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Removal of heavy metals from aqueous solution using *manihot esculenta* (cassava leaves)

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ABSTRACT
The contamination of environmental compartment with organic and inorganic compounds such as metals has motivated the development of purification and clean-up methods. A wide variety of heavy metals species enters the aquatic compartment through atmosphere, deposition, industrial discharges and these activities follow an upward curve in response to the world's growing population and its needs. Manihot Esculenta (cassava leaves) was used for adsorption experiment. The leaves were characterized using Fourier Transform Infrared (FTIR) spectrometer, Scanning Electron microscopic (SEM). To determine the percentage extraction efficiency of the leaves on the adsorption experiments of (Cu^{2+}, Pb^{2+}, Zn^{2+}) from aqueous solution using batch contact method, the following studied (effect of time, pH and dosage) was quantified using Perkins Elemer model 214 Atomic adsorption spectrometry (AAS). The manihot esculenta showed high metal uptake for tested metal ions. The effect of pH, contact time and adsorbent dosage in the removal of heavy metals from aqueous media was investigated. The optimum pH for the manihot esculenta was found to be at pH 6 for Zn^{2+}, pH 4 for Pb^{2+}, pH 4 for Cu^{2+}(99.20, 99.10, 94.00) %. Contact time was found to be at 80 minutes for Cu^{2+}, Zn^{2+} 80 minutes, Pb^{2+} 120 minutes (99.00, 83.00, 60.20) %. Adsorbent dosage for the manihot esculenta was studied between 2 g to 10 g and for theCu^{2+} has the highest dosage of 99.00 %, Zn^{2+} 94.30 %, Pb^{2+} 94.10 %. The result confirmed that cassava leaves can be employed as low cost adsorbent for Cu^{2+}, Pb^{2+} and Zn^{2+} removal from aqueous solutions.
KEYWORDS: *Proximate analysis, Mineral analysis, Fish, Micropogonias undulates, digestion*

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I. INTRODUCTION

Wastewater is a waste found to contain considerable amount of heavy metals especially from industries with high need of heavy metals in their production processes. Wastes containing heavy metals from these industries are directly or indirectly being discharge into the environment causing serious pollution and even threatening human life [1]. Water pollution in developed countries constitutes a great concern, with increasing generation of heavy metals from technological activities. Many aquatic environments face metal concentrations that exceed water quality criteria designed to protect the environment, animals and humans. Heavy metals are chemical elements with a specific gravity that is at least five times that of water and is toxic at low concentrations. Due to rapid development of industrial activities, the concentration of heavy metals in water have substantially increased and can easily enter the food chain because of they are highly soluble in water. Environmental pollution containing heavy metals has become a global concern as a consequence of industrial and metallurgical process which had lead to majority of toxic chemicals into the environment [2-6]. The widespread of these heavy metal to human health are; lead, copper, mercury, cadmium, arsenic, chromium, zinc [7]. These heavy metals have polluted the atmosphere, water, soil and food chain [8-9]. Humans are often exposed to heavy metals in various ways which are through the inhalation of metals in the workplace or polluted neighborhoods or through the ingestion of food particularly seafood that contains high levels of heavy

metals or paint chips that contain lead [10]. Eliminating heavy metal usage is often expensive and disposal of metals and metal containing materials inevitably cause pollution. On the other hand some heavy metals such as cobalt, copper, strontium, manganese, molybdenum, vanadium and zinc are required by living organisms at trace amount in moderate or harmless concentration as dietary supplements. They are also known to be part of some products such as drugs, plastics, petroleum products.

The heavy metals pollution represents an important problem with human health concerns and serious ecological consequences, it is therefore essential to remove heavy metals from industrial waste waters and drinking water. However, extensive research has been conducted on the discharge of metal ion contained in industrial effluents because of the presence and accumulation of toxic effects on living species. The discharge of metallic ions in industrial effluents is of great concern because their presence and accumulation have a toxic effect on living species. The toxicity can result in physical discomfort and sometimes life threatening illness and irreversible damage to vital body system.

Cassava is a perennial woody shrub in the spurge family native of south America but now grown in tropical and sub-tropical areas worldwide for the edible starchy roots(tubers) which are major food sources in the developing world. The scientific name is *ManihotEsculenta*. The cassava shrub may grow 2.75 m tall with leaves deeply divided into 3-7 lobes. The shrub is often grown as an annual and propagated from stem cuttings after tubers have been harvested. The fruit is small roughly 1 cm in diameter, but root tubers in cultivated varieties can be 5-10 cm in diameter. Despite the use of cassava root tubers, little or no attention are paid to the leaves and are left to rot thereby constituting wastes in the environment. The leaves are used to boost immunity, energy and brain function, soothe headache, aid digestion, lower blood pressure, rheumatoid and balances stress levels. Cassava is very versatile and its derivatives and starch are applicable in many types of products such as foods, confectionery, glues, plywood, textiles, paper, biodegradable products, drugs, alcoholic beverages, laundry starch. Cassava is also used as a livestock feed in Latin America, Caribbean, Europe, some part of Africa and is increasingly cultivated for use as biofuel in china. . However, various research have been conducted on the removal of heavy metals from industrial effluents but some of the methods used are inadequate, expensive, requires large amount of chemicals, sludge disposal and not effective. it is therefore essential to develop alternative technologies to treat metal effluents. Adsorption methods is considered as low cost, use of non-polluting biodegradable products and requires little processing with economical value, clean and safe environment. Due to their toxicity, industrial wastewaters containing heavy metals must be strictly regulated and treated before being discharged into the environment.

II. EXPERIMENTAL

2.1. Chemicals

Aqua regia solutionis a(mixture of nitric acid (HNO_3) and hydrochloric acid (HCl) in a molar ratio of 1:3). Nitric acid and HCl used in this study were purchased from Sigma Aldrich and are of analytical grade.

2.2. Sampling location

The study was carried out in Ojo, Lagos State, Nigeria. Lagos State is located in the South West part of Nigeria on geographical location between latitude 6° 35'N 3° 45'E / 6.583°N 3.750°E. It is a state approximately 3,474km^2 in land area with estimated population of 9,013,534 people (Census, 2006) [34].

2.3. Sample collection and preparation

Three fish samples were collected at different intervals from Ojo market, Ojo Local Government Lagos State, Nigeria. They were kept in cold ice box and transported to the Department of Chemistry Laboratory, Lagos State University. All procedures on proximate analysis and mineral composition were performed using the method described by Association of official analytical chemistry (AOAC) [35].

2.4. Characterization

Soxhlet extraction machine, fibertech machine, oven, furnace, Protein digestion distillation unit machine and **Varian Spectra Atomic Absorption Spectrophotometer, Buck Scientific 210 GVP model was used for elemental analysis**.

2.5. Proximate analysis and mineral composition

2.5.1. Proximate analysis

The following analysis was carried out;

2.5.1.1. Moisture content

This analysis is also called water content is the faction of total fresh tissue weight that is water[36]. It was determined using the dry oven method according to Association of Official Analytical Chemists (AOAC) [37]. The samples were oven dried for 16 hours at 100 $^{\circ}$C, then cooled down in desiccator and the moisture content was determined by calculating the difference in weight before and after oven drying.

2.5.1.2. Ash content

This fraction contains the entire element combined together. It is more useful as it allows knowing the amount of different individual elements. Ash analysis was carried out in a furnace.

2.5.1.3. Protein content

This was aided by protein digestion distillation unit machine. Protein is Integral in the human body as it is contained in every cell of the body. It builds up cell and repair worn out tissues. Fish is one of the best animal sources of protein because it gives a healthy amount of protein and has less fat compared to red meat[38].

2.5.1.4. Fat content

Fat analysis was initiated using the soxhlet extraction method. The fat content of the fish is the proportion of the fish by weight made up of fat. Sea food is considered to be low in both total fat and saturated fat. Fat is essential in human as it helps to absorb vitamins such as A, D, E, K and keeps skin healthy.

2.5.1.5. Crude fibre

It is the measure of the quantity of indigestible cellulose, pentosans, lignin and other components of this type in the present food. Dietry fibre is physiologically important as it affect gastrointestinal transit time[39]. Fibertech machine was used for its determination.

2.5.2. Mineral composition

Atomic Absorption Spectroscopy (AAS), a spectro-analytical procedure for the quantitative determination of chemical element using absorption of optical radiation (light) by free atoms in the gaseous state was used for the determination of mineral composition. Five mineral elements were considered including:

2.5.2.1. Iron (Fe)

Fe is an abundant element in earth crust and is biologically essential component of all living organism[40]. It is an essential trace element in human nutrition and its deficiency (anemia) is a world nutritional problem[41]. Iron helps the red blood cells transport oxygen to all part of the body.

2.5.2.2. Magnesium (Mg)

It plays a role in over 300 enzymatic reactions within the body including the metabolism of food synthesis of fatty acid and protein and the transmission of nerve impulses. Magnesium deficiency is rare but may affect older people; it is linked to insulin resistance, metabolic syndrome, coronary heart disease and osteoporosis

2.5.2.3. Potassium (K)

It is essential for transmission of mineral impulses and thus for muscle contraction, heat function and blood pressure regulation[42]. Potassium is a cofactor of several enzymes involved in protein and glycogen synthesis and therefore plays a crucial role in growth[43]. Its deficiency is hypokalemia.

2.5.2.4. Calcium (Ca)

It is the most abundant element in the body which makes it vital for good health. It is impotent for normal growth and development of the skeleton[44]. Human bodyneed Calcium to build up strong bones and maintain healthy communication between the brain and other part of the body. Adequate calcium intake is critical to achieving optimal peak bone mass and modifies the rate of bone loss associated with aging[45]. Hypocalcaemia is the condition where the blood has too little calcium.

2.5.2.5. Sodium (Na)

It is essential for fluid balance and cellular homeostasis[46]. Its deficiency is common in older adults especially those who are hospitalized o living in long term care facilities. Sodium deficiency (hyponatremia) can cause seizures, coma and even death.

III. RESULT AND DISCUSSION

3.1. Proximate composition

The proximate composition of the analyzed sample is shown in Figure 1. There were significant differences in each of the analysis with moisture content having the highest percentage and ash content with the lowest,this analysis was done in triplicate.

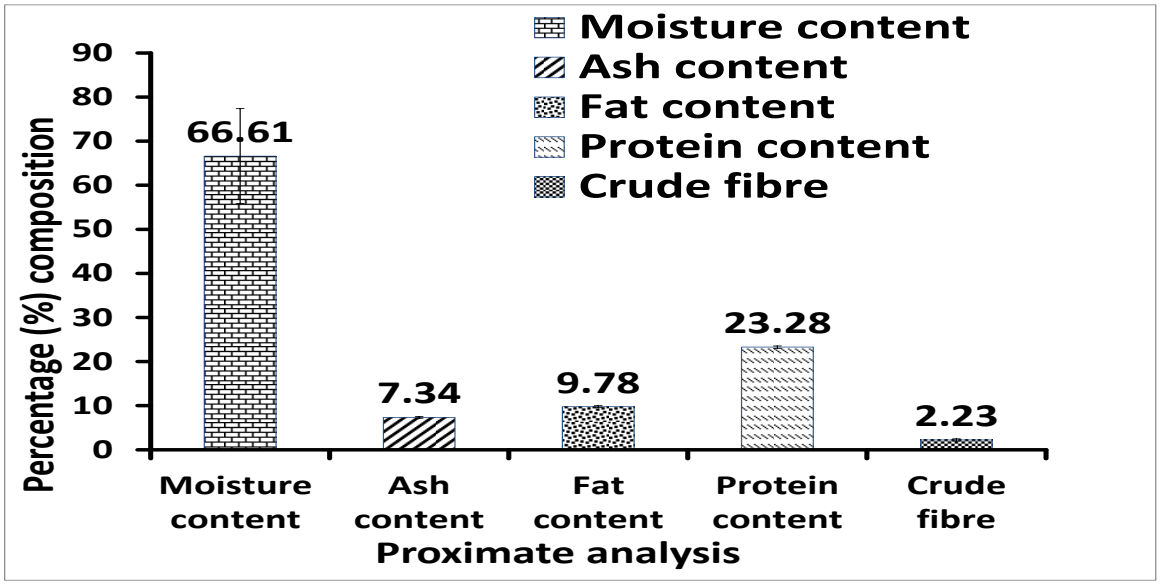

Figure 1: Proximate analysis of fresh fish species

In comparison with other fresh water species [21]carried out a study on proximate composition of croaker (*Pseudotolithus elongatus)* from retail outlets in Makoko environment, Lagos State, Nigeria and concluded that the mean proximate composition of fresh croaker was 21.43 % crude protein, 75.52 % moisture, 1.28 % ash and1.48 % lipid.[28]found out on a study of proximate composition of fish in Nigeria market that croaker (*Micropogonias furnieri*) consist 20.73 % protein and 3.09 % fat.[30] carried out a study on Proximate Composition of Nile tilapia (*Oreochromis niloticus*), African sharp tooth catfish (*Clarias gariepinus*), Nile perch (*Lates niloticus*), Barbs (*Barbus specie*), Redbelly tilapia (*Tilapia zillii*) and Common carp (*Cyprinuscarpio*) from Ethiopian Lakes and concluded the content of protein, fat, moisture and ash ranged from 13.30 to 18.50 %, 0.40 to 2.45 %, 77.24 to 80.80 % and 0.81 to 1.20 %, respectively. [33] studied *Protopterus annectens, Labeo coubie, Auchenoglanis occidentalis* and*Mormyrus rume*from lower river Benue, Makurdi and determined Crude protein in the range (61.65 - 58.52 %), fat (8.14 - 8.34 %) while Ash content was (6.17 - 4.15 %) . [47] Found proximate composition of experimental samples from Nigeria to comprise 78.19 % moisture; 17.38 % crude protein for *Latesniloticus*, 78.17 % moisture; 19.83 % crude protein for *Clariasgariepinus* and 79.40 % moisture; 18.38 % crude protein for *Oreochromisniloticus*.

The main constituent of fish flesh is water, which usually account for about 80 % of the weight of a fresh white fish fillet [48]. Different fish species vary in moisture content and other proximate constituent. The slightly lower moisture content of some larger fishes can be attributed to muscles containing more organic materials and less water than the young fish. Different researchers have also reported that moisture contents can vary with sex of fish [49, 50], absorption capability of fish and source of heat could also influence moisture content of fish.

The mean protein content in the present study is 23.28 % while in previous studies its ranges within about 17 % - 21 % which indicate *Micropogonias undulatus* is a good protein source. The moderately high protein content in *Micropogonias undulatus* among other species could be attributed to food consumption or absorption capability and conversion potential of essential nutrients from their diet or their local environment into such biochemical attributes needed by the fish. Variation in protein content can be as a result of certain factors such as season of the year, effect of spawning and migration, food availability etc[51]. Fish protein is an excellent source of lysine, methionine and cysteine and can significantly raise the value of cereal based diets, which are poor in these essential amino acids. The amount of protein in fish muscle is usually between 15 – 20 %, although it can be as low as 13.5 % or as high as 28 % in rare cases.

The mean fat content of *Micropogonias undulatus* in this study is 9.78 % (Figure 1). Previous studies have shown variations in fat content most of which are less than 10 %. [33]show a fat content range of 8.14 - 8.34 % in *Protopterusannectens, Labeo coubie, Auchenoglanis occidentalis* and*Mormyrus rume*from lower river Benue, Makurdi which is appreciably close to that of this study. The sharp increase in fat content of this study can be attributed to spawning and gonad development in the fish species. Lipids are known to play a number of roles in formation of vitellogenin, insulation of organ and buoyancy.

The mean ash content is 7.34 % (Figure 1). Variations also occur in ash content of different fishes but there is no significant difference between that of this study and [52] who found ash content of pebbly fish in

Arua, Uganda to be in the range of 7.25 - 7.56 %. Variation in ash content could be attributed to increased or decreased minerals content to correct ionic balance during starvation.

Crude fibre in fish muscle is usually very small which makes it of less significance. In this study the mean crude fibre was analyzed to be 2.23 %.

3.2. Mineral composition

The mineral content of *Micropogonias undulatus*are given in Figure 2. A larger percentage of consumers do eat fish because of its availability, flavours, palatability while fewer percentages do so because of its nutritional values. These results are important for the consumer in making an informed decision before purchasing to get the maximum nutritional benefit.

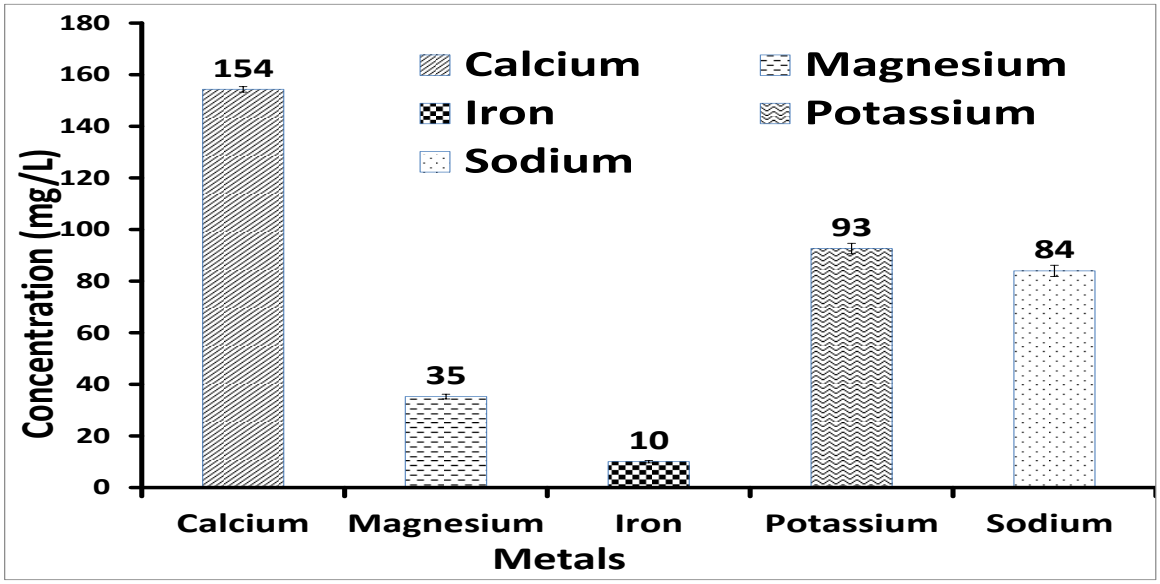

Figure 2: Mineral composition of*Pseudotolithus elongatus*

Result of the mineral composition from the present study revealed that *Micopogonias undulatus* is very rich in mineral element with calcium dominating among the five elements considered while iron is in trace amount compared to magnesium, potassium and sodium. There was significance difference in mineral composition of the various minerals analyzed. Research from previous studies has shown variations in micro elements with respect to various fish species. Accumulation of various elements depend on different factor such alas physiological needs, feeding habits and genetic composition, sex of each fish species and the biochemical significant role of each metal [53]. The high level of calcium and potassium may be attributed to their availability in the water body and the ability of fish to absorb that element from their diet in the environment where they live [54]. Generally heavy metals in the muscles of fresh water fish vary considerably among different studies possibly due to concentrations and chemical characteristics of Water from which the fish were sampled, ecological needs, metabolism and feeding patterns of fish and also the season in which studies were carried out[55, 56]. Mineral content of fish makes it unavoidable in the diet since it contributes good health.

Iron concentration in this study is 10.35 ppm. Iron serves a transport medium for electrons within cell so it is a carrier of oxygen to the tissues from the lungs by red blood cell haemoglobin and act as an integrated part of important enzyme system in various tissues. [57] Concluded that sea foods, especially darker fleshed fish are reasonably good source of iron, supplying 1 – 2 mg / 100 g muscle. Human needs adequate iron to conquer the incidence of anemia which is a major health problem. The iron content revealed in this study varies from previous researchers which can be related to specie, age, sex, size and post-harvest processing of the fish.

Magnesium mean concentration in this study is 34.24 ppm. *Micropogonias undulatus* is moderately rich in magnesium as its magnesium composition is highly variable compared to other species in other studies. Variation can be attributed to specie, season and the type of habitat.

Mean potassium concentrations was found to be 95.00 ppm.[58] Determined potassium value in trout (*onchorhynchus mykiss*) as 306 mg / 100 g while [59] reported potassium value to be 459.7mg/100g for sea bass (*dicentrarchus labrax*) and 393.8 mg / 100 g for sea bream (*sparus aurata*). They reported higher value for potassium concentration; the significantly higher value can be attributed to availability of potassium in the water body and the ability of the fish to absorb the element in its environment.

Micropogonias undulatus can be reported to be significantly rich in calcium in this study as its calcium concentration is 154.56 and it appreciably dominated all other mineral elements. The range of calcium was found in sea bream (*diplodus puntazzo*) to increase with increase in fish size[60]. The nature and flexibility in diet from *zooplankton* to *zoobenthos*, *detritus* and *macrophytes* could be a contributing factor to high level of calcium in larger fish sizes.

Sodium composition in the present study is appreciably high as it is 86.32 ppm. Fish have the tendency to concentrate large amount of some heavy metals from the water, their gills serve as respiratory organ through which ions are absorbed.

IV. CONCLUSION

The result obtained in this study has provided scientific information and detailed knowledge of the proximate and mineral content of *Micopogonias undulatus*. The fish specie is a good source of protein and fat. Consumption of *Micopogonias undulatus* is good for people's health and can be regarded as best diet for human because it has high quality protein that is essential for both infants and adults.In spite of the expected pollution threat to its habitat it shows appreciable mineral content. It is very rich in calcium, potassium and sodium which are important for human healthy living. Availability of mineral content in fish could vary on biological factors such as habitat and feeding habitat.

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