medicinal plants.

Moreover, this study has clearly demonstrated the variation in the plant parts extracts with regards to mineral elements and heavy metals could be reflected toward the difference in their uptake capabilities and their further translocation. It also gives a new perspective about the

presence of heavy metals in medicinal plants as most people believe that these natural herbal plants are safe and non-toxic unlike the modern drugs while they are completely unaware of their toxic potentials.

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