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Full Length Research Paper

HAEMATOLOGICAL CHANGES IN CATFISH EXPOSED TO JOINT MIXTURE OF PHENANTHRENE AND BENZO[A]PURENE

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ABSTRACT

Polycyclic aromatic hydrocarbons are a group of organic compounds that contain two or more aromatic rings and are found mainly as complex mixture rather than a single compound. They are ubiquitous in the environment and can be formed from either natural or anthropogenic activities. Benzo(a)purene and phenanthrene are examples of polycyclic aromatic hydrocarbons distributed in soil, water and aquatic environments. The effect of mixtures of benzo(a)purene and phenanthrene on selected haematological parameters of catfish was evaluated. Healthy juvenile catfish 100 in number weighing 18.8±1.8g were exposed to sublethal concentrations of joint mixture of benzo(a)purene and phenanthrene for a period of 40 days. Acute toxicity studies showed that phenanthrene and benzo(a)purene had LC$_{50}$ values of 1500 and 17ug/l respectively. The joint mixtures significantly ($p < 0.05$) reduced the growth rate in exposed fish. The joint mixture also led to a significant ($p < 0.05$) decline in the studied haemotological parameters including Red blood cell count (RBC), haemogolobin (Hb), haematocrit, mean corpuscular volume (MCV) and mean corpuscular haemoglobin (MCH). There were significant increases in the white blood cells (WBC) count and platelet count. These significant changes in hematological parameter in catfish reduction show that benzo(a)purene and phenanthrene mixtures are of environmental concern due to their toxicity. This study will contribute to the toxicological database and also improve on the ecological risk assessment of phenanthrene and benzo(a)purene mixtures in aquatic environment.

Keywords: Benzo(a)purene, Haematological, Phenanthrene, Sub-lethal

INTRODUCTION

Human activities have led to an upsurge in the release of hydrocarbons such as those found in petroleum. These hydrocarbons though of economic benefit however pose significant risk to both the aquatic ecosystem and human health (Ramanpour *et al.*, 2014). Polycyclic aromatic hydrocarbons (PAHs) are a major component of these hydrocarbons. Although PAHs have low water-solubility they persist and cause severe behavioural and physiological alterations in aquatic organisms (Santos *et al.*, 2011). Phenanthrene and benzo[a]purene are among the sixteen PAHs that have been identified as priority contaminants because they can bioaccumulate, in the environment and result in contamination of the food chain (Ramanpour *et al.*, 2014). . .

Both phenanthrene and benzo[a]purene occur in fossil fuels and are present in products of incomplete combustion. They are widely distributed in the aquatic environment and have been identified in surface water and tap water. They have also been identified in seafood collected-from contaminated waters and in smoked fish and other foods.

Petroleum hydrocarbons have been reported to cause structural damage to the respiratory lamellae of the gills (Prasad, 1991). The compounds tend to adsorb to organic or inorganic matter in sediments and can be trapped in long-term reservoirs. There is substantial uptake of these compounds by aquatic organisms through the diet, through exposure to contaminated water and through direct contact with sediment (Johnson et al., 2002).

Catfish was selected as the test organism, because of its hardiness, ecological and commercial importance in several tropical countries. It is also a model organism that has been used extensively in ecotoxicological research (Esenowo and Ugwumba2010).

The aim of this work is to evaluate the effects of joint mixture of phenanthrene and benzo[a]purene on the haematological parameters of catfish.

MATERIALS AND METHODS

Chemicals

Phenanthrene and benzo[a]purene were obtained from Sigma Aldrich (Germany). Acetone was obtained from BDH chemicals (UK). Every other reagent was of analytical grade.

Animals

African catfish (19.7. ±1.8 g) were obtained from a commercial aquaculture. Fish were acclimatized for 2 weeks prior to experiment. Fish were fed twice daily with commercial fish feed. Fecal matter and uneaten food were removed daily to prevent water pollution.

Acute toxicity study

A range finding test was used to determine the appropriate concentrations of exposure. Based on the obtained (pre-LC_{5o} data, the 96-hour LC_{5o} was determined for phenanthrene and benzo[a]pyrene according to the revised OECD guidelines for testing of chemicals (2019).'

Triplicate sets of seven fish each were randomly exposed to varying concentrations of phenanthrene and benzo[a]purene separately. Acetone was used as solvent carrier. The fish were placed in 30L plastic tanks containing 20L of clean tap water. Another set of 7 fish was also maintained with equal amount of tap water (and solvent carrier) but without the test chemicals and considered as the solvent control. Dead fish were removed and the mortality recorded at intervals of 24, 48, 72 and 96 h. The 96-hour LC_5o value of phenanthrene and benzo[a]purene for the fish was determined by probit analysis.

Sublethal toxicity study

Stock solutions of phenanthrene and benzo[a]purene were prepared by dissolving the chemicals in distilled water and taking acetone as solvent carrier. During sublethal studies, fish were exposed to a mixture of 50% and 25% of the LC_5o value of both chemicals (corresponding to treatment levels 1 and 2). A solvent control was included in the experimental design. Fish were kept in groups of 10 in 30L plastic tanks containing the test solutions. Experiments were performed in triplicates. Period of exposure lasted for 5 weeks

Assays

At the end of the exposure period, hypothermia was used to anaesthetize the fishes. Blood was then collected from the immobilized fish by caudal vein puncture method using a 5ml sterile disposable syringe with a 22-gauge needle. The blood was transferred to EDTA tubes and transported to the laboratory for analysis.

Statistical analysis

Results were expressed as mean standard error. Data from the different treatment groups were compared by a one-way analysis of variance (ANOVA) followed by a Scheffes test to determine statistically different groups. All differences were considered significant at $p < 0.05$.

RESULTS AND DISCUSSION

The LC_{50} for phenanthrene was 1400, ug/L. The LC_{50} for benzo[a]purene was 16 ug/L. While there were no recorded mortalities in the control group, there was 100% mortality in the highest concentration groups corresponding to 3200 and 64 ug/L for the phenanthrene and benzo[a]pyrene groups respectively.

The impact of the joint compounds on selected blood parameters is shown in Table 1. The joint compounds lead to significant ($p < 0.05$) declines in red blood cell (RBC) count. Haemoglobin (Hb) concentration, and haematocrit (Hct). Erythrocyte indices including mean corpuscular volume (MCV), mean corpuscular haemoglobin (MCV), and mean corpuscular haemoglobin concentration (MCHC) all showed significant ($p < 0.05$) declines.

Significant ($p < 0.05$) increases where observed in white blood cell (WBC) count and plate (PLT) counts.

Table 1: Haematological parameters of catfish exposed to joint mixtures of phenanthrene and benzo[a]purene. Means not sharing the same letter (a, b or c) are statistically different at $p < 0.05$.

Parameter	**Control group**	**Phen + BaP joint 350+4 ug/L**	**concentration 700+8 jig/L**
RBC	2.41±0.06^{a}	;2.35±0.13^{b}	2.17±0.43^{C}
Hb	102.66±3.71^{a}	99±1.9^{b}	91.28±2.8^{b}
Hct	34.85±2.38^{a}	34.13±2,13^{a} .	30.1±O.Q9^{b}
MCV	147.5±2.5^{a}	143.8±0,5^{b}	138.5±0.96$^{l?}$
MCH	43.3±0.24^{a}	41.15±0.52^{b}	39.6±l.l^{b}
MCHC	305,33±4.4^{a}	279.33±3.1^{b}	272±1.2^{b}
WBC	135.56±2.98^{a}	146.86±3.3^{b}	168.74±4.1^{C} .
PLT	12.66±1.33*	18.33±2.7^{b}	19±1.82^{b}

Red blood cells are essential in maintaining blood pH and regulation of blood flow to tissues and organs (Bloom and Brandt, 2008). Several chemical pollutants have been shown to reduce the measured quantities of red blood cells in circulation (Dey *et* a/., 2019). Aquatic organisms exposed to phenanthrene have been shown to have low RBC counts. The observed decline in RBC count could be as a result of internal hemorrhage or necrosis of blood cells (Khaniyan *et al,* 2016). Kim *et al.* (2007) demonstrated that subchronic benzo[a]pyrene exposure in rockfish caused a significant reduction in erythrocytes as well as haemoglobin concentration.

Haemoglobin which is synthesized in the bone marrow is the primary intracellular polypeptide of the red blood cells (Chhabra, 2013). The reduction in haemoglobin concentration as observed in the present study may be due to the disruptive effect of the PAHs on the erythropoietic tissues. Haemoglobin concentration can serve as a very sensitive bioindicator of alterations in ecological conditions (Parmar and Shar, 2021).

The low HCT values observed in this work correlated with the reduction in red blood cell count as a result of PAH toxicity. A low haematocrit level is a direct consequence of low red blood cell count (Mondal, 2021). Barcellos *et al.* 2003 showed that fish species exposed to toxic chemicals had lower Hematocrit, haemoglobin concentration and erythtocyte counts.

Erythrocyte indices are useful in understanding the etiology of anemia. Anemia is classified, according to the size of the erythrocyte, as being normocytic (normal MCV), macrotic (increased MCV), or microcytic (decreased MCV). (Walker *et al,* 1990). There were significant declines in all studied erythrocyte indices.

There was increase in the levels of circulating white blood cells in exposed fish pointing to the immunotoxicity of the PAH compounds. White blood cells are part of the immune system and participate in immune responses.

Platelets which are not cells play important roles in the inflammatory process. Under stress conditions as that obtained in the present study, platelet counts are increased to ameliorate haemorrhage (Dey *et at.* 2019).

In conclusion, the joint mixture of phenanthrene and benzo[a]purene had deleterious effects on the health status of exposed fish.

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Full Length Research Paper

PHYTOCHEMISTRY AND IN-VIVO ANTHELMINTIC PROPERTIES OF *Bambusa vulgaris* (BAMBOO) ETHANOL CRUDE EXTRACT.

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ABSTRACT

Bamboo leaves have therapeutic and nutritional properties making them good source of fodder for livestock. To be sure of the safety or otherwise, phytochemical analysis was carried out and anthelmintic effect of *Bambusa vulgaris* leave extract on adult mice infected with *Ascaris lumbricoid*e was also evaluated using carefully controlled whole animal experimental model. The result of phytochemical analysis revealed that *Bambusa vulgaris* contained saponins, general glycosides, coumarins and cyanogenic glycosides. The result of anthelmintic effect of *Bambusa vulgaris* leave extract on adult mice infected with *Ascaris lumbricoid*e compared favourably with Abendazole (40 mg/kg), which is the anthemintic agent used. This study justifies the anthelmintic activity of *Bambusa vulgaris* as it could be used in the treatment of worm infestation, particularly the *Ascaris lumbricoide.*

Keywords: *Bambusa vulgaris*, anthemintic, in-vivo, *Ascaris lumbricoide*

INTRODUCTION

The use of medicinal plants has always been part of human culture and existence and is wide spread in Africa. According to World Health Organization, medicinal plants would be the best source to obtain a variety of drugs. About 80 % of individuals from developed countries used traditional medicine, which has compounds derived from medicinal plants (Aggarwal *et.al* 2007). Anthelmintics or antihelminthics are drugs that expel parasitic worms from the body, either by stunning or killing them. The gastro-intestinal helminthes resistant to currently available anthelmintic drugs and therefore there is a foremost problem in the treatment of helminthes diseases (Sondhi and Archiana 2004). Although the majority of infections due to helminthes is generally restricted to tropical regions and cause enormous hazard to health and contribute to the prevalence of undernourishment, anemia, eosinophilia and pneumonia (Bundy 2001). Recent reports have revealed increasing cases of worm infestation globally such that the search for potent remedies appears to be the focus of most current medical researches (Udoha *et. al* 2015). The side effects and in some cases toxicity symptoms associated with the use of current orthodox antihelminthics maybe there as on for recent growing interest in medicinal plants (Ijioma and Emelike, 2014). Hence there is an increasing demand towards natural anthemintics. *B. vulgaris* is commonly known as bans and belongs to the family of *Poaceae*. It is the commonest in Nigeria, constituting almost 95% of the total bamboo resources of the country. Two distinct varieties of *Bambusa vulgaris* are found in Nigeria, the more common is the green variety bambusa vulgaris var and the yellow variety Bambusa vulgaris var. vittata (Wendal *et. al* 2007). Other species such as Bambusa ventricosa mc are cultivated for various purposes. The leaves are emmenogogue and are used for the treatment of inflammatory diseases, wound healing, ulcers and paralytic complaints (Kirtikar and Basu 2005). Furthermore, in-vitro antioxidant activity of aqueous methanol and butanol extracts and hypoglycemic activity of the aqueous extract has also been reported (Macwan *et. al* 2010). But till now, the althelmintic properties of the plant is not reported hence, the anthelminthic activity of the leave part of the plant is reported. Several species are found in Nigeria and are geographically located in the rain forest region. Young shoot of the plant contains0.3% cyanogenic acid and are lethal to mosquito larvae and used in the treatment of cough in children. The leave juice with aromatics is given in haematemesis. It is also given in chronic dysentery and internal hemorrhage. It is also used in the treatment and management of epilepsy, fainting and loss of consciousness in feverish diseases and a variety of mental disorder that develop with aging. The juice from the stem is considered antipyretic, anti-tissue, expectant and sedative and has been used for bronchial, catarrhal and cerebral infections. *Ascaris lumbricoide.*is a common parasitic nematode found in the duodenum and small intestine of wood mice and other rodents. They are 5-20mm in length and bright red due to the pigmentation of their tissues. They are usually coiled, with the female having 12-15 coils and the male 8-12. The male can be distinguished from the female by prominent copulatory bursa and two long, thin specula's at the posterior end. These worms often form cysts in the walls of the intestine (Wabo *et.al* 2013)

MATERIALS AND METHODS

Sample Collection and Preparation

Fresh leaves of *B. vulagairs* were collected from a local settlement in Umuahia South Local Government Area of Abia State, Nigeria and was authenticated and identified by a botanist at the Department of Plant Science and Biotechnology, College of Natural Sciences, Michael Okpara University of Agriculture, Umudike Abia State as *B. vulagairs.*

The leaves were separated from the stem and sliced for quicker drying. The dried leaves were crushed into homogenous powder and then stored for further experiment. Ethanol was used in soxhlet extractor at low heat of 40^0C using 80grams of the powder and obtaining 8.24g crude. The prepared crude extract was preserved in the refrigerator at40^0C until use.

Animal Collection

A total of 50 adult albino mice obtained from the laboratory animal unit of the above-mentioned college of the university were used for this study. 25 were used for toxicity study while the other 25 were used for the anthelmintic study. They were housed in ventilated caged, fed (grower guinea feed) ad libitum and clean water but starved for 24 hours prior to commencement of the experiment. All animal experiments were conducted in compliance with NIH guidelines for care and use of laboratory animals (PUB. No 85-23, Revised 1985) as expressed Akah *et al*. 2009.

This experiment was carried out partly in physiology and pharmacology laboratory and partly in parastiology laboratory of the college of veterinary medicine, Michael okpara University of Agriculture, Umudike, Abia state.

Acute Toxicity Studies (LD_{50} Determination)

25mice of both sexes weighing 30 to 40 g were divided into 5 groups of 5 mice each and were assigned graded doses of the extract in the order 200, 400, 600, 800, 100mg/kg body weight respectively. The animals were thereafter kept in aluminum cages and allowed free access to feed and water and were observed for toxicity signs and deaths within a period of 24hours. The LD_{50} value for the extract were determined according to Lorke's method as used by Ijioma et.al 2014.

Helminth Material

A mouse adapted strain of *Ascaris lumbricoide* larva (3rd stage larva) supplied by Dr. Ngongeh of the Department of Parasitology, College of Veterinary Medicine, Michael Okpara University of Agriculture Umudike. The droppings of mice artificially infected with *Ascaris lumbricoide* were collected and soaked in water for 4 hours. Excess water was then decanted, the feces crushed in a glass mortar, transferred to plastic containers in lots of about 5.0 g and shaken with glass beads. The material was then mixed with about 1 litre of water and strained through several layers of gauze**.** The filtrate was transferred to jars. The supernatant solution was then discarded and the sediment mixed with vermiculite in labeled plastic petri dishes and incubated at 4°C for 7 days .The infective 3rd stage larvae (L_3) were recovered from 7 to 14 day old vermiculite faecal cultures using modified baermann apparatus. The third stage (L_3) obtained were washed several times with distilled water and their number determined by dilution counting. The volume was adjusted to give 200 L_3in 0.2 ml.

Parasite Inoculations

The mice used for anthelmintic studies were dewormed using Albendazole in their drinking water (7 mg/ml) for three days, one month prior to the experiment. Mice body mass were measured prior to infection. The mice were infected orally with *Ascaris lumbricoide* larva, 100 L_3per 0.1ml per mice using an oral gavage on day 0.

Recovery of Eggs

After 13 days of infection, freshly passed out feaces of experimentally infected laboratory mice were collected using a tea spoon. One gram of the feaces was homogenized in a mortar using pestle with 60ml of saturated sodium chloride (NaCl) solution, this mixture was filtered using a tea sieve and 150micrlitre sieve. The filtrate were transferred into a test tube and filled until the formation of upper meniscus. A cover slip was used to cover each of the tubes and allowed to stand for 3 minutes. This was to enable eggs of the parasites to move upward, float and attach to the cover slip. The larvae were removed and placed on a slide for observation using microscope to confirm the presence of *Ascaris lumbricoide.*

Chemotherapeutic Trials/Administration

Heavily infected mice with *Ascaris lumbricoide* were randomly assigned into five groups of five mice each. They were also grouped according to similar body weight.

Group 1 – Served as normal, no treatment was given except normal animal feed and distilled water.

Group 2 - Served as positive control, mice was treated with standard drug Albandazole (40mg/kg).

Group 3 – Were administered and treated with B. vulgaris ethanol extract at doses 200mg/kg.

Group 4 - and 5 – Were administered and treated with B. vulgaris ethanol extract at doses 400 and 800mg/kg body weight respectively.

Trials commenced on the 14th day after experiment infestations. All treatments were given by the oral route using an oral gavage and lasted for a period of 15days for analysis and egg counts.

Egg Count

In-vivo parasite egg output was counted from 1-3 fecal pellets that were collected every 3 days from each group of mice (starting from the 14th day post *Ascaris lumbricoide* inoculation). Helminth eggs were recovered and examined qualitatively by flotation using saturated NaCl solution and egg output per gram of feces were calculated. For each mice sample, two grids of a McMaster slide were counted and the average was used as the eggs per gram of faeces for the parasite.

Phytochemical Screening (Quantitative) Analysis. Alkaloids and cardiac glycoside were carried out with the method by Harborne (1980), Saponin by Obadoni and Ochuko (2002), Flavonoids by Allen et al (1973) and tannins by Schanderl (1970).

RESULTS

The results of the analyses are as shown below. The phytochemical screening of *B. vulgaris* is seen in Table 1 below. Acute toxicity (LD_{50}) effect of *B. vulgaris* ethanol extract (in-vivo) is shown in Table 2 while Effect of *B. vulgaris* leaf extracts count on fecal egg count of *Ascaris lumbricoide* in mice is shown in Table 3.

Table 1: Phytochemical screening.

Phytochemicals	**Values**
Saponins	3.97
General glycosides	2.89
Cyanogenic glycosides	2.56
Coumarins	2.16

Table 2: Acute toxicity (LD_{50}) effect of *B. vulgaris* ethanol extract (in-vivo)

Group	**Dose(mg/kg)**	**No of Deaths**	**Percentage mortality**
1	200	0	0.00
2	400	0	0.00
3	600	0	0.00
4	800	0	0.00
5	1000	0	0.00

Table 3: Effect of *B. vulgaris* leaf extracts count on fecal egg count of *Ascaris lumbricoide* in mice.

Groups	**Treatment**	**Post infection egg count**	**4days post treatment**	**8days post treatment**	**% Fall in egg count**
1	Control	253.00±13.42	297.60±9.95	310.80 ±9.38	-24.19 ± 7.15
2	40mg/kg Albenzadole	264.80±16.02	65.60±3.88*	0.60 ± 0.40*	99.79±0.14*
3	200mg/kg bamboo extract	276.80±6.91	187.00±4.31*	119.20±11.66*	57.11 ±3.48*
4	400mg/kg bamboo extract	260.80±5.91	165.60±4.69*	94.80 ±2.71*	63.63 ±0.89*
5	800mg/kg bamboo extract	289.40±13.24*	179.40±3.83*	56.60 ±7.33*	80.31±2.64 *

DISCUSSION

Table 1 gave insight of some phytochemical parameters present in *B. vulgaris* leaf. These phytochemicals are responsible for the analgestic, antimicrobial, antiulcer, antidote against acute lead poising which acts as a general anthelmintic activity of *B. vulgaris.* Table 3 showed that after 13 days of infection, all mice in the test groups had significant ($p<0.05$) fecal *Ascaris lumbricoide* counts. In day zero (0), the fecal egg load in group 2 (Abendazole 40mg/kg) was 215.40±17.06 eggs/g. while in group 3 (*B. vulgaris* leaf extract 200mg/kg). Fecal loads for groups 4 and 5 (*B. vulgaris* leaf extract 400mg/kg and 800mg/kg) were 184.80±2.96 eggs/g and 245.40±33.93 eggs/g respectively. Group 1(normal control) consisted of normal mice that were not infected and hence had zero fecal egg counts. Treatment with both the standard drug (Albendazole) and *B. vulgaris* leave extract significantly ($p<0.05$) lowered fecal *Ascaris lumbricoide* egg counts in all test groups when compared with the group 1 which was treated with the standard drug. The acute toxicity and anthelminthic effect of *B. vulgaris* was evaluated. No mortality was recorded during the acute toxicity test period while result of the anthelminthic study showed significant fall in total fecal egg counts in mice initially infected with *Ascaris lumbricoid* and treated with the extract. The effect of the extract also compared favorably with that of Albendazole, a standard anthelminthic agent. These experimental studies back up the common claim of people regarding the medicinal properties of *B. vulgaris.*

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COMPARATIVE ASSESSMENT AND POTENTIAL HUMAN HEALTH RISK OF THE POLYCYCLIC AROMATIC HYDROCARBONS AND HEAVY METALS IN PEPPER (*Capsicum annuum*) GROWN NEAR MARKETS WITHIN ABA METROPOLIS, NIGERIA.

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ABSTRACT

The levels of polycyclic aromatic hydrocarbons (PAHs) and heavy metals as well as their associated health risk implications were investigated in *Capsicum annuum* fruity vegetables grown near Ahiaudele, Umungasi and Umuola market locations within Aba metropolis. The PAHs were determined using gas chromatography/mass spectrometry (GC/MS) technique while the heavy metals were determined using atomic absorption spectrophotometry (AAS) technique. Sample from Ahiaudele gave (mg kg^{-1} PAHs) 12.46; Umungasi samples gave (mg kg^{-1} PAHs) 4.10 while Umuola samples gave (mg kg^{-1} PAHs) 0.65 respectively. The risk assessment of ΣPAH4 (the sum of benzo[*a*]pyrene, benzo[*a*]anthracene, benzo[*b*]fluoranthene and chrysene) in the samples gave margin of exposure (MOE) values higher than 10,000 indicating that the health risks associated with the consumption of the vegetables were insignificant. The mean concentrations of the metals of *C. annuum* samples followed the decreasing order: Fe>Al>Cu>Pb>V>Cd>Co>Cr>Zn>Mn. The mean concentrations of all the metals were lower than the FAO/WHO maximum permissible limits for human consumption, indicating there is no risk associated with the consumption of these vegetables with respect to each metal poisoning. The human health risks involved with the intake of the heavy metals through the consumption of these vegetables were assessed through the determination of estimated daily intake (EDI), health risk index (HRI), target hazard quotient (THQ), hazard index (HI), target carcinogenic risk (TCR) and cumulative target carcinogenic risk (CTCR) factors which indicate that the exposed adult population is unlikely to be at risk of adverse health effects of the heavy metals except in Umungasi market location where the population is liable to Cd poisoning . The HI values were greater than 1 in the vegetables from all the study locations. This means that the population in all the study locations are exposed to the combined hazard effects of these heavy metals when these vegetables are consumed. From the TCR and CTCR of the studied vegetable, there are potential carcinogenic risks among the population around those study areas where the recommended threshold risks limits were exceeded and therefore mitigation measures are required in those areas.

Keywords: PAHs; *C. annuum*; Heavy metals; Risks assessment, GC/MS

INTRODUCTION

Capsicum. annuum is a fruity vegetable commonly known as pepper and widely used as a spice. It is consumed fresh, dried or in powder. (El-Ghoraba *et al*., 2013). The fruits are an excellent source of health-related phytochemicals such as ascorbic acid (vitamin C), carotenoids (provitamn A), tocopherols (vitamin E), flavonoids and capsaicinoids that are very important in preventing chronic diseases such as cancer, asthma, coughs, sore throats, toothache, diabetes and cardiovascular diseases (El-Ghoraba *et al*., 2013; Igwe, 2014). *C. annuum* fruits are used in traditional medicine in combination with cinchona in intermittent and lethargic affections, and also in atonic gout, dyspepsia accompanied by flatulence, tympanitis and paralysis (Grubben and Denton, 2004). It is also used in the treatment of acute diphtheria malignant scarlet fever where it is employed either as a gargle or administered internally (Grubben and Denton, 2004).

Polycyclic aromatic hydrocarbons are ubiquitous environmental organic pollutants arising primarily from the incomplete combustion of organic matter, with common sources including coal, oil and biomass combustion (Iwegbue *et al*., 2014; Igwe *et al*., 2022). PAHs are known to be carcinogenic and cause lung, skin and bladder cancers (Igwe *et al*, 2021). Exposure of PAHs to humans may come through inhaling of polluted air, consumption of charred or burnt food items and foodstuffs upon which PAHs had been deposited Igwe et al., 2022b).

Heavy metals are trace elements which have relatively high density compared to water (Tchounwou *et al*., 2012; Ali and Khan, 2018). Most of these heavy metals such as lead, mercury, cadmium, chromium, arsenic and thallium have been reported cause serious health hazards to humans (Tchounwou *et al*., 2012). Heavy metals contamination and human exposure results usually from anthropogenic activities such as mining and smelting operations, industrial production, domestic and agricultural use of metals and metal-containing compounds, metal corrosion, atmospheric deposition, soil erosion of metal ions and leaching of heavy metals (Tchounwou *et al*., 2012; Koller & Saleh, 2018; Edogbo *et al*., 2020; Igwe *et al*, 2021).

There are increasing global concerns regarding the possible adverse health effects of polycyclic aromatic hydrocarbons and heavy metals and their negative enduring impacts on biosystems**.** Hence the monitoring of the levels of contamination in food materials has become necessary in order to determine extent of liability to damaging exposure.

MATERIALS AND METHODS

Study Area

Sample Collection

The fruity vegetables of *C. annuum* were harvested in the month of November, 2020, from gardens near markets within Aba town in Abia State, Nigeria. The market locations were Ahiaudele, Umungasi and Umuola markets. The samples were identified and authenticated at the Taxonomy Section, Forestry Department, Michael Okpara University of Agriculture, Umudike, Nigeria.

Sample Preparation

Sample preparation and the extraction of samples for PAHs determination were done as described by Igwe *et al.* (2022a). Also, the pulverized sample (2 g) was digested as described by Igwe *et al.,* (2022).

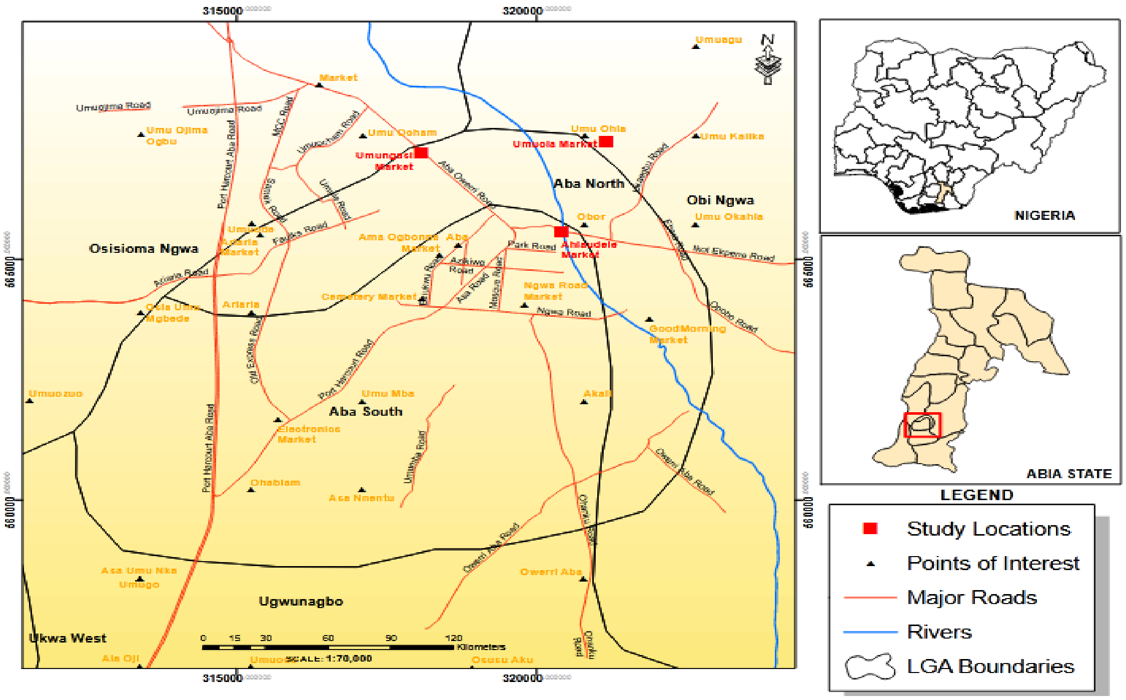

Figure 1: Map showing sample locations

GC/MS and Metal Analysis

GC/MS analysis was carried out according to the method of (Igwe *et al*., 2022a), while the concentrations of the metals (Al, Cd, Co, Cr, Cu, Fe, Mn, Pb, V and Zn) in the digests were determined with the Buck Scientific flame Atomic Absorption Spectrophotometer (AAS Model 210VGP).

Risk Assessment of the PAHs

Daily dietary exposure level by the populace to PAH4 was calculated according to Wu *et al*., (2016). The Margin of Exposure (MOE) described by Igwe *et al*., (2022a), was used for the characterization of the risk posed to humans by exposure to PAHs which can cause cancer or damage to genetic materials.

Risk Assessment of Metals

Estimated Daily Intake of the Heavy Metals

The Estimated Daily Intake (EDI) of heavy metals in Aba was calculated in accordance with USEPA (2011).

Health Risk Index

Health risk index (HRI) was calculated by dividing the EDI with the corresponding reference oral dose for each of heavy metal as described (USEPA, 2010).

Carcinogenic Risk Assessment / Non-carcinogenic Risk Assessment

Carcinogenic risk /Non-carcinogenic risk assessment methods established by USEPA (2010), are based on target hazard quotient (THQ) and hazard index (HI).

RESULTS AND DISCUSSION

The dry weight PAHs concentrations in the fruity vegetables of *C. annuum* harvested from gardens near Ahiaudele, Umungasi and Umuola markets in Aba metropolis are shown in Table 1.

Table 1: PAHs concentrations (mg kg^{-1}) in *C. Annum* fruity vegetable samples

S/N	Contaminants	Ahiaudele	Umungasi	Umuola
1.	1,2,3-Trimethylbenzene	0.22±0.009	ND	ND
2.	Naphthalene	0.98±0.008	ND	0.02±0.002
3.	2-Methylnaphthalene	0.71±0.01	0.47±0.01	0.03±0.001
4.	Acenaphthylene	0.44±0.02	0.47±0.02	0.02±0.001
5.	Acenaphthene	0.99±0.01	ND	0.01±0.005
6.	Fluorene	1.99±0.02	ND	0.07±0.003
7.	Anthracene	0.19±0.01	ND	0.10±0.008
8.	Phenanthrene	0.30±0.002	ND	0.06±0.001
9.	Fluoranthene	0.58±0.03	0.96±0.06	0.01±0.001
10.	Pyrene	0.59±0.04	ND	0.01±0.001
11.	Benzo[a]anthracene	0.84±0.02	ND	0.03±0.003
12.	Chrysene	1.00±0.07	0.01±0.001	0.01±0.002
13.	Benzo[b]fluoranthene	0.84±0.02	0.81±0.01	0.10±0.007
14.	Benzo[k]fluoranthene	0.61±0.01	0.69±0.01	0.01±0.003
15.	Benzo[a]pyrene	0.55±0.06	0.69±0.03	ND
16.	Diben[a,h]anthracene	0.82±0.02	ND	0.10±0.004
17.	Indino[1,2,3-cd]pyrene	0.64±0.05	ND	0.05±0.006
18.	Benzo[g,h,i]perylene	0.17±0.01	ND	0.02±0.001
19.	**∑PAH4**	**3.23**	**1.51**	**0.14**
20.	**∑PAH18**	**12.46**	**4.10**	**0.65**

Values are means ± standard deviation of triplicate determinations. ND means not detected

The fruity vegetable sample of *C. annuum* from Ahiaudele market location contained 12.46 mg kg^{-1} PAH18 while that of Umungasi and Umuola market locations contained 4.10 and 0.65 mg kg^{-1} PAH18 respectively. From these results, the sample of *C. annuum* from Ahiaudele market location contained the highest quantity of PAHs followed by Umungasi and then Umuola market locations. This is as a result of a more intense human and traffic activities around the Ahiaudele market location compared to other locations. Umuola location had very low PAHs content due to the fact that it is the remotest of all the locations with the least human and traffic activities and was chosen for study in order to also serve a control. Igwe *et al.*, (2022a), reported higher values of the total PAHs (∑ PAH18) content of the leaf samples of *Piper guineense* from Orieugba and Isigate markets in Umuahia, Abia State, Nigeria.

Table 3 shows the risk assessment for ΣPAH4 found in the fruity vegetable samples. The daily dietary PAH4 exposure values ranged from 9.1 to 209.95 ng/day. Igwe *et al*. (2022b), reported a daily dietary ΣPAH4 exposure level (ng/day) that ranged from 35.75 to 235.95 for *Telfairia occidentalis* obtained from Abia-Ohafia and Okagwe-Ohafia markets in Abia State, Nigeria. The use of the BMDL$_{10}$ value of 0.34 mg/kgbw/day set by EFSA, a daily vegetable consumption of 65 g per person and an adult body weight of 60.7 kg gave MOE values higher than 10,000 in all the samples containing PAH4. This means that the health risks associated with fruity vegetable samples from the gardens near the markets were low. Igwe *et al*. (2021) reported values of daily dietary exposure levels that ranged from 0.00 to 259.35 ng/day for *Talinum triangulare* and *Piper guineense* obtained from farms near markets within Aba metropolis. Wu *et al*. (2016) studied PAH concentrations in vegetables among different age groups and reported that the MOE values in most of the groups were less than 10000, indicating a certain cancer risk with respect to PAH4.

Table 2: Risk assessment of ΣPAH4 in *C. annuum* fruity vegetable samples

Risk Parameters	Ahiaudele	Umungasi	Umuola
E (ng/day)	209.95	98.15	9.1
MOE	98300	210270	2267912

E = Dietary Exposure; MOE = Margin of Exposure,

Table 3: Mean concentrations of some heavy metals (mg kg^{-1}) in *C. annuum* fruity vegetable samples

Metals	Ahiaudele	Umungasi	Umuola
Al	9.770 ± 0.227	3.130 ± 0.089	0.041 ± 0.004
Cd	0.010 ± 0.002	1.000 ± 0.057	0.440 ± 0.022
Co	0.100 ± 0.011	0.017 ± 0.003	0.733 ± 0.005
Cr	0.133 ± 0.062	0.233 ± 0.027	0.233 ± 0.081
Cu	1.433 ± 0.185	1.500 ± 0.163	0.967 ± 0.064
Fe	131.857 ± 0.588	85.203 ± 0.777	15.665 ± 0.489
Mn	0.007 ± 0.001	0.010 ± 0.001	0.100 ± 0.006
Pb	0.143 ± 0.008	0.260 ± 0.033	2.000 ± 0.072
V	0.633 ± 0.009	0.567 ± 0.009	0.667 ± 0.038
Zn	0.073 ± 0.005	0.077 ± 0.003	0.333 ± 0.035

Values are means± standard deviation of triplicate determinations

The mean concentrations of some heavy metals in *C. annuum* fruity vegetables are presented in Tables 3. The mean concentrations of the metals in *C. annuum* samples followed the decreasing order: Fe>Al>Cu>Pb>V>Cd>Co>Cr>Zn>Mn. The range of the mean concentrations of the metals (mg kg^{-1}) in the two vegetables from the three market locations are Al(0.041-9.770), Cd(0.010-1.000), Co(0.007-3.266), Cr(0.067-0.233), Cu(0.900-1.500), Fe(15.665-131.857), Mn(0.003-0.100), Pb(0.130-2.000), V(0.133-1.120) and Zn(0.063-0.700). The sample of *C. annuum* from Umungasi location contained the highest Cd, Cu, and Zn concentrations, that from Umuola location contained the highest Co, Mn, Pb and V concentrations while Ahiaudele location contained the highest Al and Fe concentrations. Umungasi and Umuola locations recorded the highest Cr concentration in *C. annuum.* The values of Pb, Cu and Cr reported herein are higher than what they reported while the values of Cd, Zn and Fe are lower than what they reported. Iwegbu *et al.* (2011), also reported the mean concentrations of the metals (mg kg^{-1}) in *C. annuum* from the same location as Pb(0.01), Cu(0.01), Cd(0.20), Zn(13.60), Cr(0.01) and Fe(15.30). The mean concentrations of Pb, Cu, Cr and Fe reported in this study are much higer than what they reported while that of Cd and Zn and lower than their report. Bedasa and Tessama (2016), reported the mean concentrations of heavy metals (mg kg^{-1}) in *C. annuum* grown in the vicinity of the industrial area of Ejersa, Ethiopia, as Cu(9.50), Pb(not detected), Cd(1.20), Cr(not detected) and Zn(100.27). These values are higher than what is reported in this study for Cu, Pb, Cd, Cr and Zn for all the market locations. The mean concentrations of the heavy metals reported *C. annuum* in this study are lower than the FAO/WHO maximum permissible limits (FAO/WHO, 2011), indicating there is no risk associated with the consumption of these vegetables obtained from the various market locations with respect to each metal poisoning.

Heavy Metals Human Health Risks Assessment

While investigating the potential health risks associated with long term consumption of these vegetables contaminated with heavy metals, it became pertinent to calculate the estimated daily intake (EDI), health risk index (HRI), target hazard quotient (THQ), hazard index (HI) and target carcinogenic risk (TCR) factors.

Table 4: Estimated daily intake (EDI) of metals in *C. annuum* fruity vegetable samples (mg/kg BW/day)

Heavy Metals	Ahiaudele	Umungasi	Umuola	RfD (mg/kg/day)
Al	0.0105	0.00335	0.000044	1.0
Cd	0.000011	0.00107	0.000471	0.001
Co	0.000107	0.000018	0.000785	0.03
Cr	0.000142	0.000250	0.000250	0.003
Cu	0.00154	0.00161	0.00104	0.04
Fe	0.141	0.0912	0.0168	0.70
Mn	0.000007	0.000011	0.000107	0.014
Pb	0.000153	0.000278	0.00214	0.0035
V	0.000678	0.000607	0.000714	0.001
Zn	0.000078	0.000082	0.000357	0.3

EDI = Estimated Daily Intake (mg/kg BW/day); CA = *C. annum;* RfD = Reference Oral Dose (USEPA, 2007)

Table 5: Health risk index (HRI) of metals in *C. annuum* fruity vegetable samples

Heavy Metals	Ahiaudele	Umungasi	Umuola
			CA
Al	0.0105	0.00335	0.0000440
Cd	0.0110	1.07	0.471
Co	0.00357	0.000600	0.0262
Cr	0.0473	0.0833	0.0833
Cu	0.0388	0.0402	0.0259
Fe	0.202	0.130	0.0240
Mn	0.000500	0.000786	0.00764
Pb	0.0437	0.0794	0.612
V	0.678	0.607	0.714
Zn	0.000260	0.000273	0.00119

Table 6: Target hazard quotient (THQ) and hazard index (HI) of metals in *C. annuum* fruity vegetable samples

Heavy Metals	Ahiaudele	Umungasi	Umuola
			CA
Al	0.01046	0.00335	0.00004
Cd	0.01071	1.07094	0.47122
Co	0.00357	0.00061	0.02617
Cr	0.04748	0.08318	0.08318
Cu	0.03837	0.04016	0.02589
Fe	0.20173	0.13035	0.02397
Mn	0.00054	0.00076	0.00765
Pb	0.04376	0.07956	0.61197
V	0.67791	0.60723	0.71432
Zn	0.00011	0.00012	0.00051
HI	1.03464	2.01626	1.96492

Table 7: Target carcinogenic risk (TCR) factors of metals in *C. annuum* fruity vegetable samples

Heavy Metals	Fruity vegetables	Ahiaudele	Umungasi	Umuola	CTCR
Pb		1.30×10^{-6}	2.37×10^{-6}	1.82×10^{-5}	2.19×10^{-5}
Cd		4.07×10^{-5}	4.07×10^{-4}	1.79×10^{-4}	6.23×10^{-4}
Cr		7.12×10^{-5}	1.25×10^{-4}	1.25×10^{-4}	3.21×10^{-4}

CTCR = Cumulative Target Carcinogenic Risk

The EDI values of metals in the adult population are presented in Table 4. Except for the EDI values of Cd in *C. annuum* from Umungasi market location, all other EDI values of the metals in the vegetables from the different market locations are less than the reference oral dose (R_{fD}) reported for the respective metals as shown in Table 4 (USEPA, 2007). A reference dose is the US Environmental Protection Agency's maximum acceptable oral dose of a toxic substance (USEPA, 2007). This indicates that the adult population is not at risk of the adverse effects of these metals except in *C. annuum* from Umungasi market location where the population is susceptible to Cd poisoning.

The HRI results for the metals detected in the *C. annuum* samples are shown in Table 5. Except for the HRI values of Cd in *C. annuum* from Umungasi market location (1.07), all other HRI values of the metals in the two vegetables from the different market locations are much less than 1. The values of HRI greater than 1 indicate that the exposed population is unsafe from the adverse health effects of the metals while values of HRI lesser than 1 indicate that the exposed population is safe from the adverse health effects of the metals. Therefore, the exposed population around the study area is not at any risk of heavy metal poisoning except in *C. annuum* from Umungasi location where susceptibility to Cd poisoning is high. Relief measures are therefore required in these areas.

The THQ of the heavy metals are given in Table 6. Except for the THQ values of Cd in *C.*

annuum from Umungasi market location (1.071), all other THQ values of the metals in the vegetable from the different study locations are lesser than 1. If the THQ is less than 1, it indicates that the exposed population is unlikely to experience adverse health effects and vice versa (Rozentale *et al*., 2015). The HI is used to evaluate the non-carcinogenic risk potential of the combined metals. If the value of HI is greater than 1, there is a potential adverse health effects on the exposed population and mitigation measures are required (Wang *et al*., 2005). The HI values are greater than 1 in the vegetables from all the study locations. This means that the population in all the study locations are exposed to the combined hazard effects of these heavy metals when these vegetables are consumed.

Not all heavy metals are carcinogenic, however, Pb, Cd and Cr are well-known carcinogenic agents (USEPA, 2010). The target carcinogenic risks (TCR) and cumulative target carcinogenic risks (CTCR) of Pb, Cd and Cr in the studied vegetables are presented in Table 7. The carcinogenic risk is the lifetime probability of an individual to develop any type of cancer due to carcinogenic daily exposure to a contaminant over a lifetime. The TCR values of Pb in the studied vegetables ranged from 1.18-E06 to 1.82-E05, Cd ranged from 4.07-E05 to 4.07-E04 while Cr ranged from 3.59-E05 to 1.25-E04. According to the United States Environmental Protection Agency, the acceptable or tolerable TCR for regulatory purposes is in the range of 10^{-6} to 10^{-4} (USEPA, 2011). The TCR values of Pb in the studied vegetables are within the range of permissible lifetime risks for carcinogens. However, except for the TCR values of Cd in *C. annuum* from Umungasi (4.07-E04) and Umuola (1.79-E04) market locations, all the other TCR values for Cd are below the threshold cancer limit. Also, except for the TCR values of Cr in *C. annuum* from Umungasi and Umuola (1.25-E04) market locations, all the other TCR values for Cr in the studied vegetables are below the threshold cancer limit. Moreover, the cumulative cancer risk as a result of exposure to multiple carcinogenic heavy metals due to the consumption of a particular type of vegetable was assumed to be the sum of the individual heavy metal risks (Sultana *et al*., 2017). The CTCR values of Pb in the studied vegetables and locations are within the acceptable or tolerable range for cancer risk. Meanwhile, the CTCR values of Cd and Cr in the studied vegetables and in all the locations are above the threshold cancer risk limit. From the TCR and CTCR of the studied vegetables, there are potential carcinogenic risks among the population around those study areas where the recommended threshold risks limits were exceeded and therefore mitigation measures are required in those areas.

Conclusion and Recommendations: The TCR and CTCR of the studied vegetable are potential carcinogenic risks among the population around those study areas where the recommended threshold risks limits were exceeded and therefore mitigation measures are required in those areas.

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EXPERIMENTAL AND QUANTUM STUDIES ON THE CORROSION INHIBITION OF ZINC IN HYDROCHLORIC ACID MEDIUM USING SCHIFF BASES.

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ABSTRACT

The corrosion inhibition of zinc plates in 0.5M HCl in the presence and absence of 4-{[(Z)-(4-chlorophenyl) methylidene} amino)-N-(5-methy-l-furan-3-yl) benzenesulfonamide herein referred to as (MMBS) and 4-{[(Z)-(4-dimethyl amino) phenyl] methylidene} amino)-N-(5-methyl furan-3-yl) benzenesulfonamide herein refers to as (CMBS) was investigated at temperature ranges of 303 K to 343 K. Their inhibition performances were tested by weight loss and quantum chemical techniques and were characterised using Fourier Transform Infrared spectrophotometer (FT-IR). The FT-IR spectroscopy showed that the synthesised Schiff bases contained some functional groups which may have aided in the inhibition of the metal species under consideration. The results obtained from the weight loss method showed that inhibition efficiencies of the inhibitors increased as the concentrations of the Schiff-base molecules increased and with the highest inhibition efficiency observed at the optimum concentration of 1.0 g/L employed but decreased with rise in temperature. The inhibition efficiencies for zinc plate, were 38.19 % and 39.98 % for (MMBS) and (CMBS) respectively. Inhibition efficiencies were also found to decrease with increase in temperature. The inhibition efficiencies followed the order; (MMBS) < (CMBS). The Kinetic data obtained showed that the corrosion process followed first order kinetics. The following adsorption isotherms models including Langmuir and Freundlich employed in the interpretation of the inhibition data showed that Langmuir model provided the best fit to the experimental data ($R^2>0.96$). Thermodynamic studies of the inhibition process showed that the ΔG_{ads} values for (MMBS) and (CMBS) were both negative indicating the spontaneity of the reaction and the values were less than -20 $kJmol^{-1}$, indicating that the mechanism of adsorption is physisorption. The enthalpy values were positive for (MMBS) (121.650 – 148.904 $Jmol^{-1}K^{-1}$) on mild steel but negative for (MMBS) (-2.1213 to - 0.4059 $Jmol^{-1}K^{-1}$) on zinc showing that the reaction was endothermic for inhibition of mild steel but exothermic for inhibition of zinc. The quantum chemical parameters such as HOMO, LUMO, $E_{HOMO;}$ E_{LUMO}, and Energy gap (ΔE), aided in the elucidation of the probable points of interaction of these inhibitors on zinc. The results obtained from the chemical studies showed that there exists a relationship between the inhibitors' efficiency and the energy gap (ΔE), energy of the highest unoccupied molecular orbital (E_{Homo}), energy of the lowest occupied molecular orbital (E_{Lumo}), dipole moment (μ), softness (σ), as well as the hardness (η) of the inhibitor. The quantum chemical parameter, as indicators to their comparative inhibition potentials, agreed with experimental data.

Keywords: Corrosion inhibitions, Schiff Bases, Experimental & Quantum studies of corrosion inhibition

INTRODUCTION: The surface of zinc, iron and steel, existing in many forms ranging from exposed metal to oxidized metal and to different degrees of states, finds many industrial applications (Ballesteros *et al*., 2015; Barros *et al*., 2016; Souza *et al*., 2016**)**. Some investigations have emphasized the importance for the protection of the metal surfaces in various applications (Amitha and Bharathi, 2012). The spontaneous destruction of metals, starting from their surfaces, due to the corrosive attack of environment brings the undesirable changes at the surfaces and reduces their lifetime, strength and changes the desirable properties of metal surfaces. In some cases, the corrosion products formed are toxic. An accurate description of surface not only helps to identify the prevailing form of corrosion but also the prescription of appropriate anti-corrosion measures. Acid solutions, (in particular HCl solutions) are widely used in industries for many purposes, such as acid pickling, industrial acid cleaning, acid descaling and oil well acidizing (Ochoa *et al*., 2013 Danaee *et al*., 2013; Gerengi *et al*., 2014; Rocha et al., 2014). Due to the general aggressive nature of acid solutions, the corrosive attack will be severed (Ochoa *et al*., 2013) and bring undesirable changes at the surface of metals. Chemical inhibitors are often used to control the corrosive attack and acid consumptions of environment (Ghasemi *et al*., 2013; Santana *et al*., 2015). Most of the well-known corrosion inhibitors are the organic compounds containing N, S, O and P atoms Santos *et al*., 2017; Barreto *et al*., 2018).

Zinc ions have long been considered as valuable corrosion inhibitors for carbon steel in aerated water because of the protection afforded by a cathodic polarization mechanism. Zinc increases the cathodic polarization and hence inhibits corrosion of steel. Its action is attributed to precipitation of zinc hydroxide on the cathodic areas because of locally high pH. Moreover, at the cathodes, oxygen is reduced with the generation of hydroxyl ions. This zinc can be added as any zinc containing salt, but most people use either zinc sulphate or zinc chloride as the source. Zinc chloride is readily available as a 50% aqueous solution for ease of handling and safety as well as economy (Thomas, 1991).

The adverse effect of corrosion can be seen in daily life. Corrosion causes accidents in industry, on highways, and in homes. It is wasteful financially, costing industrialized nations 4 -5% of their gross domestic products (GDP) annually. A little knowledge of electrochemistry, material science and corrosion could save nations some 25% of this loss (Hansson, 2011).

Corrosion chemistry is the application of science and art to prevent or control corrosion damage in a safe and economical manner. To perform this function properly, the corrosion scientist must rely on experimental research. This is because the major aspects of corrosion chemistry are largely empirical in nature. Corrosion is the degradation of the metallic properties of a metal. It progressively expends limited mineral resources and the energy utilized in the mining and processing of metals together with that employed in the production of machinery and infrastructures. Corrosion is known to affect practically all facet of contemporary development or advancement. Therefore, the deterrence of corrosion is of foremost commercial and ecological significance. The world corrosion organization has posited that the annual cost of corrosion globally is approximately 2.2 trillion US dollars. This represents more than 3 % of the World's Gross Domestic Product (GDP) (Koch *et al*., 2002). In Nigeria, the cost of corrosion has not yet been surveyed; however, the Central Intelligence Agency (CIA) world fact book on Nigeria puts it at an estimated 3.2 billion USD annually (CIA, 2006). This implies that further increases in corrosion control measures are required in every area of human life and industry.

Corrosion Inhibitors are chemical substances which can retard the corrosion of metals when added in small concentrations to the fluids in contact with the metal. When the environment is too aggressive for unprotected metal surfaces, the option to reduce corrosion problems is the use of inhibitors (Papavinasam, 1999). They belong to the surfactant category of molecules (surface-active agents), which preferentially adsorb onto any surface or interface in a system and alter the surface and interfacial free energies, even at low concentration (Hernandez *et al*., 2003). The surface-active properties come from their amphipathic, lipid like, molecular structure, which contains a polar head group having strong attraction to water, referred to as a hydrophilic head and a non-polar hydrocarbon chain having little attraction to water, called a hydrophobic tail.

Schiff Base Schiff base a compound named after Hugo Schiff has the general structures $R_2C=NR^1$ (R'=H) (IUPAC). It is synthesized from the chemical reaction between a primary amine with an aldehyde or ketone to yield imine (Schiff base). Thus, Schiff base is derived from imines being either secondary ketoimines or secondary aldimines depending on its structure.

Several special naming systems exist for this compound. For instance, a Schiff base generated from an aniline where' R' is phenyl or a substituted phenyl can be called an anil (IUPAC). The word Schiff base usually applies to these compounds when they are being used as ligands to form co-ordination complexes with metal ions. Schiff bases do not easily exist naturally but are mainly synthesize artificially and are used to form important catalyst for example Jacobsen's catalyst.

Despite the name a particular Schiff base is identified with; they have the formula shown in Figure 1 below:

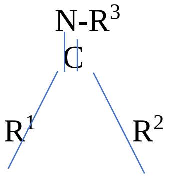

Fig. 1: showing structure of Schiff base

Materials and Methods: The Zinc whose percentage composition by weight was Fe (45.60), Si (0.50), Mn (0.12), Cu (0.08), Si (0.06), Cr (0.05) and Zn (53.48) was mechanically cut into different dimensions of 3cm x 2cm. Each coupon was sandpapered using different grades of sandpapers (rough and then smooth) until a mirror polished surfaces were obtained. The coupons were degreased by washing with ethanol, washed with de-ionised water, and cleaned with acetone and allowed to dry in the air before preservation in a desiccator.

Preparation of Schiff Base (MMBS). The Schiff bases with sulpha compound were prepared as follows: an ethanolic solution (50 ml) of p-chlorobenzaldehyde (2.8114 g, 0.01 mol) was added to the solution of sulphamethoxazol (5.060 g, 0.01 mol) in 50 ml ethanol along with two drops of HCl. The resulting solution was refluxed with stirring for 12 h and then filtered to remove the insoluble sulpha drug, observed. The filtrate so obtained was concentrated on a water bath and left overnight at room temperature when whitish-yellow crystals of Schiff bases were separated out from the solution. The crystals thus obtained were washed with ethanol and dried in a vacuum. The yield was 55 %. The Schiff base was characterized using Fourier Transform Infrared (FTIR) spectrophotometer. These processes are represented in the reaction scheme below

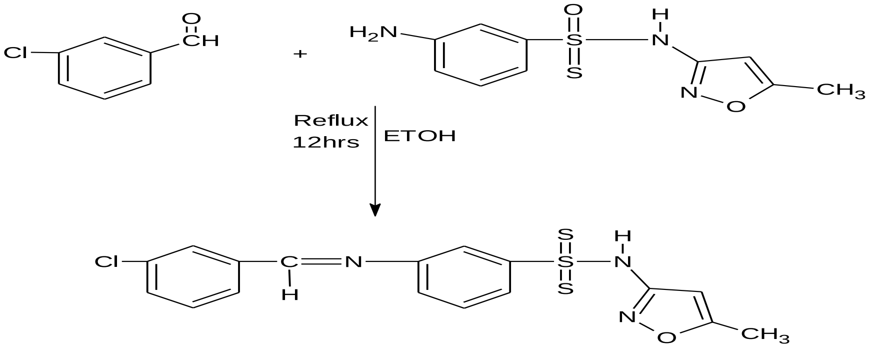

Fig: 2: [(Z)-(4-chlorophenyl)methylidene}amino)-N-(5-methylfuran-3-yl) benzenesulfonamide (MMBS).

Preparation of Schiff Base (CMBS) The Schiff bases with sulpha drugs were prepared as follows: an ethanolic solution (50 ml) of p-dimethylaminobenzaldhyde (2.9838 g, 0.01 mol) was added to the solution of sulphamethoxazol (5.060 g, 0.01 mol) in 50 ml ethanol along with five drops of HCl. The resulting solution was refluxed with stirring for 12 h and then filtered to remove the insoluble sulpha drug, if any. The filtrate so obtained was concentrated on a water bath and left overnight at room temperature until a pink crystals of Schiff bases separated out from the solution. The crystals thus obtained were washed with ethanol and dried in a vacuum. The yield was 62%. The Schiff base was characterized using Fourier Transform Infrared (FTIR) spectrophotometer. The processes are represented in the reaction schemes below.

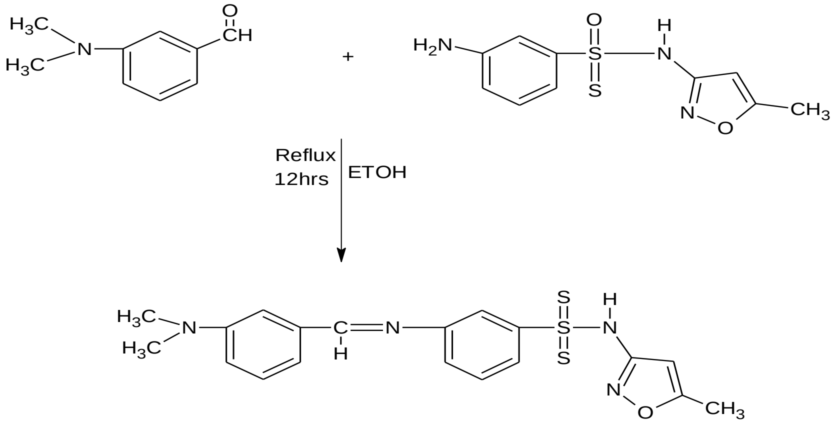

Fig.3: {[(Z)-(4-dimethylamino)phenyl]methylidene}amino)-N-(5-methylfuran-3yl)benzenesulfonamide (CMBS).

0.5 M HC1 solution was prepared from the stock solution by using dilution principle.

Preparation of Inhibitor Solutions 0.5 M HC1 was used as the test solution and was prepared from the reagent grade (E- Merck) using de-ionized water. Different concentrations of the inhibitors 0.2 g/l, 0.4 g/l, 0.6 g/1, 0.8 g/l, and 1.0 g/l were employed for the inhibition studies. These were prepared by dissolving the required amount of Schiff base compound into 100 ml of 0.5M HC1 and the mixture was stirred at room temperature.

CORROSION STUDIES: Weight loss

The pre-weighed zinc coupons were suspended vertically in aerated unstirred 100 ml of 0.5 M HCl with and without inhibitor for 2-hour interval. After every 2 hours, the coupons were removed (i.e., withdrawn from the test solution with the aid of a fishing line hung through the holes bored at their upper edge), immersed into the washing solution containing 22 % NaOH and 22 g/1 zinc dust to quench the corrosion process. The zinc coupons were washed with brush to remove the corrosion products and were rinsed with distilled water. The weight losses were recorded in grams after air drying. In each case, triplicate experiments were performed. The procedures were repeated for 2, 4, 6, 8, and 10-hour intervals. The effect of increase in temperature on zinc corrosion and corrosion inhibition was investigated by repeating the experimental at temperatures: 313 K, 323 K, 333 K and 343 K respectively under the same conditions. All tests were run in triplicate and the data obtained were tabulated. From the average weight loss (mean of three replicate analyses) results, corrosion rate of the metals (CR), surface coverage (ϴ), and inhibition efficiencies (IE%) were calculated.

Quantum Chemical Calculation

To study the effect of molecular structure on inhibition efficiency, quantum chemical calculations are usually carried out using Density Functional Theory (DFT) under the Generalized Gradient Approximation (GGA) with Pendix-Bunke-Fruzerhof (PBF) exchanging correlation function as implemented in D mol^{-1} module using material studio software package version 6.0. A double numerical basis set augmented with polarization function is employed to describe the valence electrons. The geometries were fully optimised. Spin unpolarisation schemes were implored when carrying out the calculation.

The SCF and energy convergence threshold were set at 1.0 x 10^{-5} Ha and 2.0 x 10^{-5} Ha respectively. The quantum chemical parameters determined are energies of highest occupied and lowest unoccupied molecular orbital (E_{Homo} and E_{Lumo} respectively), energy gap (ΔE) which was calculated using the equation (1) (Fang and Li, 2002).

$$\Delta E = E_{Homo} - E_{Lumo} \qquad (1)$$

Global hardness, which is a measure of the resistance of an atom to charge transfer, was estimated using equation (2).

$$\eta = 1/2[\,E_{Homo} - E_{Lumo}] \qquad (2)$$

Chemical softness (δ), a parameter which describes the capacity of an atom or group of atoms to receive electrons. It is the inverse of global hardness and was estimated using equation (3) (Yang and Parr, 1985).

$$\sigma = \frac{1}{\eta}\,2[\,E_{Homo} - E_{Lumo}] \qquad \mathbf{(3)}$$

The Maximum number of electrons transferred (ΔNmax) in the chemical reaction was calculated using equation (4)

$$\Delta N_{max} = \frac{\chi}{2\eta} \qquad (4)$$

Where χ is the electronegativity and it is estimated as

$$\chi = 1/2[\,E_{Homo} - E_{Lumo}] \qquad (5)$$

The equation used to estimate electrophilicity index (ω) was given by (Yang and Parr, 1985) as shown in equation (6).

$$\omega = \frac{\mu^2}{4\eta} \qquad (6)$$

The Mulliken charges (Q) for nucleophilic and electrophilic attacks were also determined.

RESULTS AND DISCUSSION:

Fourier Transform Infrared Spectroscopy

The Schiff base (inhibitor) molecules were characterised using infrared (IR) spectrophotometer. The (IR) spectra of the Schiff bases were recorded using a Perkin-elmer-2000 FT-IR spectrophotometer with resolving power of 4 cm^{-1}.

Fourier Transform Infrared (FTIR) Spectroscopy: The FTIR spectra of all the synthesized Schiff base compounds are shown in Figures 4 and 5. The functional groups present in the sulpha drug based synthesized Schiff base ligands in the present investigation are shown in Figures. 4 and 5. The formation of the Schiff base ligands is supported by the appearance of a strong band at 1603–1618 cm^{-1} due to s(C=N) (azomethine) in the IR spectra of these ligands. All the Schiff base ligands in the present investigation exhibit a broad band centered at 3086–3477 cm^{-1}. This suggests the involvement of the OH group in the intramolecular hydrogen bonding with the lone pair of azomethine nitrogen (Maurya *et al*., 1997). It also suggests that the ligands exist in enol form in the solid state (Maurya *et al*., 1996). All the Schiff base ligands used in this investigation exist in enol form as discussed above. Hence, they possess three potential donor sites such as the azomethine nitrogen, sulphonamide (SO_2NH) oxygen or nitrogen and the ring nitrogen of the sulpha drug. The appearance of sharp symmetric band at 1158 and 1161 cm^{-1} in the MMBS and CMBS ligands respectively is assigned s(O=S=O) to). The appearance of asymmetric band at 1314–1330 cm^{-1} in the ligands was assigned (Maurya et al., 2007). The m(NH) mode(s) of the sulphonamide group/amino group of the Schiff bases are observed at 3387 and 3378 cm^{-1} for MMBS and CMBS ligands. The ligands display a sharp and strong band due to m(C=N) of the azomethine group at 1618–1608cm^{-1}.

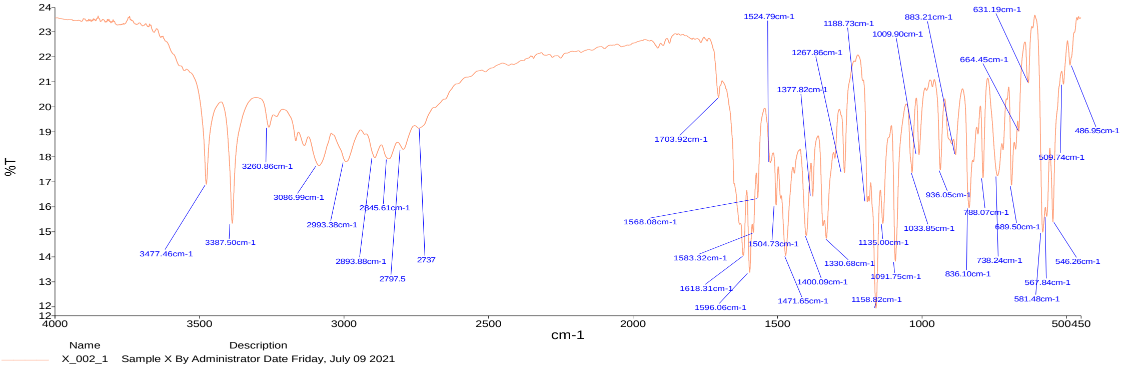

Fig 4: FTIR spectrum of MMBS

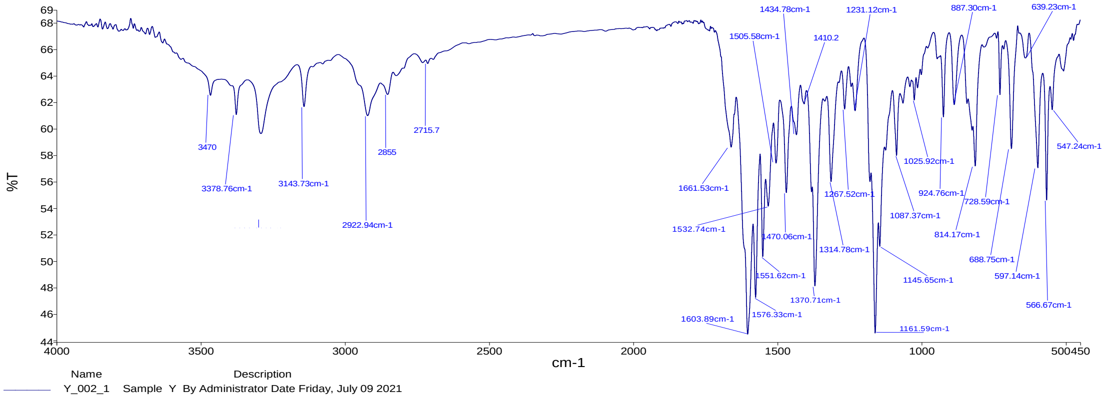

Fig 5: FTIR spectrum of CMBS.

Weight Loss Results

The weight loss of the zinc coupons in the presence of each of the inhibitors at various concentrations (0.0 g/l, 0.2 g/l, 0.4 g/l, 0.6 g/l, 0.8 g/l and 1.0 g/l) from 303 K to 343 K are presented in Tables below. The weight loss decreased with decrease in system temperature and increase in inhibitors concentration. Hence increase in temperature hindered the efficiency of the inhibitors in weight loss after 2 h interval of immersion shows that weight loss decreased with increase in concentration of inhibitors but decreased as temperature increased in the same time interval. This direct relationship shows that the adsorption mechanism may be predominantly physisorption. In the presence of inhibitor at each temperature, it is also observed that weight loss increased as temperature increased. The plot of weight loss against time is shown in Figures. 6 and 7

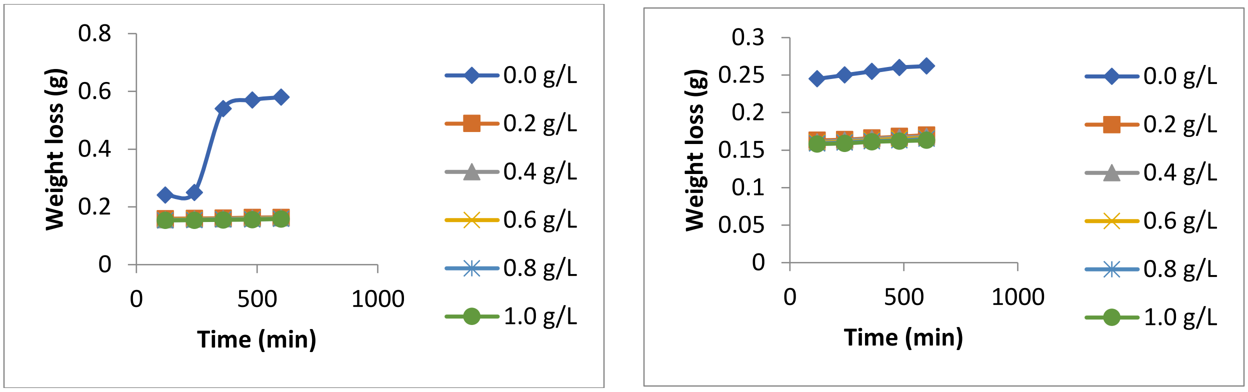

Fig. 6: Plot of weight loss (zinc plate) vs time at different concentrations of MMBS (a) at 303 K and (b) at 313 K

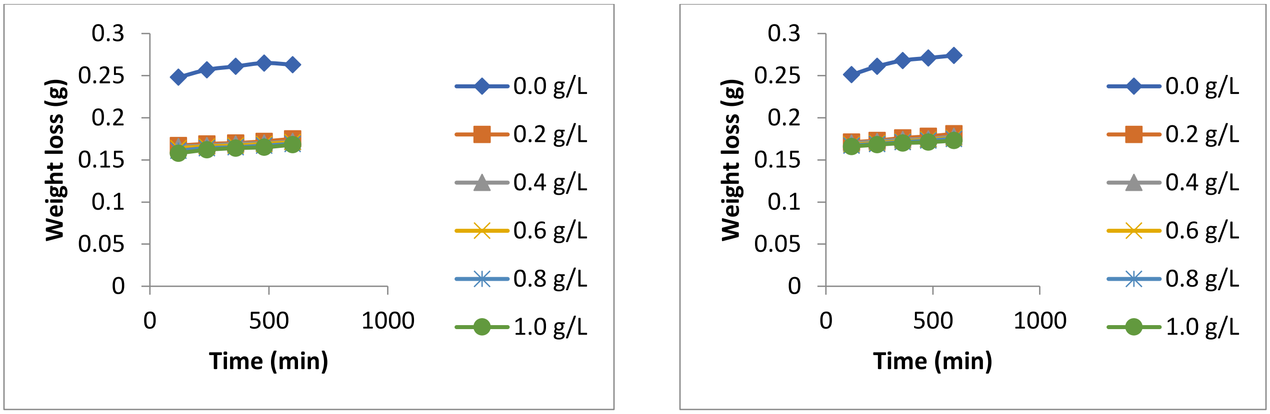

Fig. 7: Plot of weight loss (zinc plate) vs time at different concentrations of MMBS (a) at 323 K. and (b) at 333 K.

Surface Coverage and Inhibition Efficiency: The inhibition efficiencies of the various inhibitors at temperature range of 303 K – 343 K, shows that increased temperature results in the weakening of the attractive forces between the active sites of the zinc metal and the inhibitors at elevated temperatures. Moreover, increase in concentration of inhibitors that results in increased efficiency could be attributed to the formation of protective covering layers on the metal surfaces, which created a barrier between the metal surfaces and the inhibitors, resulting to decrease in weight loss (Refat and Ishaq, 2013; Eddy *et al*., 2014). Hence, the extent of adsorption decreases with increase in temperature and thus the degree of inhibition decreased with increase in temperature accordingly Ameh *et al*., 2012).

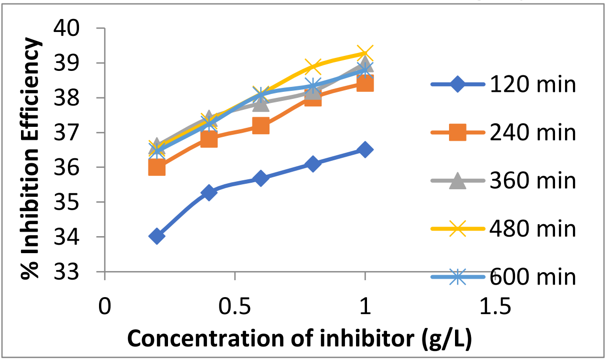

Fig.8: Plot of I.E., vs concentration of inhibitor MMBS for Zinc at 303 K.

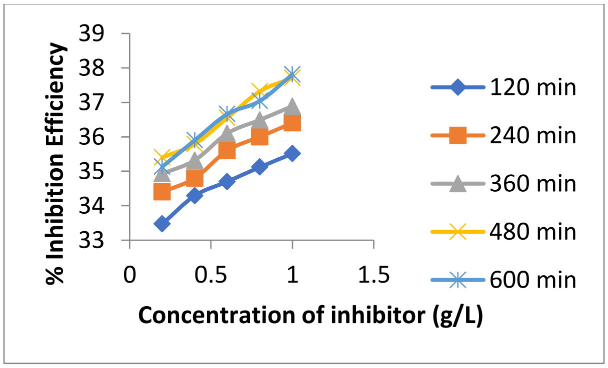

Fig.9: Plot of I.E., vs concentration of inhibitors MMBS for Zinc at 313 K

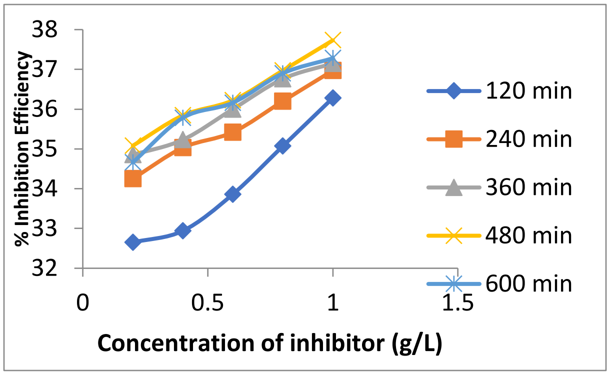

Fig.10: Plot of I.E., vs concentration of inhibitor MMBS for Zinc at 323 K

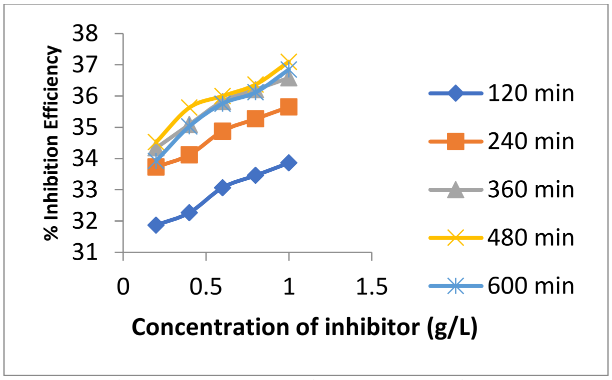

Fig.11: Plot of I.E., vs concentration of inhibitor MMBS for Zinc at 333 K.

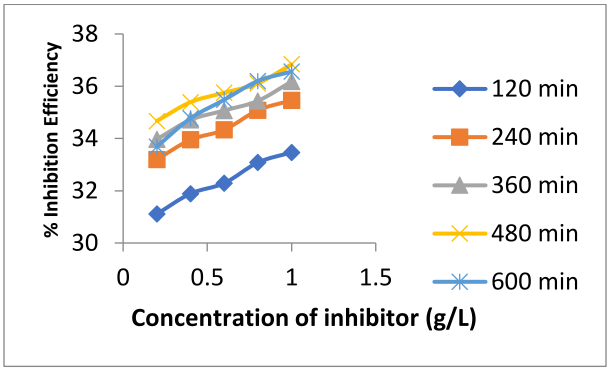

Fig.12: Plot of I.E., vs concentration of inhibitor MMBS for Zinc at 343 K.

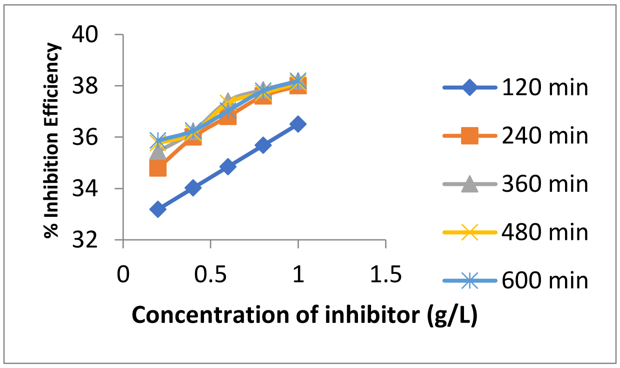

Fig.13: Plot of I.E., vs concentration of inhibitor CMBS for Zinc at 303 K.

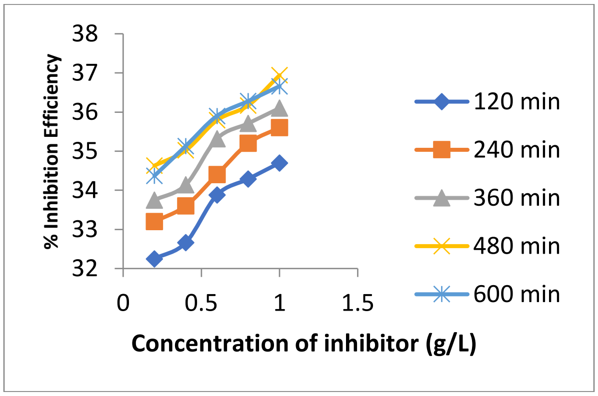

Fig.14: Plot of I.E., vs concentration of inhibitor CMBS for Zinc at 313 K.

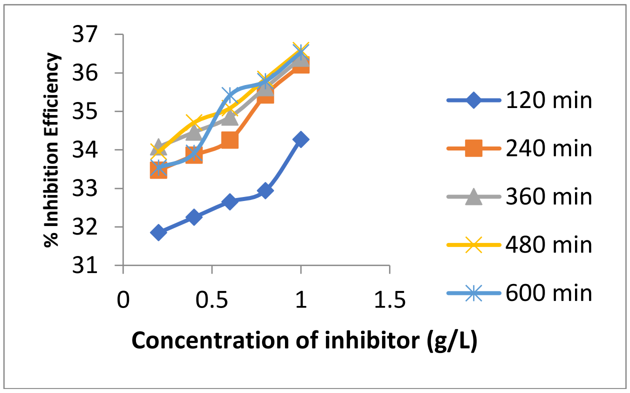

Fig.15: Plot of I.E., vs concentration of inhibitor CMBS for Zinc at 323 K.

Table 1: Surface coverage and inhibition Efficiency of MMBS on zinc at different temperature.

Temperature	Concentration	Surface coverage	% I. E
303 K	0.0 g/L	-------------	
	0.2 g/L	**0.3402**	**34.02**
	0.4 g/L	**0.3527**	**35.27**
	0.6 g/L	**0.3568**	**35.68**
	0.8 g/L	**0.3610**	**36.10**
	1.0 g/L	**0.3651**	**36.51**
313 K	0.0 g/L	--------------	
	0.2 g/L	**0.3347**	**33.47**
	0.4 g/L	**0.3429**	**34.29**
	0.6 g/L	**0.3470**	**34.70**
	0.8 g/L	**0.3512**	**35.12**
	1.0 g/L	**0.3551**	**35.51**
323 K	0.0 g/L	-----------------	
	0.2 g/L	**0.3265**	**32.65**
	0.4 g/L	**0.3294**	**32.94**

	0.6 g/L	**0.3386**	**33.86**
	0.8 g/L	**0.3507**	**35.07**
	1.0 g/L	**0.3628**	**36.28**
333 K	0.0 g/L	----------------	
	0.2 g/L	**0.3187**	**31.87**
	0.4 g/L	**0.3227**	**32.27**
	0.6 g/L	**0.3307**	**33.07**
	0.8 g/L	**0.3346**	**33.46**
	1.0 g/L	**0.3386**	**33.86**
343 K	0.0 g/L	----------------	
	0.2 g/L	**0.3111**	**31.11**
	0.4 g/L	**0.3189**	**31.89**
	0.6 g/L	**0.3229**	**32.29**
	0.8 g/L	**0.3308**	**33.08**
	1.0 g/L	**0.3347**	**33.47**

Table 2: Surface coverage and inhibition Efficiency of CMBS on zinc at different temperature.

Temperature	Concentration	Surface coverage	% I. E
303 K	0.0 g/L	-------------	
	0.2 g/L	**0.3319**	**33.19**
	0.4 g/L	**0.3402**	**34.02**
	0.6 g/L	**0.3485**	**34.85**
	0.8 g/L	**0.3568**	**35.68**
	1.0 g/L	**0.3651**	**36.51**
313 K	0.0 g/L	--------------	
	0.2 g/L	**0.3225**	**32.25**
	0.4 g/L	**0.3266**	**32.66**
	0.6 g/L	**0.3388**	**33.88**
	0.8 g/L	**0.3429**	**34.29**
	1.0 g/L	**0.3470**	**34.70**
323 K	0.0 g/L	-----------------	
	0.2 g/L	**0.3185**	**31.85**
	0.4 g/L	**0.3225**	**32.25**
	0.6 g/L	**0.3265**	**32.65**
	0.8 g/L	**0.3294**	**32.94**
	1.0 g/L	**0.3427**	**34.27**
333 K	0.0 g/L	----------------	
	0.2 g/L	**0.3068**	**30.68**
	0.4 g/L	**0.3107**	**31.07**
	0.6 g/L	**0.3147**	**31.47**
	0.8 g/L	**0.3187**	**31.87**
	1.0 g/L	**0.3227**	**32.27**
343 K	0.0 g/L	----------------	
	0.2 g/L	**0.2914**	**29.14**
	0.4 g/L	**0.3032**	**30.32**
	0.6 g/L	**0.3111**	**31.11**
	0.8 g/L	**0.3150**	**31.50**
	1.0 g/L	**0.3229**	**32.29**

Corrosion Rate

The corrosion rates of the zinc plates in the presence and absence of inhibitors from 303 K – 343 K are presented in Tables 3-4. The tables show that corrosion rate decreased in the presence of inhibitors, which indicates that the compounds have inhibitory effect on the corrosion process. The decrease in the corrosion rate in inhibited acid solutions suggests the mitigating effect of the inhibitors on the corrosion rate of zinc plate. This phenomenon also supports physical adsorption mechanism (Olasehinde *et al.*, 2012; Eddy *et al.*,2014, Kazaure *et al.*, 2015).

Table 3: Corrosion Rates of zinc using MMBS at various Concentrations and Temperature

Temperature (K)	Concentration (g/L)	Weight Loss, ΔW (g)	Rate of corrosion (mgcm^{-2}min^{-1})
303	0.0	0.241	0.3347
	0.2	0.159	0.2208
	0.4	0.156	0.2167
	0.6	0.155	0.2153
	0.8	0.154	0.2139
	1.0	0.153	0.2125
313	0.0	0.245	0.3403
	0.2	0.163	0.2264
	0.4	0.161	0.2236
	0.6	0.160	0.2222
	0.8	0.159	0.2208
	1.0	0.158	0.2194
323	0.0	0.248	0.3444
	0.2	0.167	0.2319
	0.4	0.166	0.2306
	0.6	0.164	0.2278
	0.8	0.161	0.2236
	1.0	0.158	0.2194
333	0.0	0.251	0.3486
	0.2	0.171	0.2375
	0.4	0.170	0.2361
	0.6	0.168	0.2333
	0.8	0.167	0.2319
	1.0	0.166	0.2306
343	0.0	0.254	0.3528
	0.2	0.175	0.2431
	0.4	0.173	0.2403
	0.6	0.172	0.2389
	0.8	0.170	0.2361
	1.0	0.169	0.2347

Table 4: Corrosion Rates of zinc using CMBS at various Concentrations and Temperature

Temperature (K)	Concentration (g/L)	Weight Loss, ΔW (g)	Rate of corrosion (mgcm^{-2}min^{-1})
303	0.0	0.241	0.3347
	0.2	0.161	0.2236
	0.4	0.159	0.2208
	0.6	0.157	0.2181
	0.8	0.155	0.2153
	1.0	0.153	0.2125
313	0.0	0.245	0.3403
	0.2	0.166	0.2306
	0.4	0.165	0.2292
	0.6	0.162	0.2250
	0.8	0.161	0.2236
	1.0	0.160	0.2222
323	0.0	0.248	0.3444
	0.2	0.169	0.2347
	0.4	0.168	0.2333
	0.6	0.167	0.2319
	0.8	0.166	0.2306
	1.0	0.163	0.2264
333	0.0	0.251	0.3486
	0.2	0.174	0.2417
	0.4	0.173	0.2403
	0.6	0.172	0.2389
	0.8	0.171	0.2375
	1.0	0.170	0.2361

343	0.0	0.254	0.3528
	0.2	0.180	0.2500
	0.4	0.177	0.2458
	0.6	0.175	0.2431
	0.8	0.174	0.2417
	1.0	0.172	0.2389

Kinetics Studies of Zinc Corrosion in HCl Solution in The Presence of Inhibitor.

The kinetics of the zinc's corrosion in 0.5 M HCl solution and inhibitor systems were studied at 303 ^{0}K – 343 ^{0}K by fitting the corrosion data into first order rate law. Figures. 16-17 show the dependence of log W_t (weight of zinc at time, t) as a function of time. As depicted in the figures 18-19, the corrosion data fitted into the rate law for first – order reaction as expressed in equation 5 (Abiola and James, 2010; Abiola *et al*., 2013; Abiola *et al*., 2013).

$$\log [W_i - \Delta W_t] = -\frac{k}{2.303} t + \log W_i \qquad (7)$$

Where k is the first – order rate constant, Wi is the initial weight of zinc sample

ΔW_t is the weight loss of zinc sample at time t and the term ($W_i - \Delta W_t$) is the residual weight of zinc sample at time t and can be designated as W_t.

The obtained plots of -log (weight loss) vs. time are linear with negative slopes. These confirm a first – order kinetics for the corrosion of zinc in HCl solution in the absence and presence of inhibitor.

Figures 16 – 19 reflects the reaction order with respect to zinc plates. This result (Figures.16 - 19), suggests that the adsorption of the inhibitor's molecules do not influence the anodic reaction order. As seen from Figures. 16 – 19, similar plot was obtained when log (weight loss) Wt was plotted against time for mild steel in HCl solution with and without inhibitor (control). The rate constants (K) and half-lives ($t_{1/2}$) of the corrosion process were calculated and presented in Tables 5-6. The tables show that rate constant decreased with increase in concentration of inhibitor and study temperatures which suggests physisorption (Odiongenyi *et al*., 2015). The plots intervals that the corrosion reaction follows first order for zinc plates due to high R^2 values. This suggest that the corrosion process is a linear one and physisorption (Eddy *et al*., 2012). This suggest that the rate of the corrosion inhibition is directly proportional to the concentration of the inhibitor. Moreover, half-life ($t_{1/2}$) increased as the inhibitors concentration increases. However, half-life did not actually increase with the increase in the inhibitors concentration as should have been expected, though increase in temperature results to decrease in half-life. Similar results were reported on the adsorption of corrosion inhibitor on metals in HCl solution (Abiola and James, 2010; Abiola *et al*., 2013; Abiola *et al*., 2013). The corrosion rate calculations from eexperiment indicate that the zinc weight loss decrease with increase in the concentration of the inhibitors (MMBS and CMBS) and increases with decreases in the concentration of the inhibitor (MMBS and CMBS). This is graphically shown in Figures 16 to 19. The calculated values of the corrosion rate of zinc are also shown in Tables 4.10 to 4.29 (Dim *et al*., 2012).

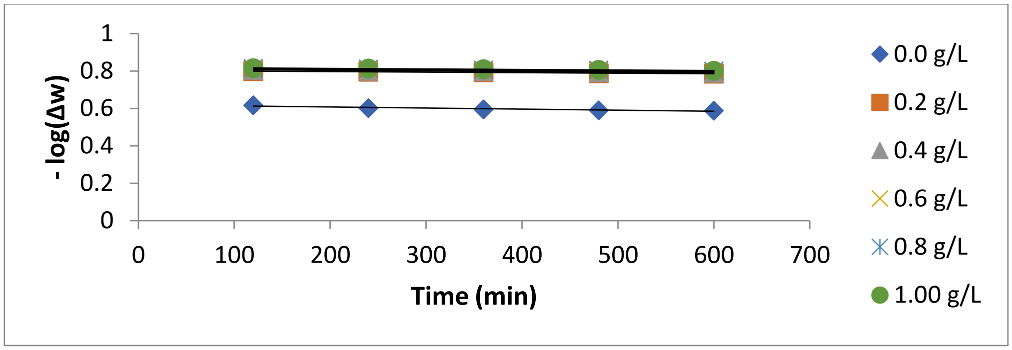

Fig.16: A plot of –log (weight loss of zinc) vs. time for MMBS at 303 K

Table 5: Rate constants and half-lives of zinc for MMBS at 303 K

Concentration (g/L)	Slope	R^2 value	Rate Constant, $k(min^{-1})$	Half-life (mins)	Intercept
0.0	6.00E-05	0.8909	32.5612	2.128 x 10^{-2}	0.6192
0.2	3.00E-05	0.9823	13.7806	16.712 x 10^{-2}	0.8026
0.4	3.00E-05	0.9857	13.7806	16.712 x 10^{-2}	0.8104
0.6	3E-0.5	0.9702	13.7806	16.712 x 10^{-2}	0.8119
0.8	3.00E-05	0.9476	13.7806	16.712 x 10^{-2}	0.8158
1.0	3E-0.5	0.973	13.7806	16.712 x 10^{-2}	0.8192

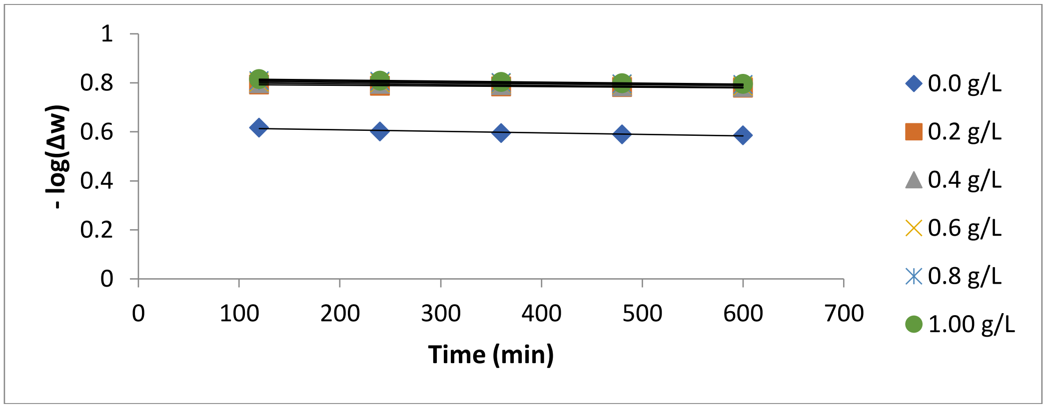

Fig. 17: A plot of –log (weight loss of zinc) vs. time for CMBS at 303 K

Table 6: Rate constants and half-lives of zinc for CMBS at 303 K

Concentration (g/L)	Slope	R^2 value	Rate Constant, $k(min^{-1})$	half-life (mins)	Intercept
0.0	6.00E-05	0.9052	32.5612	7.073 x 10^{-2}	0.6208
0.2	3.00E-05	0.9711	13.7806	16.712 x 10^{-2}	0.7953
0.4	4.00E-05	0.985	20.0408	11.492 x 10^{-2}	0.8034

0.6	3.00E-05	0.9713	13.7806	16.712×10^{-2}	0.8092
0.8	4.00E-05	0.9845	20.0408	11.492×10^{-2}	0.8146
1.0	4.00E-05	0.9867	20.0408	11.492×10^{-2}	0.8197

This process was repeated using the two inhibitors of MMBS and CMBS and at varying temperatures of 303K, 313K, 323K, 333K,343K. The rate constants seen from the tables were determined from the slopes from which the half-lives were calculated by an equation $t_{1/2} = 0.693/k$. In this study, the rate is dependent on the concentration of the aggressive medium. The fitting of the corrosion data into the first order model shows that the corrosion of the zinc in 0.5 M HCl in the presence and absence of inhibitors follows first-order kinetics. This agrees with the results of other researchers (Kazaure *et al*., 2015; Ijuo *et al*., 2016). As observed from the tables, the rate constant decreases with inhibitor concentration. However, at initial temperature (303 K), the rate constants were observed to increase with concentration, though this did not follow a regular pattern. The increase in half-life observed by the addition of inhibitor shows that inhibition process actually took place. This indicates that the time taken for weight of zinc to come to half its original weight has been elongated. Therefore, the half-life increases as corrosion rate decreases. Except for some few occasions where there were inconsistencies.

Activation Energy and Frequency Factors

In acidic solution, the corrosion rate is related to temperature by the Arrhenius equation.

$$K = Ae^{-Ea/RT} \qquad (8)$$

where Ea is the apparent activation energy and A - frequency factor, R - gas constant, T - Temperature. The activation energy and the Arrhenius constant of the corrosion reactions were obtained, by making use of eqn. 8. A plot of ln CR vs. $\frac{1}{T}$ according to Arrhenius equation and the results are shown in Tables 7-8. Linear plots were obtained for all the corrosion of the surfaces in the absence and presence of the inhibitors. The values of Ea were computed from the slope of the linear plots. It is clear from the data that Ea values in the presence of inhibitors are higher than that in the absence. The higher activation energies imply a slow reaction, and that the reaction is sensitive to temperature. Similar results have been reported by Ebenso, *et al*. (2004) in the corrosion inhibition of steel by Alizarin. It is also noted that frequency factor decreased with the addition of inhibitors. The frequency factors generally decreased with increase in concentration of the inhibitors in agreement with Manimegalai and Manjula, (2015). The plots of ln CR vs. $\frac{1}{T}$ are shown in Figures. 18- 19.

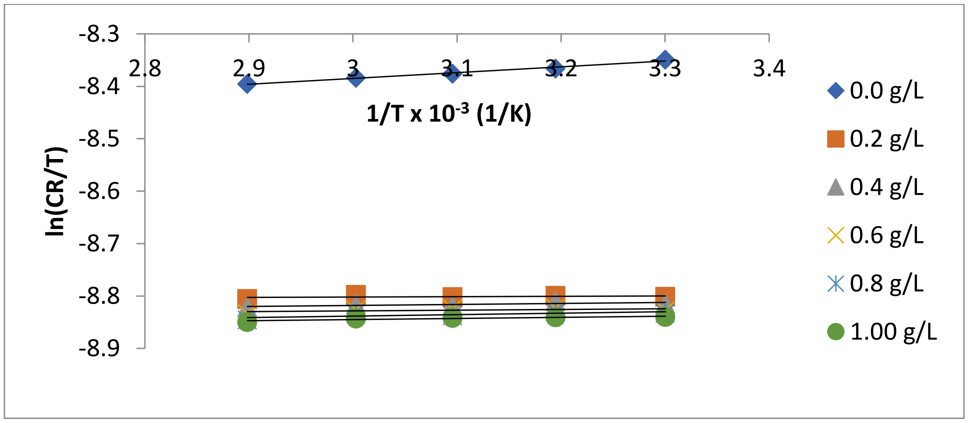

Fig.18: Eyring plot of ln (CR/T) vs. 1/T for MMBS on zinc

Table 7: Entropies and enthalpies of activation values for MMBS on zinc

Concentration	Slope	Intercept	ΔH (J/mol)	ΔS ($Jmol^{-1}K^{-1}$)	R^2 values
0.0 g/L	0.1108	-8.7173	-2.1213	-364.768	0.9841
0.2 g/L	0.0069	-8.8226	-0.1321	-366.786	0.1329
0.4 g/L	0.0191	-8.8755	-0.3657	-367.799	0.5117
0.6 g/L	0.0135	-8.8691	-0.2585	-367.677	0.2795
0.8 g/L	0.028	-8.9223	-0.5361	-368.697	0.5127
1.0 g/L	0.0212	-8.9087	-0.4059	-368.436	0.7492

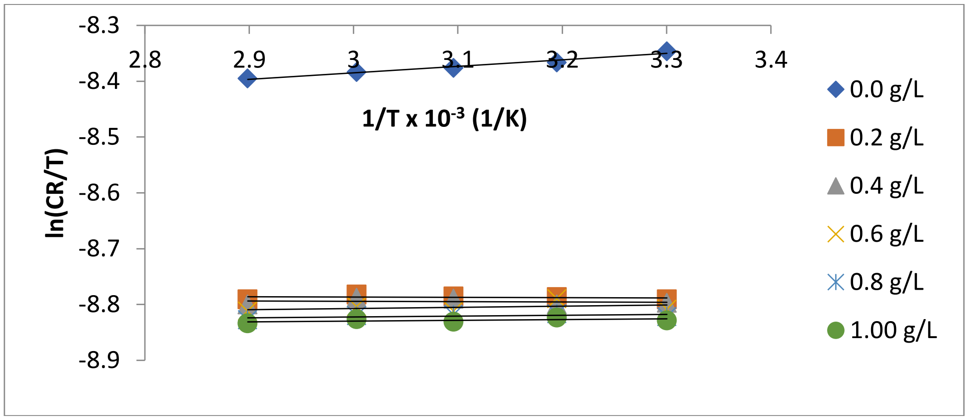

Fig.19: Eyring plot of ln (CR/T) vs. 1/T for CMBS on zinc

Table 8: Entropies and enthalpies of activation values for CMBS on zinc

Concentration	Slope	Intercept	ΔH (J/mol)	ΔS ($Jmol^{-1}K^{-1}$)	R^2 values
0.0 g/L	0.1165	-8.7344	-2.2304	-365.096	0.9727
0.2 g/L	-0.0053	-8.7706	0.1015	-365.789	0.0549
0.4 g/L	-0.0058	-8.777	0.1110	-365.912	0.0252
0.6 g/L	0.021	-8.8702	-0.4020	-367.698	0.1282
0.8 g/L	0.0152	-8.8680	-0.2910	-367.659	0.3356
1.0 g/L	0.0137	-8.8708	-0.2623	-367.710	0.2810

The results in Tables 4.7 -4.8 indicate that the enthalpies activation increased moderately in the presence of inhibitors. This indicates that the inhibitor molecules adsorbed physically on the zinc surface. By increasing the temperature, the percent Inhibition Efficiency (% IE) decreased due to desorption of inhibitor molecules from the metal. The study of the activation parameters reveals that the activation energy (Ea) in Tables 4.30-4.33 increases when the concentration of inhibitor increases. This shows that as the energy barrier of corrosion reaction increases, the corrosion rate decreases. It is clear from the data that activation energy (Ea) values in the presence of inhibitors are higher than that in the absence. The higher activation energies imply a slow reaction, and that the reaction is sensitive to temperature. Moreover, the interpretation of the values and positive sign of the enthalpies (ΔH) reflect the endothermic nature of the corrosion of zinc in hydrochloric acid solution. On the other hand, the values of entropy ΔS for both the uninhibited and inhibited acid solutions are negative (Fouda *et al*., 2013; Singh *et al*., 2014) Analysis of the data in Table 4.34 -4.37 clearly shows that the negative sign of enthalpy reflects the exothermic nature of dissolution of steel. Absolute values of enthalpy of activation are lower than 41.86 KJ/mol indicates physical adsorption whereas values approaching 100 KJ/mol indicate chemical adsorption. In this study, the values of ΔH are less than 41.86 KJ/mol confirming physical adsorption. The ΔS values are negative which means that the process of adsorption is accompanied by a decrease in entropy. The negative value of ΔS decreases in the presence of inhibitor as compared to that of in their absence i.e. There is an increase in entropy in the presence of inhibitor. This indicated that the increase in randomness or disorder at the interface is due to adsorption-desorption phenomenon at high temperature (Shivakumar and Mohana, 2012). In the present study, the ΔG_{ads} values (Table 9-10) obtained ranges from -22 to -30 KJ/mol, which are lower than -20 KJ/mol but higher than - 21 KJ/mol. This indicates that the adsorption is neither typical physisorption nor typical chemisorption, but it is a complex mixed type in which physisorption may be predominant (Mohammed *et al*., 2012). This assumption is supported by the data process reported in Tables 4.2 – 4.5, which shows that inhibition efficiency decreases with increase in temperature (physisorption) (Solomon *et al*., 2010).

The adsorption of an organic inhibitor on the surface of a corroding metal may be regarded as a substitution process between the organic compound in aqueous phase and water molecules on the metal surface. The adsorption of an organic adsorbate at metal-solution interface can occur because of substitutional adsorption process between organic molecules present in aqueous solution (org sol) and water molecules previously adsorbed on the metallic surface (H_2O_{ads}) (Abboud *et al*., 2009).

$Org_{sol} + nH_2O \rightarrow Org_{ads} + nH_2O_{sol}$ (9)

where Org_{sol} and Org_{ads} are the organic species in the bulk solution and that adsorbed on the metallic surface respectively, nH_2O_{ads} is the H_2O molecule adsorbed on the metallic surface and 'n' is the size ratio representing the number of H_2O molecules replaced by one organic adsorbate.

The Langmuir model:

The Langmuir model is given by Eqn (9).

$C/\Theta = I/K_{ads} + C$ (9)

The plot of log (C/ϴ) against log C produces a straight-line with slope of 1 and - log K_{ads} as intercept, then

$\frac{\theta}{1-\theta} = b + C$ (10)

The terms shown in the above equation are defined as follow: $K_{ads} = (1/b)$ is the adsorption-desorption equilibrium constant and Ci_{nh} is the inhibitors concentration. The ΔG_{ads} values (free energy of adsorption) were calculated using the following equation (Olasunkanmi *et al*.,. 2016):

$\Delta G_{ads} = -RT\ln(K_{ads} \times C_{solvent})$ (11)

where $C_{solvent}$: is the molar concentration of solvent (For H_2O, it is 55.5 mol/L). From equation 8, a plot of $(\theta/1-\theta)$ versus C should give a straight line if the assumptions of Langmuir are valid (Ashassi-Sorkhabi *et al*., 2006). Langmuir plot for the inhibited corrosion reaction is shown by Figs.20 – 21. The fact that lines on the figures are linear and very close to each other (with R^2 ranging from 0.890 - 0.999) confirms that Langmuir isotherm is obeyed. The applicability of Langmuir adsorption isotherm to the adsorption of MMBS and CMBS on mild steel and zinc surfaces suggests that there is a high increase in the free energy as compared to the uninhibited system. The results show strong adsorption of inhibitors on the metal surfaces and the existence of mono layers of adsorption. That is, there is interaction between the active sites on the metal surfaces and adsorbed species leading to the formation of spread firms on the surfaces which consequently inhibited the corrosion process.

To mitigate the dissolution of mild steel, the inhibitor molecules got adsorbed onto the metal surface by replacing the pre-adsorbed water molecules. The adsorption of inhibitor molecules can be through physical, chemical, or physical-chemical adsorption. In this regard, the free energy of adsorption can give useful information about the adsorption mode involved in the interaction of the inhibitors to the zinc and mild steel surfaces. According to many authors (Chaitra *et al*., 2016; Lgaz *et al*., 2020). The values of ΔG_{ads} equal to-40 kJ mol^{-1} or more negative, is mainly counted to be chemisorption, whereas, if ΔG_{ads} equal to -20 kJ mol^{-1} or less negative, the adsorption is mainly classified as physisorption.

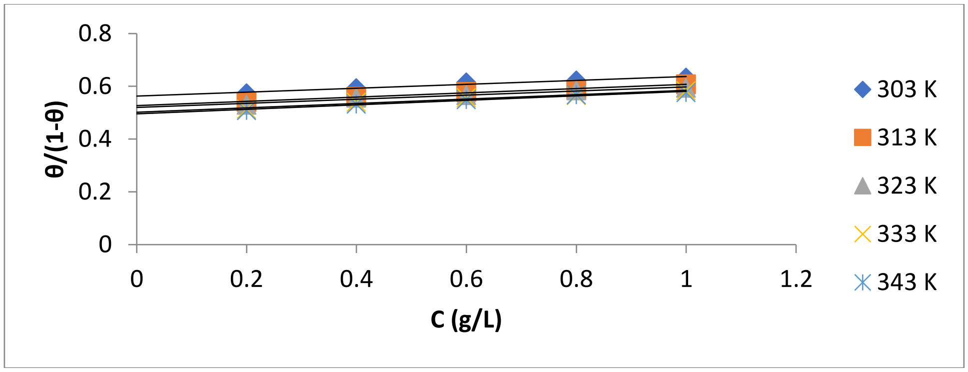

Fig. 20: Langmuir plots for MMBS on zinc at various temperatures

Table 9: Free Energy and Adsorption Parameters for MMBS on zinc the plots

Temperature (K)	K_{ads}	$-\Delta G_{ads}$ (KJ/mol)	R^2 values
303	1.7759	11.565	0.9629
313	1.8975	12.118	0.9903
323	1.9231	12.542	0.9682
333	1.9928	13.029	0.9728
343	2.0173	13.455	0.9749

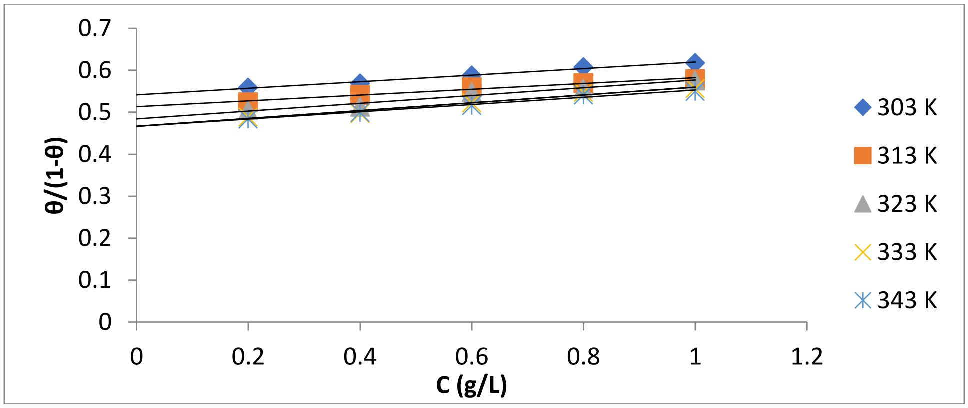

Fig. 21: Langmuir plots for CMBS on zinc at various temperatures

Table 10: Free Energy and Adsorption Parameters for CMBS on zinc the plots

Temperature (K)	K_{ads}	$-\Delta G_{ads}$ (KJ/mol)	R^2 values
303	1..8471	11.664	0.9844
313	1.9482	12.187	0.9724
323	2.0657	12.734	0.9605
333	2.1432	13.230	0.9684
343	2.1444	13.629	0.9839

It can be seen from the tables above that, ΔG_{ads} values become less negative, as the temperature increased. This suggests that the adsorption process occurred by the electrostatic attraction. The negative values of ΔG_{ads} suggest that the adsorbed layer on the metal surfaces is stable and the adsorption process is spontaneous (Tang *et al.*, 2009). The values of ΔG_{ads} were less negative than -20 kJ mol^{-1}, indicating that the adsorption mechanism of the investigated inhibitor on zinc in 0.5 M HCl solution is consistent with physisorption (Abboud *et al.*, 2009).

The Freundlich Isotherm Model.

In Frumkin isotherm, the relationship existing between the adsorbate concentration, C, and the degree of surface coverage (θ) is expressed in equation (8). The plot of Freundlich isotherm model for adsorption of MMBS and CMBS inhibitors on zinc are shown on figures 22 to 23 at various temperatures.

The experimental data were also fitted into the Freundlich adsorption isotherm using equation 2.9. A plot of log ϴ vs log C were made as in figures 4.66-4.69 for mild steel and zinc respectively.

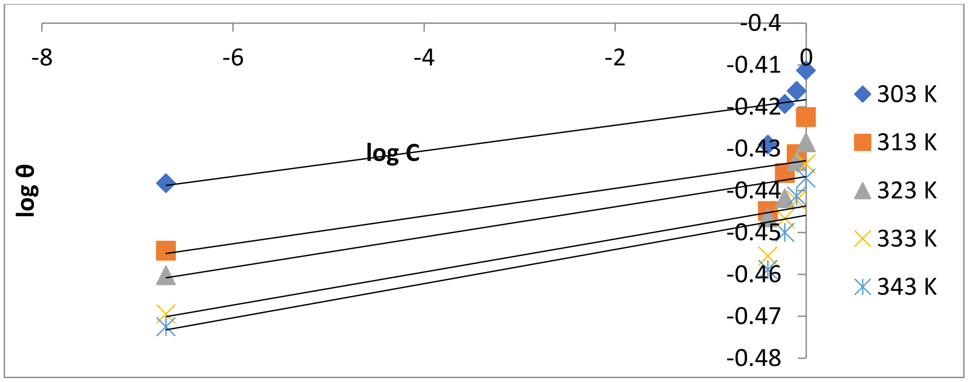

Fig. 22: Freundlich isotherm plots for adsorption of MMBS on zinc at various temperatures.

Table 11: Free Energy and Adsorption Parameters for adsorption of MMBS on zinc

Temperature (K)	n	logK_{ads}	K_{ads}	-ΔG_{ads} (J/mol)	R^2 value
303	0.0031	-0.4183	0.3817	4.6627	0.687
313	0.0033	-0.4328	0.3691	4.9844	0.615
323	0.0036	-0.4366	0.3659	5.1886	0.7217
333	0.0039	-0.4437	0.3600	5.4358	0.7099
343	0.0041	-0.4459	0.3582	5.6265	0.7011

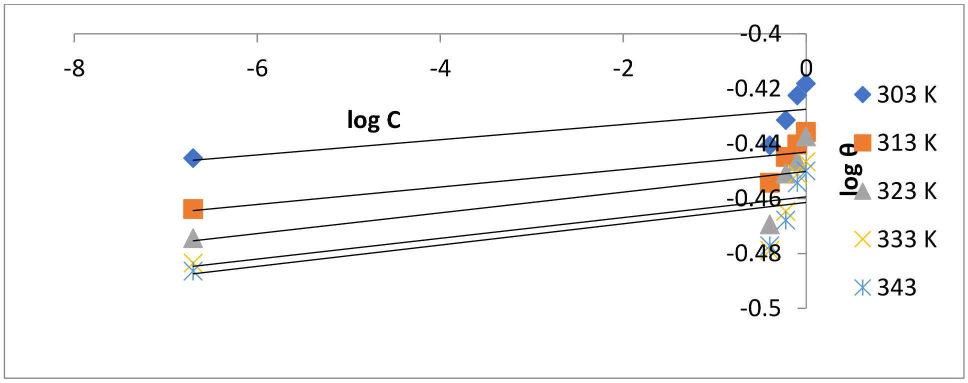

Fig. 23: Freundlich isotherm plots for adsorption of CMBS on zinc at various temperatures.

Table 12: Free Energy and Adsorption Parameters for adsorption CMBS on zinc

Temperature (K)	n	logK_{ads}	K_{ads}	-ΔG_{ads} (J/mol)	R^2 value
303	0.0028	-0.4275	0.3736	4.7665	0.4887
313	0.0032	-0.4431	0.3605	5.1024	0.678
323	0.0038	-0.4501	0.3547	5.3491	0.493
333	0.0038	-0.4594	0.3472	5.6284	0.4548
343	0.0039	-0.4614	0.3456	5.8228	0.5491

The observed R^2 values for zinc with MMBS and CMBS inhibitors in Langmuir, were within the of range 0.8409 – 0.9601 and the parameters obtained are shown in Table 12 – 13. The Freundlich constants K_{ads} and 1/n which represents the adsorption capacity and intensity respectively are also presented in Tables 13-14. The Freundlich constant K_{ads} is the ratio of the amount of inhibitor adsorbed to that remaining in solution provided the Freundlich exponent is approximately equal to unity.

Satisfactory adsorption takes place when the computed n value is between 1 – 10, that is if the value of 1/n is less than one, and this indicates a normal adsorption, but when value is greater than one, it means cooperative adsorption (Villarantine *et al*., 2018).

It can be observed from Table 13– 14, the values of strength of adsorption, 1/n which were more than unity in zinc, suggests that the adsorption intensity of the adsorbate on the adsorbent or surface is non heterogenicity and non-satisfactory (Saadi *et al*., 2015). Moreover, n values range from 0.0678 – 0.066 i.e., n values suggest cooperative adsorption of the inhibitor on the metal indicating that inhibitors concentration has little influence in the adsorption processes (Makkar and Goodchild, 1996).

Additionally, it has been seen that lower temperature favours high K_{ads} value, and this suggests that the inhibitor is more efficient at lower temperature than at higher temperature.

To further support the non-interpretation of the experimental data by Freundlich isotherm model, the correlation coefficient K^2 for zinc is found to be low when compared to Langmuir isotherm model that satisfactorily interpreted the experimental data. The R^2 values obtained for zinc from the Langmuir model suggest good adsorption of the inhibitor molecules on the zinc surfaces.

Quantum Chemical Study

The effects of molecular structure on inhibition efficiency of the Schiff bases were determined through quantum chemical study using semi-empirical (PM3) method. The semi-empirical parameters were determined using the full optimized structures of each of the Schiff bases (MMBS and CMBS) employing the Polar Ribiere algorithm.

The geometry of the optimized lowest energy conforms together with the Homo and Lumo densities for each of the studied structures of MMBS and CMBS are shown in Table 13.

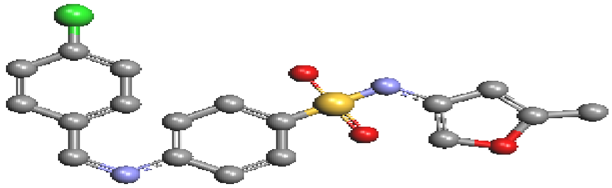

Fig. 24: Optimised geometry of MMBS Schiff base (inhibitor)

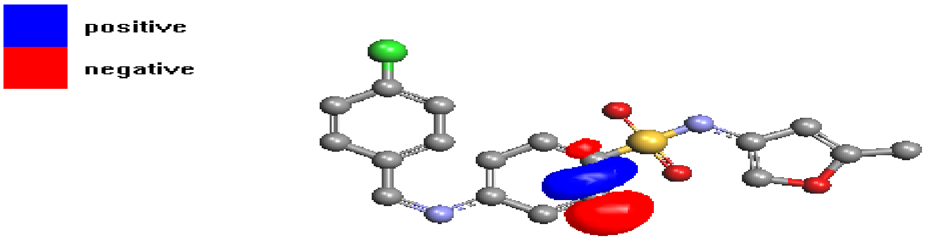

Fig. 25. Homo orbitals of MMBS Schiff base (inhibitor)

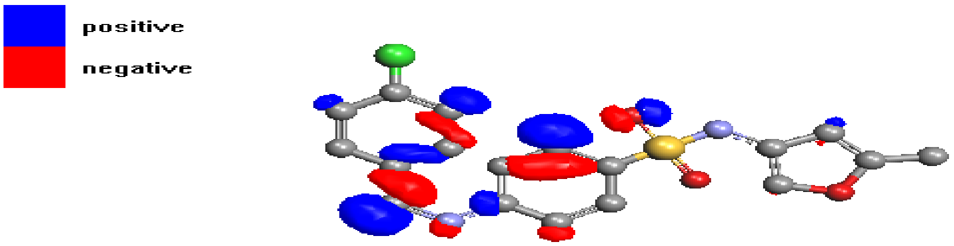

Fig. 26 Lumo orbitals of MMBS Schiff base (inhibitor)

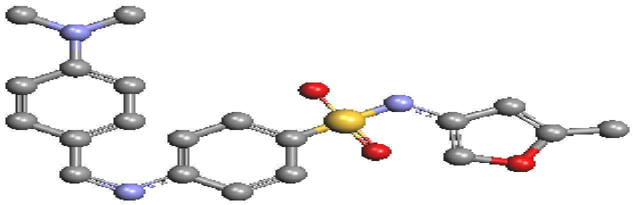

Fig. 27: Optimised geometry of CMBS Schiff base (inhibitor)

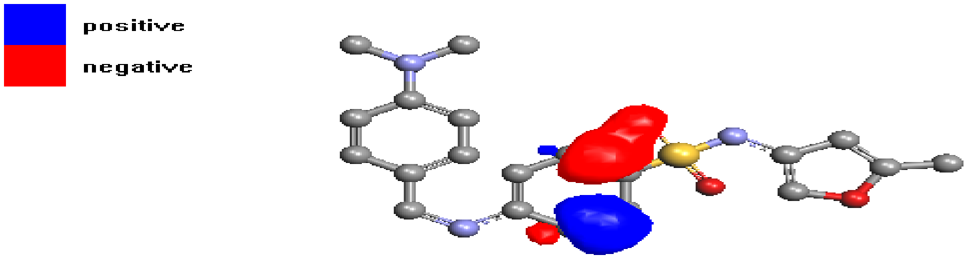

Fig. 28 Homo orbitals of CMBS Schiff base (inhibitor)

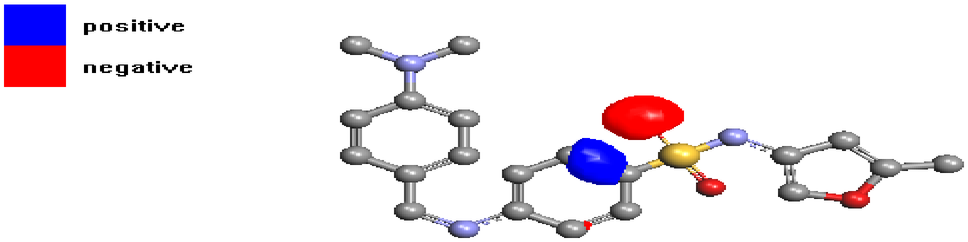

Fig. 29. Lumo orbitals of CMBS Schiff base (inhibitor)

Table 13: Derived quantum chemical parameters from semi-empirical (PM3) method for the Schiff bases MMBS and CMBS.

S/N	Quantum chemical parameters	P- Chloro- (MMBS)	P-dimethyl (CMBS)
1	E_{HOMO} (eV)	-0.135584	-0.140308
2	E_{LUMO} (eV)	0.008026	-0.006767
3	Total Energy ($kJmol^{-1}$)	-1166.60	-1149.0201
4	Energy gap (ΔE) (eV)	0.14361	0.13354
5	Electronegativity (χ)	0.063779	0.0735375
6	Global hardness (η)	0.071805	0.066772
7	Global softness (σ)(eV^{-1})	13.9266067	14.976337
8	Global electrophilicity index (ω)	0.028325	0.0333845
9	No of transferred electrons (ΔN)	48.2990	51.866519
10	Dipole moment (μ)	-0.063779	-0.066771
11	$\Delta E_{\text{back donation}}$	0.01594475	0.0166926
12	Electron Affinity (E. A.)		
13	Ionization potential (I. P)		
14	Molecular volume (mv)		

Table 14: Comparative study of Calculated Quantum Parameters of Inhibitors.

S/N	Name of Schiff Base	Energy Gap (ΔE) (eV)	E_{HUMO}	E_{LUMO}	Dipole Moment (μ)	References
1.	2,20-(1,4-phenylenebis(methanylylidene)) bis(N-(3-methoxyphenyl) hydrazinecarbothioamide) (PMBMH)	6.49	-8.826	-2.336	2.7364	(Bahaa *et al*., 2022)
2.	Metformin	0.23133	-0.19043	0.04090	3.2432	(Ambrish *et al*., 2012)
3	Ampiclox	5.731	-7.5543	-1.823	0.821	(Nnabuk *et al*., 2009)
4.	MINDO (Modified Intermediate Neglect of Differential Overlap (MINDO)	8.84	-9.16	-0.32	2.65	(Abdulfatai *et al*., 2013)
5.	N'-[4-(dimethylamino) benzylidene]-4-hydroxybenzohydrazide (SB)	3.8962	−4.9290	-1.0328		(Preethi Kumari & M. Lavanya, 2021).
6.	Isatin	− 6.143	− 8.927	− 2.784		(Ahmed *et al*., 2022b)
7.	P- Chloro- (MMBS)	0.14361	-0.13558	0.008026	-0.063779	This work
8.	P-dimethyl (CMBS)	0.13354	-0.14030	-0.006767	-0.066771	This work

CONCLUSION

The study of the inhibition potentials of two Schiff bases synthesized from p-chlorobenzaldehyde and sulphamethoxazol for (MMBS): p-dimethylaminobenzaldhyde and sulphamethoxazol for (CMBS) shows that the Schiff bases act as effective corrosion inhibitors for zinc metals in 0.5 M HC1 acid. The FTIR spectra showed that the studied Schiff bases contained nitrogen, oxygen, and sulphur atom in addition to the π - electrons in their molecules and these may be responsible for the high inhibition efficiencies of the of the Schiff bases.

The experimental data obtained from weight loss method show that the inhibition efficiencies increase upon increasing the concentration of the Schiff bases (inhibitors) but decrease as temperature of the reaction increases, indicating that physisorption may be the likely mode of the inhibition process.

From various isotherms, such as Freundlich, Temkin and Langmuir, Langmuir was applied for the analysis of the corrosion process, it showed a good fit for the experimental corrosion data with R^2 value ranges within 0.8409 - 0.9601. From the thermodynamic point of view, the adsorption process was characterized by a decreasing degree of disorderliness as the concentration of the inhibitor increases for the values of entropy of adsorption (ΔS_{ads}) were negative for MMBS onto zinc. Judging from the calculated negative values of free energy of adsorption (ΔG_{ads}), the mechanism of adsorption of the two Schiff bases onto the zinc surfaces was found to follow physisorption since the energy values were less than -20 kJmol-^{1}. The negative values obtained for both entropy of adsorption (ΔS_{ads}) and free energy of adsorption (ΔG_{ads}) show that the adsorption of the inhibitors on the surfaces of zinc was a spontaneous process. The quantum chemical studies showed that there exists a relationship between inhibition efficiencies of the inhibitors, (MMBS and CMBS) and the quantum chemical parameters: E_{LUMO}, E_{HOMO}, ΔE, dipole moment (μ), hardness (η), softness (σ) and ΔN. The values obtained for the experimental inhibition efficiency agreed with values obtained from quantum chemical studies. The negative values obtained for E_{HOMO} further suggest that the mechanism of adsorption was physisorption. Conclusively, the inhibition of the zinc can be attributed to the adsorption of the studied Schiff base molecules onto the surfaces of the metals which leads to the blocking of the active sites of the metals and consequently resulting in increase in inhibition efficiency. The presence of functional groups with high electron density and hetero atoms such as O, N, S *etc* with conjugated double bonds on the inhibitors (Schiff base molecules) facilitate the adsorption of the inhibitors on to the surface of the metals.

The inhibition efficiencies obtained from the different methods employed in the studies: weight loss and quantum chemical studies were in agreement.

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PHYTOCHEMICAL STUDIES OF *Annona muricata* LEAF EXTRACTS

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Abstract

Annona muricata has a wide range of ethnomedicinal values, and indigenous communities in Nigeria, extensively use it to supplement pharmaceuticals. The purpose of this study was to determine the phytochemical constituents of *A. muricata* extracts using a phytochemical screening test and TLC profile studies. Cold maceration yielded chloroform crude extract. The crude chloroform extract was further fractionated into hexane, ethyl acetate, and methanol via column chromatography. The qualitative phytochemical screening revealed that saponin was absent in all extracts except the methanol extract, which had a high saponin content. Also, the methanol extract, unlike the other extracts (crude chloroform, hexane, and ethyl acetate), contained no alkaloids. Furthermore, terpenoid was found to be more abundant in hexane extract than in the other extracts. The quantitative phytochemical result revealed a very significant percenatge of saponins in the methanol extract and terpenoid in the hexane extract. TLC profile study revealed that the polar extracts were best separated using a solvent combination of chloroform and methanol, whereas the non-polar extracts were separated using a solvent combination of hexane and chloroform.

Keywords: *Annona muricata, TLC,* Phytochemical screening

INTRODUCTION

The term phytochemical refers to plant chemicals that have a variety of structures and functions. Colour and odour for protection and insect attraction for pollination, phytoalexins for pathogen defense, hormonal functions for growth and signaling, antifeedants and toxins for insect protection, and allelochemicals for herbivore defense (Mamta *et a*l., 2013). Phytochemicals may have biological activity when consumed by humans. Fruits, vegetables, whole grains, nuts and seeds, and other plant foods are the most abundant sources of phytochemicals.

Medicinal plants are regarded as the foundation for health preservation and care worldwide. *Annona muricata* is a species of the Annonaceae family that has been extensively researched in recent decades due to its therapeutic potential. *Annona muricata* commonly known as soursop, is a member of the Annonaceae family, which includes over 130 genera and 2300 species. A. muricata L. contains a variety of compounds with pharmacological properties. This plant is widely grown in tropical and subtropical regions, including Southeast Asia, South America, and Africa's rainforests.

Different parts of *A.muricata* serve distinct functions. The plant produces edible fruit all year and is widely used in traditional medicine to treat skin diseases, respiratory illnesses, fever, bacterial infections, diabetes, hypertension, and cancer (Moghadamtousi *et al*., 2015; De Souza *et al*., 2009). The seeds combat parasitic infections, the fruit treats arthritis, nervous disorders, and diarrhoea, and the leaves treat cystitis, diabetes, headaches, hypertension, insomnia, and liver problems, in addition to acting as an antidysenteric, anti-inflammatory, and antispasmodic agent (Wélé *et al*., 2004). The leaves, bark, and roots of A.muricata have been used for anti-inflammatory, antihypertensive, sedative, antidiabetic, smooth muscle relaxant, and antispasmodic properties (Mooghadamtousi *et al*., 2015; Adewole and Ojewole, 2019; Mishra *et al*., 2013). Cooked leaves are applied topically to treat abscesses (De Sousa *et al*., 2010). In tropical African countries such as Nigeria, the leaves are traditionally used to treat skin diseases (Adewole and Ojewole, 2019).

A. muricata leaf extract contains flavonoids, terpenoids, saponins, coumarins, lactones, anthraquinones, glycosides, tannins, and phytosterols (Gavamukulya *et al*., 2014). The A.muricata plant also contains acetogenins, essential oils, vitamins, carotenoids, amides, and cyclopeptides (Coria-Téllez *et al*., 2018; Vijayameena *et al*., 2013). The plant also contains minerals such as potassium, calcium, sodium, copper, iron, and magnesium (Gyamfi *et al*. 2011).

The purpose of this study is to report on the phytochemical composition of various extracts of A. muricata using TLC and phytochemical screening. The different phytochemicals found in the extracts highlight their potential pharmacological properties. In the future, phytochemicals may be used as chemo-preventive agents, also knowledge of the chemical constituents of plant is desirable because such information will be of value for isolation and synthesis of complex chemical substance.

MATERIALS AND METHODS

Plant Sample Preparation

On April 6, 2019, a large quantity of fresh plant parts (leaves) was collected from Ahiazu - Mbaise in Imo State, Nigeria. The plant material was cut up into small pieces and air dried at room temperature. 250 g of *A. muricata* was transferred to an extraction container, and 1.5L of chloroform was added. It was left to stand for 48 hours before filtering. After filtration, the filtrate was allowed to stand for 15 days, yielding concentrated chloroform crude extract. Column chromatography was used to separate the constituents of the chloroform extract based on their solubility in various solvent polarities, ranging from non-polar to less-polar, and then polar, in the order of hexane, ethyl acetate, and methanol which on evapouration afforded hexane, ethyl acetate and methanol extract.

TLC Profiling Procedure

All the extracts (hexane, chloroform, ethyl acetate and methanol) were dissolved with little quantity of methanol. The solutions were used for TLC profiling. Each of samples was applied on the TLC plate by using a capillary tube. The sample loaded plates were developed in a developing chamber containing a mixture of solvents with different proportions (hexane and chloroform). The developed plates were and taken to iodine tincture chamber.

Qualitative Phytochemical Analysis.

Phytochemical screening for alkaloids, flavonoids, saponins, tannins, and terpenoids, were performed according to the standard procedures described by Harbone (1998).

Quantitative Phytochemical Analysis.

Quantitative phytochmical analysis was carried out according to the according to the standard procedures described by Harbone (1998).

RESULTS

The phytochemical analysis result of the research showed that the different extracts of *a. muricata* contained different phytochemicals in varying quantities, as shown in tables 1 and 2 below. Tables 3 is showing the result obtained from subjecting the extracts to TLC in a solvent system of

Hexane (30%) and Chloroform (70%), from the result, the different extracts exhibited different characteristic in the same solvent mixture. Tables 4 is showing the result obtained from subjecting the extracts to TLC in a solvent system of Chloroform (70 %) and methanol (30 %), from the result, the different extracts exhibited different characteristic in the same solvent mixture

Table 1: Results of Quantitative Phytochemical Analysis

Phytochemical	Chloroform	Ethyl acetate	Methanol	Hexane
Tannins	++	+	-	+
Flavonoids	++	++	-	+
Saponins	-	-	+++	-
Terpenoids	-	+	-	+++
Alkaloids	++	++	-	++

Table 2: Results of Quantitative Phytochemical composition of A. muricata extracts (% Mean ± S.D)

Phytochemical	Chloroform	Ethyl acetate	Methanol	Hexane
Tannins	6.14 ± 0.3	1.9367± 0.02082^{a}	0.0000 ± 0.000^{a}	1.0967±0.08963^{a}
Flavonoids	5.33 ± 0.4	6.3567±0.05033^{a}	0.0000 ± 0.000^{a}	0.3533 ± 0.02082^{a}
Saponins	0.0000 ± 0.000	0.0000 ± 0.000^{a}	16.3553±0.9142^{a}	0.0000 ± 0.000^{a}
Terpenoids	0.0000 ± 0.000	1.1700±0.0002^{a}	0.0000 ± 0.000^{a}	14.2420 ± 0.6000^{a}
Alkaloids	6.10 ± 0.8	5.9246±0.03611^{a}	0.0000 ± 0.000^{a}	6.9400 ± 0.03000^{a}

Values indicated by superscript ‘a’ are significantly different down the group from the ethyl acetate extract using one way anova (dunnett’s test) p (<0.05)

Table 3: Thin layer chromatography result.

Extract	Spot	Colour	R_f
Hexane	1	Light green	0.1090
	2	Greenish yellow	0.2363
	3	Deep green	0.6909
	4	Light green	0.7818
Chloroform	1	Green	0.1090
	2	Light green	0.1818
	3	Green	0.3636
	4	Light green	0.40
	5	Yellow	0.5090
	6	Deep green	0.7272
	7	Yellow	0.9454
Ethyl Acetate	No movement	Deep Green	-
Methanol	No movement	Deep Green	-

Table 4: Thin layer chromatography result

Extract.	*Spot*	*Colour*	R_f
Hexane	Moving with solvent font	-	-
Choloroform	1	Yellow	0.2830
	2	Light green	0.3120
	3	Green	0.3851
	4	Green	0.0482
	5	Light green	0.5200
	6	Green	0.6751
	7	Light green	0.7520
	8	Yellow	0.9142
Ethyl Acetate	1	Yellow	0.4250
	2	Light green	0.5020
	3	Green	0.6235
Methanol	1	Yellow	0.4320
	2	Light green	0.6540
	3	Light green	0.6930
	4	Green	0.7080
	5	Green	0.8150

DISSCUSION

The result of the phytochemical composition of *A. muricata* leaves is summarized in Tables 1 and 2. The results revealed that the plant contain alkaloids, flavonoids, tannins, saponin and terpenoids.

From the obtained result chloroform crude extract (6.1400 %) contain higher tannin content compared to hexane (1.0967 %) and ethyl acetate (1.9367 %) extract. Tannins appears to be absent in methanol extract. Tannins have been reported to exert physiological effects, such as to accelerate blood clothing, reduce blood pressure, decrease the serum lipid level, produce liver necrosis, and modulate immune responses. Tannins have potent astringent properties. They are known to hasten the healing of wounds and inflamed mucous membranes.

The ethyl acetate (6.3567 %) and choloroform extracts (5.3300 %) have a moderately higher flavonoid content than the hexane extract (0.3533 %), whereas the methanol extract has no flavonoid. Flavonoids primarily protect plants and, at the cellular level, act as cell cycle regulators. Flavonoids, when consumed as food, have high biological activity and exhibit antioxidant, anti-inflammatory, and antiallergic properties. According to Sharififar et al. (2009), these compounds have strong antioxidant properties and can scavenge free radicals, making them useful in various biological. Additionally, they protect the human body from the negative effects of oxidative stress. (Kim *et al*., 2017). They have been found to have antimicrobial properties against various microorganisms in vitro. Flavonoids have gained popularity due to their potential health benefits, including antiviral, anti-diabetic, anti-inflammatory, anti-tumor, anti-carcinogenic, and anti-aging properties (Cook and Samman 1996; Ren et al., 2003;

Zhou et al., 2009; Patra and Chua, 2010).

In comparison, methanol contains a high concentration of saponins (16.3553 %). The results showed that saponins are only found in methanol extract and completely absent in hexane, chloroform, and ethyl acetate extracts. Saponins have antimicrobial properties, which protect your body from fungi, bacteria, and viruses. At the same time, they boost immune function by stimulating the production of T cells. They also act as antioxidants, scavenging oxidative stress. According to Just et al. (1998), saponins have been shown to inhibit inflammation. Saponins have the ability to precipitate and coagulate blood cells. Saponins have properties such as foaming in aqueous solutions, haemolytic activity, cholesterol binding, and bitterness (Sodipo *et al*., 2000; Okwu, 2004).

Hexane extract contains a high concentration of terpenoid (14.2420 %) compared to chloroform (0.0000 %) ethyl acetate (1.1700 %) and methanol (0.0000 %). Plant-based terpenoids have traditionally been used by humans in the food, pharmaceutical, and chemical industries, and have recently been investigated for the development of biofuels. Terpenoids have been shown to help prevent and treat diseases such as cancer. Terpenoids exhibit antimicrobial, antifungal, antiparasitic, antiviral, antiallergenic, antispasmodic, antihyperglycemic, antiinflammatory, and immunomodulatory properties (Wagner and Elmadfa, 2003; Rabi and Bishayee, 2009). Terpenoids have been found to be useful in the prevention and therapy of several diseases, including cancer. Terpenoids are also known to possess antimicrobial, antifungal, antiparasitic, antiviral, antiallergenic, antispasmodic, antihyperglycemic, antiinflammatory and immunomodulatory properties (Wagner and Elmadfa, 2003 and Rabi and Bishayee, 2009). In addition, terpenoids can be used as protective substances in storing agriculture products as they are known to have insecticidal properties as well (Sultana and Ata, 2008). Terpenoid's diverse functional roles have been extensively researched and are now widely accepted.

The phytochemical analysis result shows that alkaloids are moderately present in all extracts except the methanol extract. Alkaloids have a variety of pharmacological activities, including antimalarial (e.g., quinune), antiasthmatic (e.g., ephedrine), anticancer (e.g., homoharring tonine), analgesic (e.g., morphine), and antibacterial (Kaur and Arora, 2015). Ng et al. (2015) found that two alkaloids (galantamine and rivastigmine) have a significant impact on Alzheimer's disease (AD). Natural herbs contain alkaloids that have antiproliferation and antimetastasis effects on cancers in vitro and in vivo. Camptothecin and vinblastine, two alkaloids, have been successfully developed as anticancer drugs (Lu et al., 2012).

Tables 3 and 4 show the results of TLC analysis; it can be seen that the hexane extract revealed four different coloured spots, the chloroform extract revealed approximately seven spots, and the methanol and ethyl acetate extract did not separate in a solvent system of hexane (30%) and chloroform (70%). Meanwhile, chloroform, ethyl acetate, and methanol extracts produced 8, 3, 5 spots in a solvent system containing 70% chloroform and 30% methanol.

The Rf value is a physical constant for organic molecules that can be used to determine their identity. Rf values are used to calculate polarity, relative masses, and relative solubility, among other things.

The various Rf values obtained from the TLC profiling results (Tables 3 and 4) provide insight into the polarity of the various extract fragments, as the greater the Rf value, the less attraction to the polar stationary. The more polar the compound, the better it adheres to the adsorbent, travels a shorter distance from the baseline, and has a lower Rf value. So, the lower Rf, the greater the attraction to the stationary phase. The higher the Rf value, the less polar the compound. Manik et al. (2016).

CONCLUSION

The methanol, hexane, and chloroform extracts of the whole A. muricata plant contain therapeutic components such as alkaloids, tannis, flavonoids, terpenoids, and saponins in varying amounts. In the methanol extract, saponin is predominant, while the hexane extract is rich in terpenoid. Secondary metabolites found in studied species may play a role in traditional medicine and pharmacology.

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CHEMICAL SOCIETY OF NIGERIA (CSN) ABIA CHAPTER
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Conference Proceedings

Full Length Research Paper

EVALUATION OF THE ANTINUTRIENT COMPOSITION OF UMUNNEOCHI DELICACY (Ighu Ayo).

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ABSTRACT

Umunneochi delicacy (Ighu ayo) also known as African Salad or Abacha is a Staple food of African Origin mostly popular among the people of Umunneochi Local Government Area in Abia State Nigeria. It is mostly loved by the Igbos due to it's composition, taste and easy method of preparation. The Ighu ayo was purchased from Ahia Ohuru (Modern Market) in Aba Abia State. The anti-nutrient composition was evaluated using the Assocation of Official Analytical Chemist (AOAC) method, spectrophotometric method and colorimeric method. The Study showed that the antinutrients present in Ighu ayo were hydrogen cyanide 0.0016mg/100g, trypsin inhibitor 44.08mg/100g, Oxalate 109.39mg/100g, tannin 136.89mg/100g. The result showed that the delicacy contains high level of antinutrients which might be as a result improper processing of the ingredients such as potash used in preparing the meal. Therefore, it is recommended that the Umunneochi delicacy should be consumed in a lower amount.

KEYWORDS: Antinutrients, Ighu ayo. Umunneochi, Spectrophotometry, Colorimetry.

INTRODUCTION

Cassava (*Manihot utilisma)* also known as manioc, tapioca or yacca, is a widely grown crop in most countries in e tropical regions of Africa, Latin America and Asia and it ranks in one of the main crops in the tropical countries (Alabi *et.al*, 2011). It is among the starchy staples which gives a carbohydrate production of about 40% higher than rice and 25% more than maize. More than two third of the total production of cassava is used as food for animal feed and industrial purposes (Nwokoro *et.al*, 2002). Although cassava is the third most important food source in the tropical world after rice and maize, it provides calories for over 160 million people of Africa (Parma and Hensel, 2017). It's food value is greatly compromised by the endogenous presence of cyanogenic glucosides. Through drying it's been found that the toxicity of cassava products is reduced (Twe 1991).

Abacha (ighu ayo) and its local salad are cassava that are popular and relished by the Eastern and Southern Nigerians. It is usually soaked in water and eaten with or without coconut or peanuts are snack (Ihekoronye and Ngoddy 1985), while the local salad is softened. Abacha cooked with vegetable, palmoil, fish and other additives. It is an exotic delicacy and a special salad recipe native of Nigeria. It is widely accessed for its composition of food ingredients known to be rich in protein, carbohydrate, vitamins and minerals. African salad also known as Ighu ayo in Umunneochi is used as a special delicacy during traditional festivals (Abacha Ncha, Africansalad, 2013). The aim of this work was to determine the antinutrients present in Umunneochi delicacy (Ighu ayo).

MATERIALS AND METHODS

Materials:

Fresh butter, cassava tubers are purchased from Ahia Ohuru (Modern Market) in Aba, Abia State. The tubers were peeled the same day and cut into small pieces, It was processed into dry Abacha of about 100g by further cuttings into smaller pieces of about 10cm long, followed by washing with distilled water. The washed sample was boiled for 10mins at 100^0C and cooled. After cooling, product was shredded into thread like strands using a locally made shredder. The shredded product was then washed gently four times with distilled water, followed by soaking in distilled water for 24hrs. It was then rinsed thoroughly drained and thinly spread on tray and sun dried at about 60^0C for five days.

Methods

Preparation of Local salad dish (Umunneochi delicacy) Ighu ayo.

Only the laboratory Abacha sample was used in preparation of the local salad as there was no raw data for the market sample with which to compare 500gof laboratory prepared dry Abacha was soaked in distilled water for ten minutes to rehydrate, removed and drained through a sieve. Palmoil was fried for two minutes, followed by addition of dehulled smoked fish, stockfish, fresh pepper, ugwa (local pea), salt and maggi, drained abacha was added to the mixture of oil and stirred. Garden egg leaf was added and stirred very well to form the local salad. The whole mixture was left steam for ten minutes.

Determination of Antinutrient

The phytate content was determined according to the methods of Nkama and Gbenyl 2001, hydrogen cyanide was determined using the procedure of AOAC 2005. Trypsin inhibitor determination was done by using the spectrophotometric method, oxalate was determined using the AOAC 1990 method, Tannin determination was done by Folin Denis Colometric method. Saponin was done by the double solvent extraction gravimeter.

Statistical analysis

All data obtained in 3 replicates were analysed by using SPSS package version 21 using one way analysis of variance.

RESULTS

Antinutrient Composition of Ighu Ayo

The antinutrient compositions present in Ighu Ayo are presented in the Table below.

Table 1: Antinutrient compositions present in Ighu Ayo

ANTINUTRIENT	**VALUES (Mg/100g)**
Trypsin inhibitor	44.08
Saponin	76.73
Phytate	86.69
Oxalate	109.39
Tannin	136.89
Hydrogen Cyanide	0.0016

DISCUSSION

The result revealed trace amount of Cyanide (0.0016mg/100g) which can be negligible, trypsin inhibitors (44.08mg/100g), tannin (136.89mg/100g). The low concentration of Cyanide in the delicacy indicates that the delicacy may be threatening to human nutrition at any level and state of consumption. Hydrogen Cyanide is known to be harmful to the body therefore consumption of food with large amount of Cyanide can result to chronic neuropathy. The Oxalate content was very high(109.39mg/100g), this might occur due to the type of cassava used in making the delicacy or the potash (akanwu) used in preparing the delicacy. Oxalates form insoluble complexes with some metals thus leading to reduced calcium availability/ metabolism. The Saponin, phytate and tannin contents are significantly high especially tannin (136.89mg/100g). Tannin have been reported to have anti-carcinogenic effects. However, reports reveal that higher intake of tannin acid has been associated with poor protein utilization, liver and kidney toxicity. High levels of antinutrients such as oxalate, phytate, tannin is known to be very poisonous to humans. However, the toxicants can be eliminated during processing.

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CHEMICAL SOCIETY OF NIGERIA (CSN) ABIA CHAPTER

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Conference Proceedings

Full Length Research Paper

DETOXIFICATION OF CADMIUM (II) IONS IN SIMULATED EFFLUENTS USING BIO-SYNTHESIZED ALUMINIUM OXIDE NANOPARTICLES WITH *Terminalia cattapa* LEAF EXTRACT.

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ABSTRACT

The ability of nanomaterials to detoxify toxic heavy metals in solution colorimetrically is on the increase as low-cost and easiest method. ln this study, biological synthesis of aluminium oxide nanoparticles was carried using Terminalia cattapa leaf extract. Characterization of the synthesized aluminium oxide nanoparticles were determined by various spectroscopic techniques such as UV-visible spectroscopy, FTIR, SEM and XRD. UV-visible analysis of the aluminium oxide nanoparticles showed surface plasmon absorption with maximum absorption at 420nm. FTIR analysis indicated that O-H of acid at 2900 cm^{-1} and C-O of alcohol at 1320 cm^{-1} functional groups were responsible for the formation of aluminium oxide nanoparticles while SEM analysis revealed that the surface morphology of the aluminium oxide nanoparticles had a porous irregular granulated shaped morphology of various sizes. It also revealed smooth surface of the particles upon magnification. The XRD result showed the formation of the aluminium oxide nanoparticles that are crystalline in nature with crystallite size of 26.5. The colorimetric detection of Cd (II) ions in aqueous solutions using colloidal aluminium oxide nanoparticles showed highest detection point at wavelength of 600nm when the concentration of aqueous solution of Cd (II) ions was at 20µM. This indicated that aluminium oxide nanoparticles have the ability to detoxify Cd (II) ions in solutions even at low concentrations. Therefore the obtained results encourage the use of economical synthesis of aluminium oxide nanoparticles in the development of nano-detoxifier to detoxify pollutants present in effluents solutions and other metal bearing effluents.

Keywords: Terminalia cattapa, aluminium oxide nanoparticles, Cd (II) ions, colorimetric.

INTRODUCTION

Although heavy metals are ubiquitous in most natural material, anthropogenic activities have resulted in elevated concentrations of metals in the environment (Ankley *et al.,* 1994). Some significant anthropogenic sources of heavy metals in the environment include; metalliferous mining and smelting, fossil fuel combustion, agriculture and electronics (Alloway and Ayre, 1997). Heavy metal contents in water, soils, crops and vegetables in mining and smelting areas have been extensively documented in China, with elevated concentrations of heavy metals measured (Shu *et al.,*2005). Generation of heavy metals through combustion processes such as power generation, smelting, incineration and the internal engine combustion have been equally documented (Nriagu, 1989). Agricultural activities increase the trace metal content of soils and waters and therefore have significant effect on metal content of crops (Alegria, *et al.,*1990). Agriculture constitutes one of the major non-point sources of metal pollutants and such sources include: fertilizer application which has impurities as Cd, Cr, Mo, Pb, U, V, Zn; Pesticides: Cu, As, Hg, Pb, Mn, Zn; Desiccants: As for cotton; wood preservatives: As, Cu, Cr; wastes from intensive pig and poultry production: Cu, As, and Zn; Sewage Sludge: Cd, Ni, Cu, Pb, and Zn (Khan and Shadid, 2004). The use of heavy metals (Cu, Zn, Au, Ag, Pb, Sn, Y, W, Cr, Se, Sm, Ir, In, Ga, Ge, Re, Sn, Tb, Co, Mo, Hg, Sb, As and Gd) in the manufacture of semi-conductors and other electrical components have created serious global problem due to their poor management (UNEP/GPA, 2006). According to Alloway and Ayre (1997), cadmium is a highly toxic non- essential metal because of the absence of homeostatic control for this metal in human body. The increasing use of this metal has generally increased the potential for human exposure (Waalkes *et al.,* 1991). Acute exposure to cadmium can result in damage to numerous tissues such as kidney, liver, lung, gastrointestinal tract, central nervous system ovaries and testes (Goering *et al.,* 1994). Kidney is a primary target of chronic cadmium toxicity (Friberg *et al.,* 1986). Cadmium acts as inhibitor of sulphydryl enzymes (Goering *et al.,* 1987). It can cause stress by increasing lipid peroxidation or by changing intracellular glutathione (GSH) levels (Pereira *et al.,* 1998). In vitro experiments have reported that cadmium can displace essential metal components such as zinc, Cu and Fe from metalloenzymes and thereby alter their activities (Vallee and Ulmer, 1972). Based on histologic analysis, cadmium can cause chronic toxic effects within the pancreas which includes the induction of pancreatic cancers (Poirier *et al.,* 1983) and cellular trans-differentiations (Konishi *et al.,* 1990). Carcinogenic and teratogenic effect has also been observed in epidemiological studies on animals (USEPA, 1999). Chronic cadmium poisoning due to mining complex result in "itai-itai" disease by the residents that consumes cadmium contaminated rice (Watanabe *et al.,* 2000). Chronic cadmium inhalation is also suspected to be a possible cause of lung cancer (Sorahan and Esmen, 2004). However, due to the toxicity of cadmium, there is need for its detection and detoxification in any medium especially in effluents before discharge. Synthesis of nanoparticles of size ranging from 1 to 100nm via nanotechnology is a recent technology (EU, 2011) and bio-nanotechnology that integrate principles of biology with physical and chemical procedures to generate nano-sized particles with specific functions equally exists (Kathiresan, 2009). This bio-based protocols for synthesis of metal nanoparticles are environmentally and economically green as they are based on green chemistry principles and are simple, relatively in-expensive, and easily scaled up for larger scale production (Prabhu and Poulose, 2012). Three main steps are involved in green synthesis method, i.e reaction medium selection, biological reducing agent selection, and selection of non-carcinogenic substances for stability of nanoparticles (El-Shishtawy *et al*., 2011). Yet, plant-mediated preparation of nanoparticles can be advantageous over other bio-based synthesis because the procedure of maintaining cell cultures can be omitted and it is also suitable for large scale production under non-aseptic environment (Makarov *et al.,* 2014). Generally, nano-materials can be fabricated through two main methods, i.e "top-down" and "bottom-up" approaches Forough and Farhadi (2010) but "bottom-up" approach is more preferable for the preparation of nanoparticles, which involves a homogeneous system where in catalysts (eg reducing agent and enzymes) synthesize nanostructure that are controlled by catalyst property's reaction media, and conditions (eg solvents, stabilizers and temperature). Hence, there is need to develop a sustainable preparation of nanoparticle that get rid of using harmful organic chemical substances, since noble particles are widely applied to areas of human contact (Shams *et al.,* 2013). According to Ahmed *et al.,* (2016) and Saranya *et al.,* (2017), phytochemicals in plant extracts such as proteins, polysaccharides, organic acids, vitamins, as well as secondary metabolites, such as flavonoids, alkaloids, polyphenol, terpenoids and heterocyclic compounds have significant roles in metal salt reduction and furthermore, act as capping and stabilizing agents for synthesized nanoparticle. Several phytochemical components of the plant extracts of *Terminalia cattapa* exist including, alkaloids, tannins, terpenoids, saponins, flavonoids, polyphenols, anthraquinones, cardiac glycosides, anthracene, glycosides (Bikanga *et al.,* 2019). Therefore, this work investigated the detoxification ability of bio-synthesized aluminium oxide nanoparticles with *Terminalia cattapa* via detoxification of Cd (II) ions in simulated effluents using a colorimeter.

EXPERIMENTAL Collection of plant materials Fresh leaves of *Terminalia cattapa* were collected from the premises of Michael Okpara University of Agriculture Umudike Abia State Nigeria, identified and equally authenticated at the Taxonomy Unit in the Forestry Department in Michael Okpara University of Agriculture Umudike.

Preparation of aqueous plant extract

Thoroughly washing of the sliced leaves of *Terminalia cattapa* with deionized water was done, air dried at room temperature for three weeks and milled to a fine powder using a blender. 50 grams of the milled sample was dispersed in a 500 mL of deionized water in 1000 mL glass beaker and boiled at 100°C for 15 minutes in a hot plate and was allowed to cool. Then, the solution was filtered using a Whatman No. 1 filter paper (Springfield Mill. Maidstone. Kent, England) and the immediate use of the filtrate was done for the synthesis of aluminium oxide nanoparticles.

Synthesis of aluminium oxide nanoparticles

Aluminium oxide nanoparticles were synthesized by adding 100 mL of the aqueous leaves extract to 900 mL of 1×10^{-3} M aqueous ($Al_2O_3.8H_20$) solution in a 1000 mL round bottom flask and stirred for about 35 mins. After 18 minutes of stirring, change in colour was observed from ochre yellow to amber brown indicating the formation of aluminium oxide nanoparticles. Repeated centrifugation of aluminium oxide nanoparticles solution was carried out at 4000 rpm for 15 minutes for purification followed by re-dispersion of the pellet in deionized water. Finally, the aluminium oxide nanoparticles were dried in an oven at 80°C and allowed to cool and stored in an airtight container for further analysis.

UV-visible spectroscopy analysis

1mL of aqueous aluminium oxide nanoparticles was measured by sampling 1 mL aliquot and compared with 1 mL of distilled water used as blank. UV-visible spectrum was monitored on Cary Series UV-visible spectrophotometer Agilent Technology that was operated within the wavelength range of 200 to 800 nm.

FT-IR spectroscopy measurement

FTIR analysis of *Terminalia cattapa* leaves extract and aluminium oxide nanoparticles were carried out and their measurements were performed using FTIR-Cary 630 Fourier Transform Infrared Spectrophotometer, Agilent Technology, in an absorbance method at a resolution of 14 cm^{-1} in potassium bromide (KBr) pellets in the wave number range of 4000-500 cm^{-1}.

Scanning electron microscopy (SEM)

analysis

SEM analysis of the aluminium oxide nanoparticles was studied in order to ascertain it's morphology using electron magnification of 80 - 150,000x (MODEL-PHENOM ProX Scanning Element Microscope manufactured by Phenom World Eindhoven, Netherlands).

X-ray diffraction (XRD) analysis

XRD analysis was carried out using a diffractometer (Empyrean Model, Netherlands) that operated at a voltage of 45 KV and a current of 40 mA using Cu-K(alpha) radiation in a -2 configuration with a wavelength (λ) of 0.1541. Smoother portion of aluminium oxide nanoparticles was fed on a slide which was then charged into the machine after adjusting the machine parameters and was The Uv-visible analysis of zero-valent aluminium oxide nanoparticles was determined using ultraviolent visible spectrophotometer. The absorption spectrum of the zero-valent aluminium oxide nanoparticles is shown in Fig. 1 with maximum absorption at 420 nm.

Fourier transform infrared spectroscopy

FTIR analysis of *Terminalia cattapa* leaf extract before and after synthesis of the operated via a monitor.

Colorimetric detection of Cd (II) ions from simulated effluents using aluminum oxide nanoparticles (AlNPs).

For the detoxification of Cd (II) ions in simulated effluents, 2 mL of colloidal aluminium oxide nanoparticles solution was added to various concentrations (10- 50) µM of nickel chloride salt solution that was prepared by serial dilution from 1mM of stock solution of nickel salt. The mixtures were allowed to stand for 15 minutes before subjected to colorimeter. Absorbance was in the range of 200–800 nm.

RESULTS

Uv-visible analysis

aluminium oxide nanoparticles were determined to ascertain the possible functional group/s responsible for the reduction of aluminium oxide ions to magnesium oxide nanoparticles. Fig. 2 depicts the FTIR spectrum of *Terminalia cattapa* leaf extract before synthesis while it's functional groups are presented in Table 1. Equally Fig. 3 shows the FTIR spectrum of aluminium oxide nanoparticles after synthesis and its functional groups are also shown in Table 2.

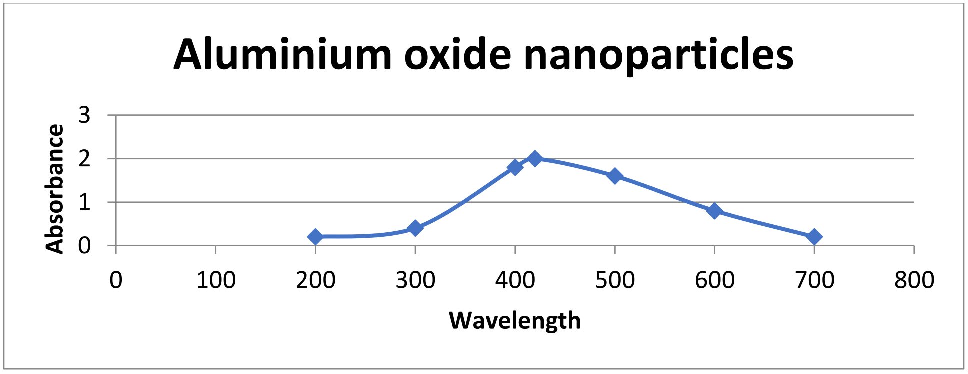

Fig 1. UV- visible spectrum of aluminium oxide nanoparticles

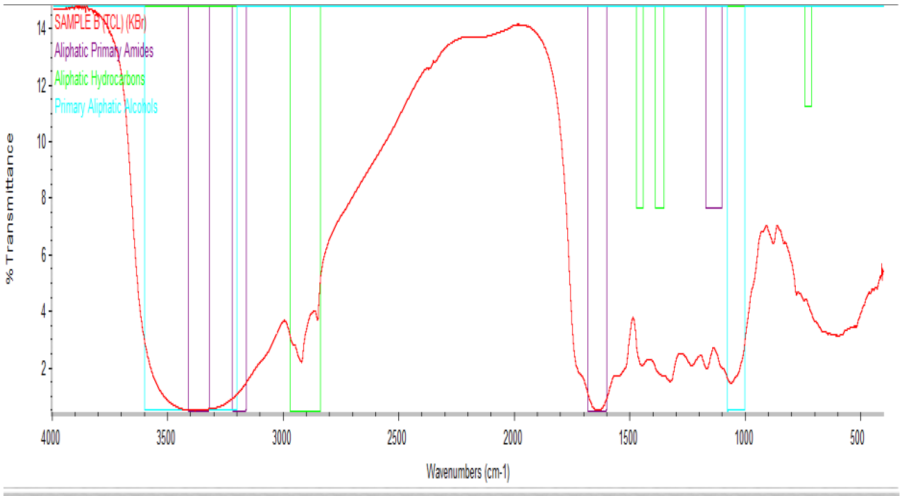

Fig. 2: FTIR spectrum of *Terminalia cattapa* leaf extract

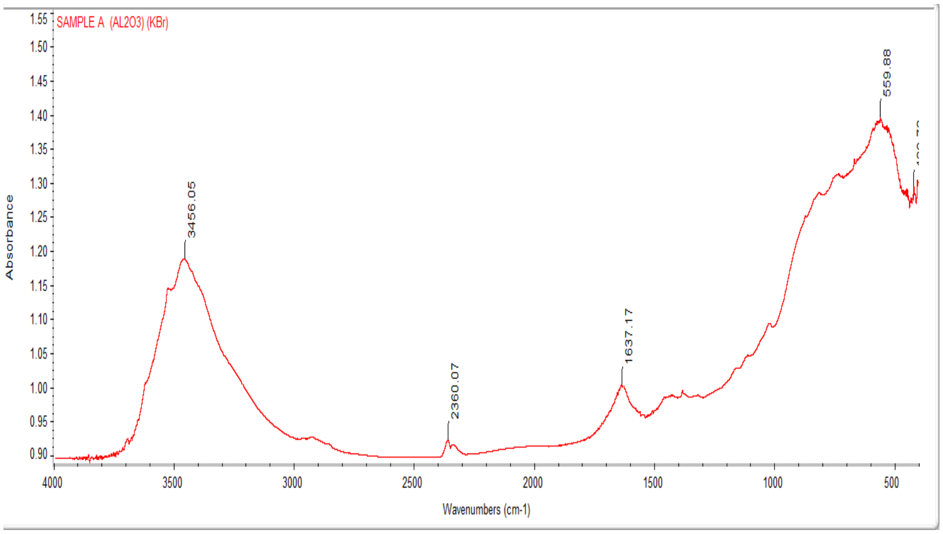

Fig. 3. FTIR spectrum of aluminium oxide nanoparticles

Table 1: Functional groups present in *Terminalia cattapa* leaf extract

Wavenumber (cm^{-1})	Functional groups
3400	O-H of alcohol
2900	O-H of acid
2850	O-H of acid
1650	C=C of aromatic compound
1320	C-O of alcohol
1070	C-O of alcohol

Table 2: Functional groups present in aluminium oxide nanoparticles

Wavenumber (cm^{-1})	Functional groups
3456.05	O-H of alcohol
1637.17	C=C of aromatic compound

Scanning electron microscopy analysis (SEM)

Aluminium oxide nanoparticles SEM images are depicted in Fig. 4 and Fig. 5. The morphology of this nanoparticle showed coarse granulites irregular shape of various sizes that are porous and agglomerated. Upon magnification, the image possesses smooth surface.

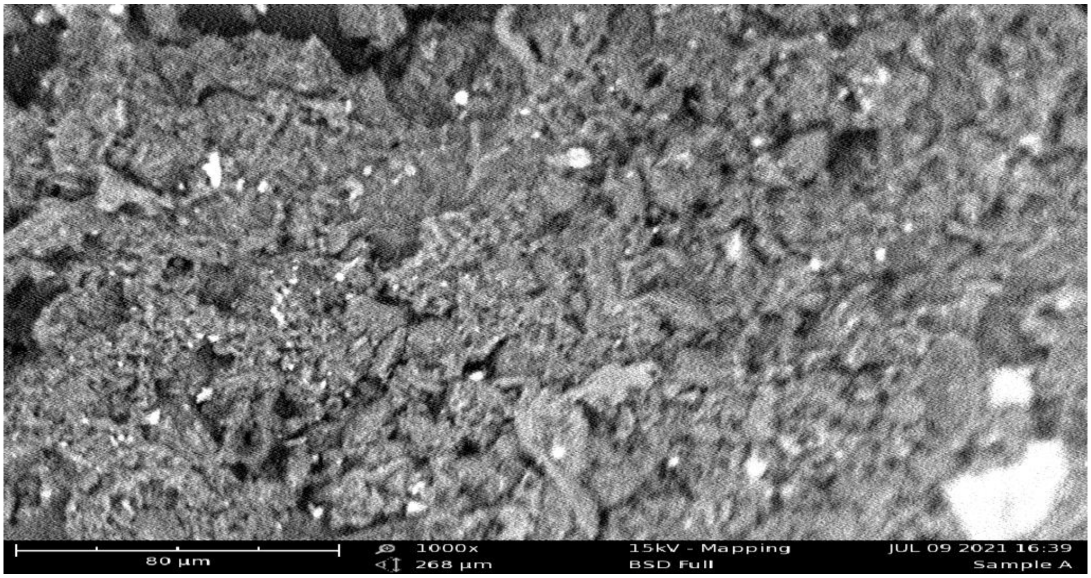

Fig 4: SEM image of aluminium oxide nanoparticles

Fig 5: Zoom SEM image of aluminium oxide nanoparticles

X-ray diffraction analysis (XRD)

The XRD pattern of aluminium oxide nanoparticles is shown in Fig.6. Characteristics reflections are shown to appear at 2θ values of 10.70, 20.00, 30.40, 30.90, 40.20, 40.55, 50.75 and 60.70 within the angle range of 10 to 100.

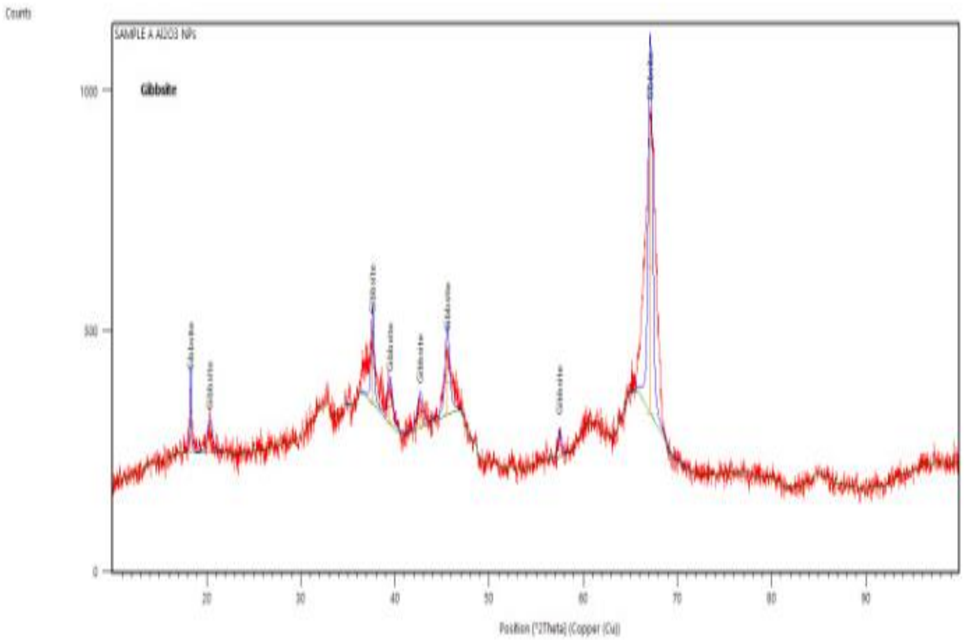

Fig. 6: X-ray diffraction spectrum of aluminum oxide nanoparticles.

Colorimetric analysis

Detection was carried out against various concentrations (10-50) µM of Cd(II) ions. The aluminum oxide nanoparticles response was observed visually through the colour change of the solution. Among the five solutions tested, solution with concentration of 20 µM showed the most significant colour change, from dark brown to clear solution. Other solutions of different concentrations showed a change in colour but not as significant as solution of 20 µM. This indicated that the aluminum oxide nanoparticles were more sensitive to Cd (II) ions at concentration of 20 µM than other concentrations tested. Colorimetric plot of absorbance versus wavelength is shown in Fig. 7, while Table 3 depicts the quantity of Cd (II) ions detected by aluminum oxide nanoparticles in various concentrations.

Table 3: Amount of Cd (II) ions detected by aluminum oxide nanoparticles.

Concentration (µM)	200	300	400	500	600	700	800
	Wavelength (nm)						
10	0.42	0.41	0.32	0.31	0.77	0.44	0.20
20	l0.54	0.44	0.42	0.42	0.92	0.45	0.45
30	0.51	0.46	0.32	0.33	0.52	0.41	0.31
40	0.31	0.32	0.31	0.32	0.52	0.42	0.32
50	0.33	0.30	0.33	0.30	0.53	0.41	0.32

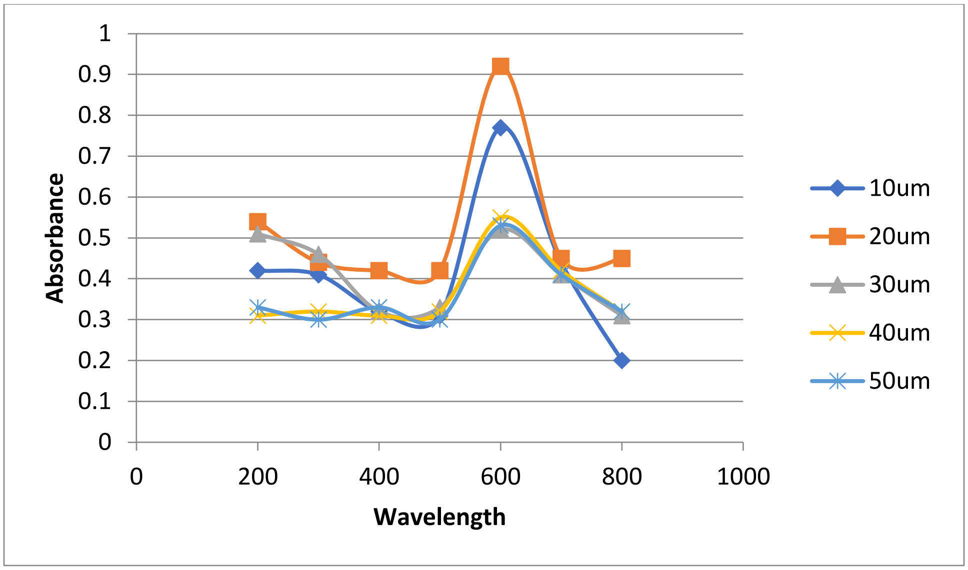

Fig.7: Colorimetric plot of absorbance versus wavelength.

DISCUSSION

Maximum absorption at 420 nm by aluminum oxide nanoparticles via Uv-visible analysis indicate surface plasmon absorption and this is similar with the work of Okwunodulu *et al.*, (2020) on the use of zinc nanoparticles in sequestering Hg (II) ions in simulated effluents. According to the FTIR analysis, it was revealed that O-H of acid at 2900 cm^{-1} and C-O of alcohol at 1320 cm^{-1}functional groups were involved in bio-reduction process. Therefore, these functional groups were responsible for the capping, stabilization and reduction of aluminum oxide ions to aluminum oxide nanoparticles while SEM analysis of the aluminum oxide nanoparticles indicated coarse granulites irregular shape of various sizes that are porous and agglomerated. Upon magnification, the image possesses smooth surface. Based on the XRD analysis, aluminum oxide nanoparticles formed are crystalline in nature with irregular shapes and sizes. It's crystallite size is 26.5 based on Debye-Scherrer equation. The peaks displayed very sharp and had strong intensities. Detoxification of Cd (11) ions by aluminum oxide nanoparticles colorimetrically could be attributed to the porous nature of the aluminum oxide nanoparticles based on SEM result. Occurrence of colour shift could be due to aluminum oxide nanoparticles aggregation that was induced by the presence of Cd (II) ions at 20 µM and interference of the Cd (II) ions on the interaction of aluminum oxide nanoparticles with any radical present Shrivas etc al., (2019) which then reduced the stability of aluminum oxide nanoparticles and resulted in the aggregation. Based on the results, aluminum oxide nanoparticles detoxified some reasonable quantities of Cd (11) ions at every wavelength but the highest detection point was observed at wavelength of 600nm when the concentration of aqueous solution of Cd (II) ions was at 20µM. This indicated that aluminum oxide nanoparticles has the ability to detect Cd (II) ions in solutions even at low concentration.

CONCLUSION Aluminum oxide nanoparticles were synthesized biologically with *Terminalia cattapa* and characterized using a few spectroscopic techniques such as UV–vis spectroscopy, Fourier transform infrared spectroscopy, scanning electron microscopy and XRD. FTIR analysis revealed the functional groups present in *Terminalia cattapa* leaf extract that are responsible for the reduction of aluminum oxide ions to aluminum oxide nanoparticles. The use of the colloidal aluminum oxide nanoparticles in detoxifying Cd (11) ions in aqueous solutions was this colorimetric method should be adopted for easy detoxification. Moreover, the obtained results encourage the use of economical synthesis of aluminum oxide nanoparticles in the development of nano-detoxifier to detoxify the pollutants present in industrial effluents.

successful because detoxification was made even at low concentrations.

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CHEMICAL SOCIETY OF NIGERIA (CSN) ABIA CHAPTER

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Conference Proceedings

Full Length Research Paper

THERMODYNAMIC INVESTIGATION OF DICLOFENAC ADSORPTION ONTO PROTONATED AMINO ACID INTERCALATED BENTONITE

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ABSTRACT

Among pharmaceutical products (PPs) recalcitrant to water treatments, diclofenac shows a high toxicity and remains at high concentration in natural aquatic environments. In this study, the effectiveness of protonated forms of L-Arginine (BTA) and L-Phenylalanine (BTP) intercalated bentonite clay for effective uptake of pharmaceutical diclofenac (DCF), in aqueous medium was assessed. Batch experiments were conducted to determine the influences of temperature on adsorption efficiency. Adsorbents were characterized by specific surface area evaluation, contact angle measurement and Cation exchange capacity. Results showed that the modification of the adsorbents by biosurfactants resulted to structural changes in the adsorbents. It was found that optimum adsorption condition was achieved with surfactant loading rate of 150% of the cation exchange capacity (CEC) of the adsorbents for a period of 120 minutes at 25 ^{0}C, corresponding to adsorption capacities of 23.93 mg/g and 21.79 mg/g for BTA and BTP respectively. Thermodynamic investigation revealed a spontaneous, feasible, endothermic and random process for DCF removal by protonated L-arginine and L-phenylalanine modified bentonite.

Keywords: Thermodynamics, organoclay, adsorption, diclofenac, hydrophobicity, temperature.

INTRODUCTION

The presence of pharmaceutical compounds in the environment has become a significant concern due to the potential consequences of long-term exposure, which are still not fully understood (Lonappan *et al.*, 2016). Diclofenac, a nonsteroidal anti-inflammatory drug, has been extensively studied in recent years. It is commonly prescribed in both human and veterinary medicine for its anti-inflammatory and pain-relieving properties (He *et al.*, 2017). Given its widespread production and consumption, diclofenac and its metabolites have been detected in aquatic environments in various countries, with concentrations ranging from 0.7 to 0.44 ng L^{-1} in surface waters and up to 8.5 mg L^{-1} in wastewater (Lonappan *et al.*, 2016). The transformation products of diclofenac have also been found in concentrations ranging from 0.08 to 1.80 mg L^{-1} (Scheurell *et al.*, 2009). In Brazil, diclofenac has been observed in water at levels ranging from 3.3 to 785 ng L^{-1} (Starling *et al.*, 2019).

Research on Diclofenac has focused on finding it in water bodies (Biel-Maeso *et al.*, 2018; Starling *et al.*, 2019), removing or breaking it down (Maia *et al.*, 2019), and understanding its effects on the environment (Klaudia *et al.*, 2019). Studies have shown that Diclofenac can be detected in water, removed, or degraded, and its impact on the environment has been examined. It has been found that Diclofenac can be toxic and accumulate in aquatic life, even at low levels (Klaudia *et al.*, 2019). Diclofenac has been linked to the death and decrease in vulture numbers in Pakistan (Oaks *et al.*, 2004). Research has also found that Diclofenac can break down into more toxic substances through natural processes or sunlight exposure (Klaudia *et al.,* 2019).

Because of issues related to the environment, various techniques for removing diclofenac have been examined, including coagulation, flocculation, and activated sludge treatment (Carballa *et al.,* 2005; Vieno and Sillanpää, 2014); adsorption using natural or artificial substances (Andrew Lin *et al.,* 2015; Maia *et al.,* 2019); and breakdown through sophisticated oxidation methods, like ozonation (Beltrán *et al.,* 2009), photo-Fenton (Pérez-Estrada *et al*., 2005), and photocatalysis (Mugunthan *et al.,* 2018).

In this scenario, adsorption stands out due to its simplicity in operation and the prevention of unwanted by-products. Organophilic clay minerals have been utilized as effective adsorbents for the removal of drugs from water sources (Maia *et al.,* 2019; Ghemit *et al.,* 2019). The effectiveness of these clay minerals is attributed to their improved compatibility with organic pollutants, thanks to their hydrophobic properties and the availability of additional adsorption sites (Oliveira and Guégan, 2016). Therefore, clays modified by addition of surfactants that contain aromatic rings, have been used to adsorb various pollutants (Luo *et al*., 2015; Onwuka *et al.,* 2020). The adsorption process involves both π-π interactions among the aromatic rings of the surfactant and the pollutant, as well as other organic interactions (hydrogen bonding, London forces, etc.), which enhances the adsorption capacity of these modified clays (Oliveira and Guégan, 2016; Oliveira *et al.,* 2017).

In our previous studies (Onwuka *et al.,* 2020; 2020a; 2020b), we have investigated the adsorption efficiencies of Hexadecyltrimethyl ammonium cations ($HDTMA^+$) and Trimethylphenyl ammonium cations ($TMPA^+$) intercalated bentonite for the efficient removal of BTEX compounds, pyrene and 2,4-Dichlorophenol in aqueous medium under various experimental conditions. Generally, the use of other clay mineral like kaolinite, montmorillonite, and rectorite, etc. intercalated with Quaternary Alkyl ammonium Cation for the successful removal of organic pollutants have been widely reported (Nourmoradi *et al*., 2012 Onwuka *et al.*, 2022). On the other hand, the continuous application of chemically synthesized modifiers like Quaternary Alkyl ammonium surfactants and other anionic surfactants for removal of organic pollutants may result to secondary pollution and non-biodegradability. Therefore, investigation into the possibility of applying alternative organic modifiers like biosurfactants becomes necessary.

Amino acids or biopeptides, which are building blocks of proteins, are expected to be compatible with protein-biopeptide matrices when used as modifiers. Compared with chemically synthesized modifiers, amino acid biosurfactants have the important advantages of being biodegradable, low toxicity, and capable of diverse structures. Previous studies have been performed linking the adsorption of certain amino acids to clay minerals. The results obtained suggest that the structure and properties of the resulting organoclay are influenced by both the type of surfactant used and the nature of the clay mineral (Kitadai *et al.,* 2009).

Therefore, this study investigates the potency of a novel organoclay based on L-arginine and L-phenylalanine biosurfactants for efficient uptake of diclofenac (DCF) in aqueous medium via batch adsorption mode. Variation in temperature was employed to optimize sorption process, and thermodynamics of the adsorption of DCF by the adsorbents was also investigated.

MATERIALS AND METHODS

Adsorbent

Calcium bentonite clay mineral (with CEC =13.71 cmol (+)/kg) used in this study was obtained from a clay deposit in Amuro

(Imo Clay shake) Community in Okigwe Local Government Area of Imo State Nigeria. The bentonite clay mineral was beneficiated according to our previous study (Onwuka *et al.*, 2020), and stored prior to organophilicization.

The amino acid biosofactants: L-arginine CAS 74-79-3 and L-phenylalanine CAS 63-91-2 employed as modifier were supplied by Merck Germany. Hydrochloric acid, sodium hydroxide and other chemicals used in this study were obtained from BDH Chemicals England and were of analytical grades.

Synthesis of novel organoclay

The calcium bentonite which was earlier pre-modified to sodium bentonite was further modified via cation exchange method. In this method, the cations (Na^+) present in the surface of the bentonite was exchanged with those of the protonated amino acids. This was achieved by applying the method of Mallakpour and Dinari (2011) with little modification. 3 g of beneficiated bentonite clay (BT) was agitated with 70 ml of deionized water at 60° C for 6 hours to enable swelling of the layered silicates. Aqueous solution of the amino acids was prepared separately by differently dissolving 50%, 100%, 150% and 200% CEC equivalent of clay in 100 ml of deionized water at 60° C, after which a stoichiometric amount of HCl was individually added to the different mixtures and the dispersed clay was then added to the different mixtures followed by agitation using a mechanical Stirrer for 12 hours. The precipitates of the modified clays were filtered, washed in 200 ml of deionized water for up to three times to remove excessive ammonium salts of the amino acids. The final product obtained after further filtration were vacuum dried at 80° C for 24 hours and the dried cake was pulverized and sieved with a 250mesh size to obtain a uniform particle size novel organoclay. The novel organoclays were labeled as BTA (L-arginine modified bentonite) and BTP (L-phenylalanine modified bentonite), and they were stored in the desiccator prior to characterization and adsorption experiments.

Adsorbate

Diclofenac (2-[(2,6-dichlorophenyl) amino] phenylethanoic acid) (purity > 98 %) was supplied by Sigma Aldrich Chemicals, and was further prepared by simple dilution with deionized water. Stoichiometric amount of diclofenac was mixed with deionized water to obtain DCF solution of 1000 mg/L standard solution which was used as a working standard to prepare other concentrations. Direct spectrophotometric method was used to quantify DCF concentration and absorbance was ascertained via a double beam UV/VIS spectrophotometer at 276 nm wavelength. A calibration curve was generated by plotting concentration of DCF vs absorbance using standard solutions of DCF ranging from 25 mg/L to 250 mg/L.

Adsorbent Characterization

The determination of specific surface areas of the adsorbents was ascertained by Sears procedure (Trivedi *et al.*, 1973), and ammonium acetate procedure was employed to determine the individual CEC of BT, BTA and BTP. Surface hydrophobicity of the absorbents was obtained by measuring individual contact angle via the capillary rise technique.

Batch adsorption studies

For the batch adsorption experiment, L-arginine and L-phenylalanine modified bentonite clay (BTA and BTP) were separately dispersed in 20 ml of 100 mg/L of DCF solution at different temperature ranges of 25°C to 55°C using 0.5 g absorbent (150% CEC), at a pH of 2, for 120 minutes. The solids were recovered after each test by centrifugation and the supernatant quantified for DCF at 276 nm using UV visible molecular spectrometry (UV-1800 spectrophotometer, Japan) and the adsorption capacity of the absorbents for DCF uptake was estimated according to equation (1):

$$q_e = (C_i - C_e)\frac{V}{m} \qquad (1)$$

Where the drug concentration (mg/L) before and after adsorption are represented by C_i and C_e respectively, V is the volume of DCF solution and m represents the mass of the organoclay absorbents. The experiments were conducted in triplicate to ensure accuracy.

RESULTS AND DISCUSSION

Surface Characterization

Table 1a represents the result of the experiments involving the chemical composition of raw bentonite (BT). Results for measured contact angles, specific surface area and Cation exchange capacities (CEC) for Bentonite (BT), L-arginine modified bentonite (BTA) and L-phenylalanine modified bentonite (BTP) are included in table 1b. From table 1a it is obvious that the chemical constituent of bentonite clay used in this study is in accordance with standard bentonite clay. Noumoradi *et al.* (2012) reported closer values for montmorillonite clay.

The Specific surface area of BT reduced from 32.60m^2/g to 26.20m^2/g and 16.60m^2/g after modification for BTA and BTP respectively. The reason for reduction in specific surface area for BTA and BTP may be due to the fact that the interlayers between organic cations contained scanty micropores. We have reported similar results for surface area of bentonite supplies by Mansid Chemicals Ltd in our previous work (Onwuka *et al.*, 2020) and Noumoradi *et al.* (2012) also reported similar trend for raw and TTAB modified montmorillonite clay.

The cation exchange capacity (CEC) of clay (BT) increased from 13.71 cmol/kg to 27.43 cmol/kg and 40.65 cmol/kg for BTA and BTP respectively after modification (table 1b). Noumoradi *et al.* (2012) Reported similar trend for raw and TTAB modified montmorillonite clay. The increase in cation exchange capacity of the modified clay could be due to the inter layer micro environment established by the protonated amino acid which is highly favorable for partitioning the organic molecules, clay surface charge density and size of alkyl Chain which are all responsible for rearrangement of intercalated cations.

The essence of measuring contact angles of the adsorbents was to glean little insight into the adsorbents' hydrophobicity. Adsorbent surface is said to be more hydrophobic when a large contact angle between solid phase and water droplet is observed. Initially, the contact angle of 33° was observed for BT, but after modification, contact angle increased to 59° and 49° for BTA and BTP respectively, reflecting an increase in surface hydrophobicity (table 1b and figure 1(a-c). Sun *et al.* (2018) Reported similar results for organokaolin.

Table 1a. Chemical composition of Raw Bentonite (BT)

Chemical composition (%)	Bentonite
SiO_2	2.87
Al_2O_3	11.98
Fe_2O_3	1.05
Na_2O	2.13
MgO	2.99
P_2O_5	1.45
K_2O	2.04
CaO	1.13
TiO_2	0.66
MnO	0.12
H_2O	0.23

Table 1b. Values for cation exchange capacity, contact angle and specific surface area of bentonite (BT) and results forcontact angle measurement, specific surface area and cation exchange capacity (CEC) of bentonite (BT), L-arginine modified bentonite (BTA) and L-phenylalanine modified bentonite (BTP)

Adsorbents	CEC (cmol/kg)	Contact Angle	Surface area m^2/g
BT	13.71	33^o	32.60
BTA	27.43	59^o	26.20
BTP	40.65	49^o	16.60

Thermodynamic Studies

The influences of temperature in the range of 298 K to 328 K for the effective removal of diclofenac by the adsorbents (BTA and BTP) were investigated at optimum experimental conditions (figure 2a). The adsorption capacities of BTA and BTP decreased as a temperature of the system increased from 298 K to 328 K, implying that the adsorption of DCF drug molecules by BTA and BTP were favorable at decreased temperature. A decrease in adsorption capacity resulting from increase in temperature for the adsorption of DCF in aqueous solution by cyclamen persicum tuber based activated carbon has been reported by Jodeh *et al.* (2015).

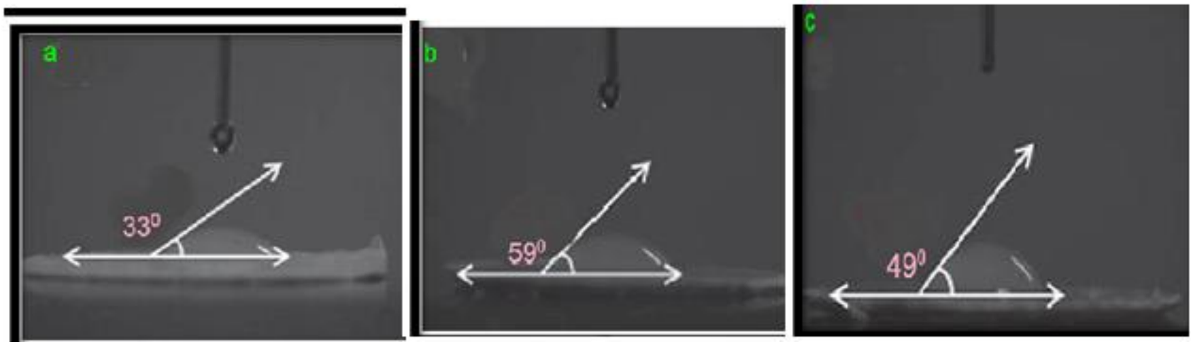
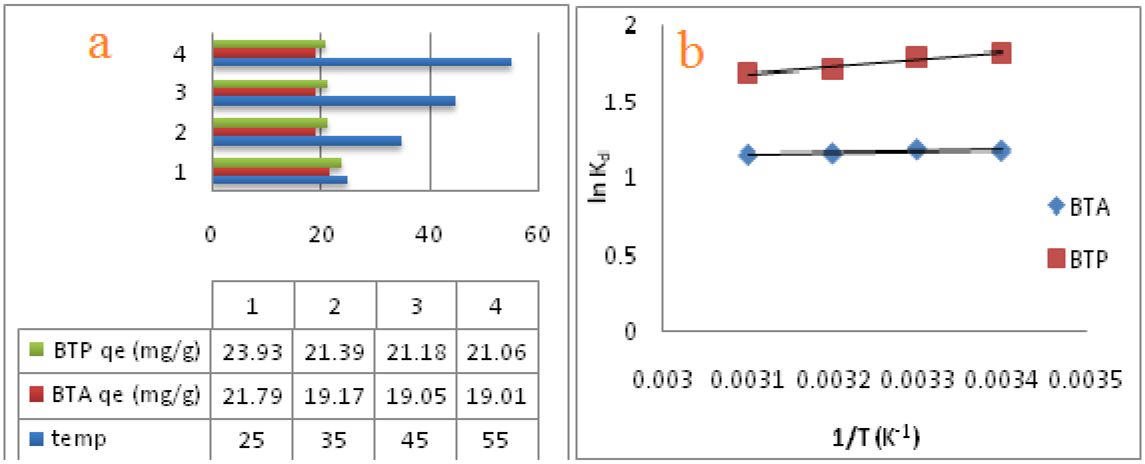


Figure 1: Measured contact angles for BT (a), BTA (b), BTP(c)



	1	2	3	4
🟩 BTP qe (mg/g)	23.93	21.39	21.18	21.06
🟥 BTA qe (mg/g)	21.79	19.17	19.05	19.01
🟦 temp	25	35	45	55

Figure 2: Effect of variation in temperature on adsorption of DCF onto BTA and BTP (a) and Plots of ln K versus 1/T (b)- (C_o = 100 mg/L, mass= 0.5 g, contact time =120 minutes, CEC =150 %, pH =2)

In addition, thermodynamic parameters such as entropy change (ΔS^0), enthalpy change (ΔH^0) and Gibbs free energy (ΔG^0) at aforementioned temperature range was evaluated according to equations (2) - (4) below:

$$K = \frac{C_O - C_e}{C_e} \qquad (2)$$

$$\ln K_d = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \qquad (3)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \qquad (4)$$

Where C_o and C_e are the initial concentration and equilibrium concentration, R is the universal gas constant (8.314 J/mol K), and T is the absolute temperature (K).

Information regarding thermodynamic parameters is detailed in Table 2 and figure 2(b). Obviously, the Gibbs free energy (ΔG^0) presented negative values within the temperature range of 298 to 328 K, suggesting that the absorption of DCF by BTA and BTP is spontaneous and feasible, and a noticeable successive increase in the negative value of ΔG^0 as temperature increases implies that the adsorption of DCF by BTA and BTP is favorable at lower temperature, and this confirms our previous assumption (figure 2a). Also, the adsorption of DCF by BTA and BTP occurred around 1 to 20 kJ/mol, suggesting physisorption.

Table 2: Thermodynamic parameters for the adsorption of DCF onto BTA and BTP

Adsorbent/Adsorbate	**ΔS^0 ($Jmol^{-1}k^{-1}$)**	**ΔH^0 ($Jmol^{-1}$)**	**ΔG^0 ($kJmol^{-1}$)**			
			298K	**308K**	**318K**	**328K**
BTA/DCF	0.78	12.56	-0.56	-1.17	-1.99	-3.12
BTP/DCF	0.25	16.34	-1.78	-2.22	-2.76	-3.01

A positive value of enthalpy (ΔH^0) was observed, lower than 84 kJ/mol: this implies that the adsorption of DCF by BTA and BTP was an endothermic process, governed by physical adsorption (Mahmoodian *et al.*, 2015). The positive value of entropy (ΔS^0) observed indicates high disorderliness (DS>0) within the adsorbent/adsorbate system. With high positive values of enthalpy and entropy, the negative values and the trend observed for ΔG^0 for the adsorption process becomes expected. Salaa *et al*. (2020) reported a spontaneous, feasible, endothermic and random process for DCF removal by organahalloysite intercalated via a novel route. The adsorption of diclofenac sodium from water using oxidized activated carbon followed similar process (Bhara *et al.*, 2016).

CONCLUSION The use of protonated L-arginine and L-phenylalanine biosurfactants to enhance the structural properties of bentonite via cation exchange mechanism for effective removal of pharmaceutical diclofenac (DCF) in aqueous medium displayed favorable adsorption for this aforementioned emerging micro-pollutant which has always been present at significant concentrations in numerous natural water environments. Optimum adsorption capacity was obtained at lower temperature, and information gleaned from thermodynamic investigation confirmed that the adsorption of DCF by these novel adsorbents is spontaneous, feasible, endothermic and disorderly. Also, the adsorption of DCF by BTA and BTP is governed by physisorption. In sum, results obtained in this study have substantiated the potency of these novel organoclays (BTA and BTP) for effective uptake of DCF in aqueous solution. Although there is need to carryout column/continuous experiments, competitive adsorption, as well as mechanistic studies, even possibly exploring molecular simulations.

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CHEMICAL SOCIETY OF NIGERIA (CSN) ABIA CHAPTER

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Full Length Research Paper

SYNTHESIS, CHARACTERIZATION AND XRD ANALYSIS OF Fe(III) AND Zn(II) COMPLEXES OF ACETONE BENZOIC ACID HYDRAZONE

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ABSTRACT

A new series of metal complexes of Fe(III) and Zn(II), namely Iron (III) acetone benzoic acid hydrazone and Zinc (II) acetone benzoic acid hydrazone have been prepared. The complexes and ligands were characterized by X-ray Diffraction Analysis (XRD), Fourier Transform Infrared Spectra Analysis, UV-VIS and Solubility Test. The FTIR analysis indicated that the ligand ABAH coordinated with the metal ions through the carbonyl oxygen and azomethine nitrogen. The BAH coordinated through carbonyl oxygen and the primary amine nitrogen. This is an indication that the ligands acted as bidentate donors to the metal ion. The X-ray Diffraction (XRD) patterns of the metal complexes provide a detailed comparative account. The solubility test on the ligands and its metal complexes revealed their solubility in ethanol and dimethylsulphoxide (DMSO). The Electronic Absorption Spectra of Zn(II) complex showed absorption band located at 36,486 cm^{-1} showing a tetrahedral geometry while Fe(III) ABAH and BAH ligand show absorption band at a shoulder around 16041 cm^{-1} with 4A2 → 4T1 (P) respectively, consistent with a four coordinate tetrahedral geometry. In view of the Relative Half Value Width (FWHM), it may be concluded that the ABAH-Zn is partially crystalline and ABAH-Fe shows an amorphous nature.

Keywords: **ligands, Zinc (II) complexes, benzoic acid, hydrazone, electronic spectra, Iron (III) complex, XRD**

INTRODUCTION

A coordination compound or complex is a class of substance with a chemical structure where the central atom is a metal and surrounded by non-metal atoms or a group of atoms (or ligands). Both the central atom and ligands are joined by chemical bonds like covalent bond, ionic bond and coordinate bond. Complex compound is also called a coordinate compound as it contains the coordinate bonds in its structure, Examples of complexes are $[Co^{3+}(NH_3)_6]^{3+}$,$[Ni(CN)_4]^{4-}$,$[Fe^{2+}(CN)_6]^4$,etc. The central metallic atom of a complex is often transition metal, like copper, zinc, cobalt, manganese etc. Some main group elements also form complexes. Aluminum, tin, and lead, for example, form complexes such as the AlF_6^{3-}, $SnCl_4^{2-}$ and PbI_4^{2-}ions. The number of ligands bound to the transition metal ion is called the coordination number. Coordination number of the metallic atom predicts the geometry of the complex compound. Hence for the coordination number 2,3,4,5 and 6 the geometry of the complex compound is linear, trigonal, planar, tetrahedral (or square planar), trigonal-bypyramidal and octahedral respectively. A ligand is an ion or small molecule that binds to a metal atom (in chemistry) or to a biomolecule (in biochemistry) to form a complex, such as the iron-cyanide coordination complex

Prussian blue or the iron-containing blood-protein hemoglobin. The ligands are arranged in spectrochemical series which are based on the order of their field strength. It is not possible to form the entire series by studying complexes with a single metal ion; the series has been developed by overlapping different sequences obtained from spectroscopic studies. The above spectrochemical series help us to for determination of strength of ligands. A major application of coordination compounds is their use as catalysts, which serve to speed up the rate of chemical reactions. Hydrazides are known as a class of organic compounds with the formula $RNHNH_2$ where R is an acyl (R^1CO--), a sulfonyl (R^1SO_2-), or phosporyl ($R^1_2P(O)$-). They are prepared by the reaction of esters with hydrazine hydrates. Due to the inductive effect of acyl, sulfonyl, or phosphoryl, hydrazides are non-basic. In the synthesis of certain amines, aldehydes and heterocyclic compounds that are otherwise difficult to prepare, hydrazides are important starting and intermediate materials. Hydrazines have traditionally been used as reagents for the derivatization and characterization of carbonyl compounds. Hydrazide reacts with aldehydes and ketones to give the grouping R_1R_2 C=N-NHR known as hydrazide derivatives. Recently hydrazides have gained great important due to their diverse biological properties including anti-bacterial, anti-fungal, anti-inflammatory, anti-malarial and anti-tubercular activities. However, reported that hydrazide has strong ability to form metal complexes and they exhibit a wide range of biological activities. Hydrazide forms complexes through two potential binding sites, i.e., oxygen and nitrogen. Hydrazones are a class of organic compounds which have the structure $R1R2C=NNH_2$. They are correlated to ketone and aldehyde in which oxygen has been replaced with NH_2 group. These azometine NHN=CH- proton constitute an important class of Hydrazones are more reactive than carbonyl groups (aldehyde or ketone) due to the presence of alpha active hydrogen atoms. According to, hydrazones are used as precursor in organic reactions particularly in the preparation of Schiff base ligand which formed coordination bond with transition metals in vivo, with promising biological properties, and also used as ligands in coordination chemistry. Hydrazones and their byproducts constitute a resourceful class of organic compounds that are important for drug design, inferred that hydrazones obtained by the condensation of 2-hydroxy or methoxy aldehydes and ketones with hydrazides are considered potential polynucleating ligands because they have amide, azomethine and phenol/methoxy functions, thus offering a variety of bonding possibilities in metal complexes. The dramatically rising prevalence of multi-drug resistant microbial infections lately has become a serious health care problem, hence has necessitate the study of hydrazones and their metal complexes for their, antifungal, antibacterial, anticancer and herbicidal properties. Reported the inhibition of *Staphyloccocus aureus* by 4-fluorobenzoic acid ((5-nitro-2-furyl) methylene-hydrazide, a hydrazide derivative. Equally, found 5-bromoimidazo[1,2-a]pyridine-2 carboxylic acid benzylidenehydrazide and 5-bromoimidazo[1,2-a]pyridine-2-carboxylic acid 4-methoxybenzylidenehydrazide to possess 3.9 μg/mL against *E. fecalis* and *S. epidermis*. However, reported the anti-malaria activity of 1-Substituted phenyl-N′-[(substitutedphenyl) methylene]-1H-pyrazole-4-carbohydrazides. Benzoic acid [(5-nitro-thiophene-2-yl) methylene hydrazide series has been tested against M. *tuberculosis* H37Rv. It was inferred that 4-Methoxybenzoic acid [(5-nitrothiophene-2-yl)methylene] hydrazide demonstrated highest activity, with a MIC value of 2.0 μg/mL compared to other series of the hydrazides.

The two zinc complexes derived from tridentate ligand gave rise to trinuclear and dinuclear metal complexes. Geometry and coordination number around trinuclear reveals two terminal Zn atoms displays five-coordination in a distorted square pyramidal geometry and the central Zn atom shows 6-coordination in octahedral geometry. On the other hand dinuclear complexes exhibits 4 coordination in tetrahedral and other zinc atoms shows 6-coordination number and geometry around the zinc atoms was octahedral. Trinuclear Zn(II) metal complex with luminescent properties has been reported. The potentially multidentate Schiff base Zn(II) complex display strong emission in solid state with a slightly blue shift. Single crystal X-ray diffraction studies show an incomplete cubane-like structure contains $[Zn_3O_4]^{2+}$ cores in which all metal atom were hexa-coordinate whose geometry display distorted octahedral.

Iron is an abundant element on earth and is a biologically essential component of every living organism. However, despite its geologic abundance, iron is often a growth limiting factor in the environment. This apparent paradox is due to the fact that in contact with oxygen iron forms oxides, which are highly insoluble, and thus is not readily available for uptake by organisms. The body requires iron for the synthesis of its oxygen transport proteins, in particular hemoglobin and myoglobin, and for the formation of heme enzymes and other iron-containing enzymes involved in electron transfer and oxidation-reductions evaluated the Novel azo-acetohydrazide complexes Fe^{3+} with 2-hydroxy-5-((4-nitrophenyl)diazenyl)benzylidene)-2-(p-tolylamino)acetohydrazide (scheme 2.5) using well diffusion method against *Escherichia coli* and *Aspergillus niger* at different concentration. It was inferred that bioactivities data elucidated that as the concentration of the tested solutions increases the activities increase. Hydrazone ligands and their complexes act as anti-microbial agents against gram-negative, gram-positive bacteria, fungi and yeast. Nevertheless, hydrazone have been intensively investigated mostly because of their potential application as anticancer and antiviral. These compounds display a versatile behavior in metal coordination and the biological activity is often increased by bonding to transition metals, [35] reported the Synthesis of 2-hydroxy-5-Bromo-3-nitroacetophenone, isonicotinoyl hydrazone [HCNAIH] (ligand) by reacting a solution of isonicotinoyl hydrazide ethanol and 2hydroxy-5-Bromo-3-nitroacetophenone Scheme 2.6. The zinc complexes were prepared by reacting hot solution of ligand HCNAIH in ethanol a suspension of Zn (II) acetates. From biological evaluation, it was concluded that structural changes of the complex have remarkable effect on the sensitivity and sensitivity varies with organisms. Zinc complexes of the type ZnX_2B,, where X is a halogen or thiocyanate and B a heterocyclic base, the zinc atom may have coordination number 4, 5, or 6 in the solid state, but in solution heterocyclic base is lost from the latter compounds to give the 4-coordinate . However, in zinc complexes of the type ZnA_2B, where A is a p-diketone anion and B a heterocyclic base, we have found that, although the zinc atom may have coordination number 4, 5, or 6 in the solid state, the preferred coordination number in solution appears to be five. A recent single-crystal X-ray analysis3 of bis(N-methylsalicylaldiminato) zinc(II) has shown that in this compound the zinc atoms achieve an approximately trigonal- bipyramidal, 5-coordinate environment in dimeric molecules with oxygen bridges. Incomplete structure determinations on bis(N-n-butylsalicylaldiminato) zinc(11)4~5 indicate that this compound consists of discrete tetrahedral molecules. The atomic number of iron is 26 and its electronic configuration is $[Ar]4s^2\ 3d^6$. Iron has 14 isotopes. Among them, the mass of iron varies from 52 to 60 Pure iron is chemically reactive and corrodes rapidly, especially in moist air or at elevated temperatures. Iron is vital to plant and animal life.

Materials and Methods

Methyl benzoate and hydrazine hydrate were obtained from Maldich Co Ltd and other reagents used were analytical grade and used without further purification while the metal sulphates and other reagents and solvent used where mainly from BDH chemicals Co Ltd.

Preparation of Benzoic Acid Hydrazide (BAH).

10 ml of hydrazine hydrate (10.32g, 0.2 mole) was added to 30 ml of methyl benzoate (32.64g, 0.239 mole) in 100 ml of absolute ethanol and anti-bumping granules were added to prevent bumping. The mixture was refluxed for six hours in a 250 ml round bottom flask. The mixture was poured into a beaker and concentrates with a water bath, and then left overnight to crystalize, the resulting crystals was then recrystallized with minimum ethanol, filtered, dried over silica gel in a desiccator for two days and weighed. The yield of benzoic acid hydrazide was given as 6.238 g (14%)

Preparation of Acetone Benzoic Acid Hydrazone (ABAH).

Exactly 5.44g of BAH was dissolved in 10 ml of absolute ethanol. 4.10 ml of acetone was added to the mixture and heated for some minutes in 250 ml beaker and concentrated with water bath. The mixture was left overnight to crystalize. The resulting crystals was recrystallized with minimum ethanol, filtered and dried over silica gel in a desiccator for two days and weighted.

The yield of acetone benzoic acid hidrazone was given as 3.5g, and the percentage yield (64.3%)

Preparation of Zinc (II) ABAH Complex.

1.00g of the ligand (ABAH) in 50 ml of ethanol in 250 ml beaker was added dropwise to 0.85g of zinc sulphate

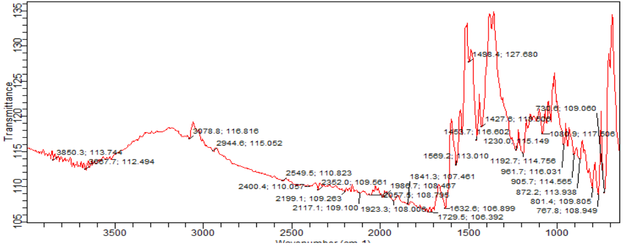
($ZnSO_4.7H_20$) in 10 ml of distilled water with constant stirring. The mixture was concentrated in water bath for 30 min and left to crystalized. The crystal formed was white in color. It was filtered, dried over a silica gel desiccator for two days and weighed; the yield is given as 1.625g and percentage yield (87 %).

Preparation of Iron (II) ABAH Complex.

Exactly 1.00g of the ligand (ABAH) in 50 ml ethanol in 250 ml beaker was added dropwise to 0.85g of hydrated ferric sulfate ($Fe_2(SO_4)_3.6H_2O$) in 10 ml of distilled water with constant stirring, the mixture was the concentrated in a water bath for 30 min and left to crystalized. The crystal formed was black in color. It was filtered, dried over a silica gel desiccator for two days and weighed. The yield was given as 0.447g (24%)

Solubility Test

The solubility test for the ligands and complexes was carried out by dissolving 0.8g of BAH, ABAH Fe^{3+} and Zn^{2+} complexes in 20 ml in 250 ml beaker in solvents such as water, methanol, ethanol, chloroform, DMSO, hexane of the ligands and complexes.



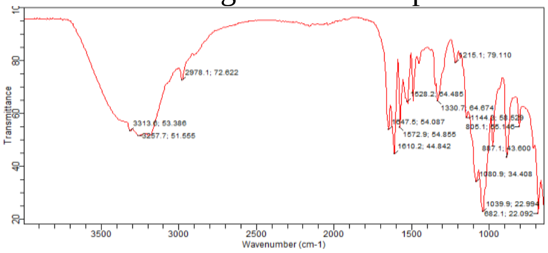
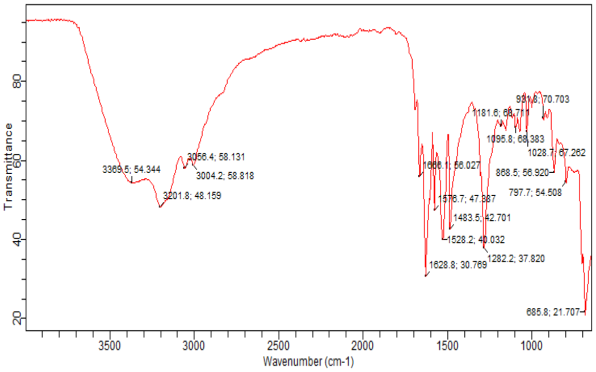


Fig. 3.2 FTIR result of the ABAH

Fig 3.4 FTIR result of Zn^{2+} ABAH



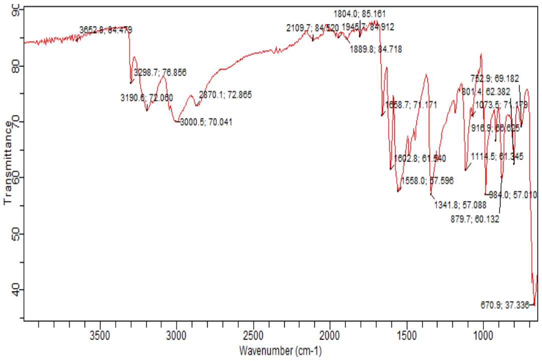


Fig. 3.1 FTIR result of the BAH

Fig. 3.3 FTIR result of Fe^{3+} ABAH-

Table 1: Analytical data of ligands and complexes

Compounds	Formula	Weight	Colour	Yield	%Metal	%SO4
BAH	$C_7H_8N_2O$	136	Milky	6.238	___	____
ABAH	$C_{10}H_{11}N_2O_2$	191	White	3.5	_______	____
$[Fe_2(ABAH)_2](SO4)_3.H_2O$	$C_{20}H_{24}N_4O_9S_3Fe_2$	799.6	Dark brown	0.447	6.97 % (6.22 %)	12%(23%)
$Zn(ABAH)_2SO_4.H_2O$	$C_{20}H_{24}N_4O_9SZn$	561.3	White	1.625	11.60 % (11.21%)	17.1%(24.70%)
$Zn(BAH)_2SO_4.H_2O$	$C_{14}H_{18}N_4O_6SZn$	435.3	Milky	1.42	15 % (14.5%)	22 % (34.3%)

Key: BAH = benzoic acid hydrazide; ABAH = acetone benzoic acid hydrazone; Fe $(ABAH)_2]$ $(SO_4)_3$ = acetone benzoic acid hydrazone iron (III)sulphatre; Zn $(ABAH)_2]SO_4$ = acetone benzoic acid hydrazone zinc (II) sulphate; Zn $(BAH)_2]SO_4$ = benzoic acid hydrazide zinc(II) sulphate

FT-IR SPECTRA

The relevant infrared spectra data is presented in Table 2. From the data, the band due to (C=O)v vibration was observed at 1632.60 cm^{-1} for ABAH. These were lowered in the complexes by 15.46-34.72 cm^{-1} indicating the involvement of the carbonyl group in the bonding metal (46); Nakamoto (1997) state that compounds containing weak coordination ligand oxygen such as ketones, aldehydes, esters and some nitro compounds upon coordination show a shift in the absorption band of (C=O)v either to the lower or higher frequencies. A weak peak with medium intensity was also observed at 1558 cm^{-1} was assigned to an imine group(C=N)v stretch showing the possible formation of a hydrazone from the condensation between the benzoic acid hydrazide and acetone, ABAH at 1589.2 cm^{-1} was lowered by approximately -11.9 in the $[Fe(ABAH)_2]$ and -16.3 cm^{-1} in $[Zn(ABAH)_2]$ this suggest that the lowering in the vibrational band due to the imine group (C=N)v in the complexes is involve in the coordination of this site to the metal ions (Manjulata, 2003). The vibration band due to (N-H)v stretch in the BAH was observed at 3296 cm^{-1} which , when compared lowered in the complexes of ABAH by 34.6- 54.8 cm^{-1}, this could be as a result of a hydrogen bonding (N-H)v stretching of the ligand is not much altered in the spectra of the complexes showing the non-involvement of the nitrogen atom (Sonmez and Sekere,2002). In the complexes of ABAH and BAH, it appears broad and unresolved suggesting the presence of OH of water of crystallization. Other peaks, between 3000 to 3400 cm^{-1} was found showing there is an aromatic structure of (=C-H)v (sp^2 aromatic) corresponding with a characteristic strong signal at 1453.1 cm^{-1} suggesting that there is an aromatic ring in the structure of the compound. A narrow band at about 2978.1 cm^{-1} which was assigned to a (-C-H)v stretch (sp3 C-H) bond of an alkane. Based on the above analysis, the analysis showed that the materials have aromatic ring and functional bonding

Solubility Test for the Ligand and Complexes

The solubility test for the ligand and complexes were carried out in different solvents and the results are shown in table 4. It shows that both the ligand and complexes are insoluble in most organic solvents. This may be due to the polymeric nature of the complexes (Salawau and Aliyu, 2012)

Table 4: Solubility result of Ligands and Complexes

COMPOUNDS	water	Methanol	Ethanol	chloroform	DMSO
BAH	insoluble	Soluble	Soluble	Slightly Soluble	Soluble
ABAH	Insoluble	Insoluble	Soluble	Insoluble	Slightly soluble
$Fe(ABAH)_2SO_4.H_2O$	Insoluble	Insoluble	Soluble	Insoluble	Insoluble
$Zn(ABAH)_2SO_4.H_2O$	Insoluble	Insoluble	Soluble	Insoluble	Insoluble
$Zn(BAH)_2SO_4.H_2O$	insoluble	Soluble	Insoluble	Insoluble	Insoluble

Electronic Spectra for the Ligand and Complexes

The electronic spectrum gives information on the electronic environment of the metal; the electronic absorption spectra are determined in DMSO in the range of 200-1000 nm. The pure ABAH ligand showed three intensive bands at 44642 cm^{-1}, 38314 cm^{-1}, 27173 cm^{-1} suggesting the presence of the π→π* and the n→π* transitions 27. The π→π* transition in the complexes is shifted to a longer wavelength as a consequence of coordination to the metal, confirming the formation of a metal complexes .the Fe(III) complex display maximum absorption band display at 44247-36630 cm^{-1} ascribed to an intramolecular charge transfer transition in the complexes ligand in addition it can be attributed to charge transfer from ligand to metal(M—L) furthermore this is followed by a long broad tail at 36630 cm^{-1} due to a d—d transition in an octahedral arrangement.

Table 5: Electronic spectra of Ligands and Complexes

COMPOUNDS	λmax (nm)	εmax cm^{-1}	Geometry	Transition
BAH	205	48,780	-----	π→π*
ABAH	**224,261,368**	**44642 ,38314 271713**	-------	π→π*
$Fe^{3+(}ABAH)$	**226,273**	**44247,36630**	octahedral	π→π*
$Zn^{2+(}ABAH)$	**265, 231 ,236**	**437735,43290, 42372**	tetrahedral	π→π*

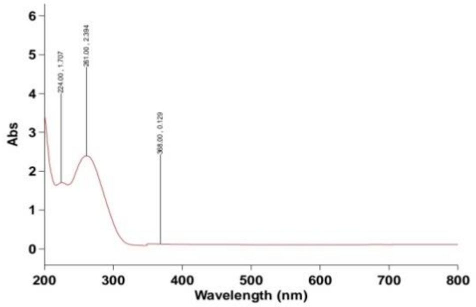


Fig. 3.7 UV-VIS result of the ABAH

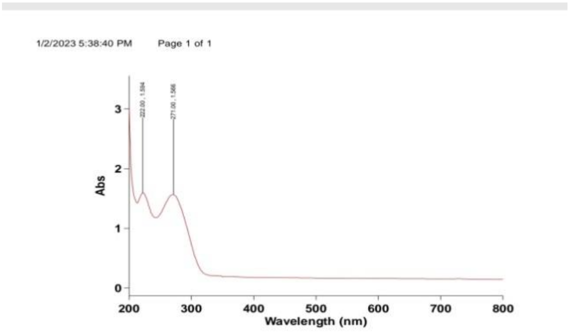


Fig 3.9 UV-VIS result of Zn^{2+} ABAH

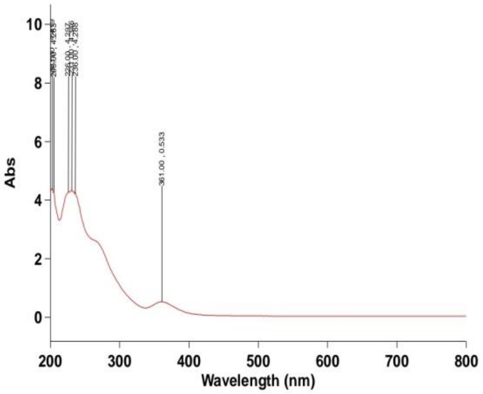
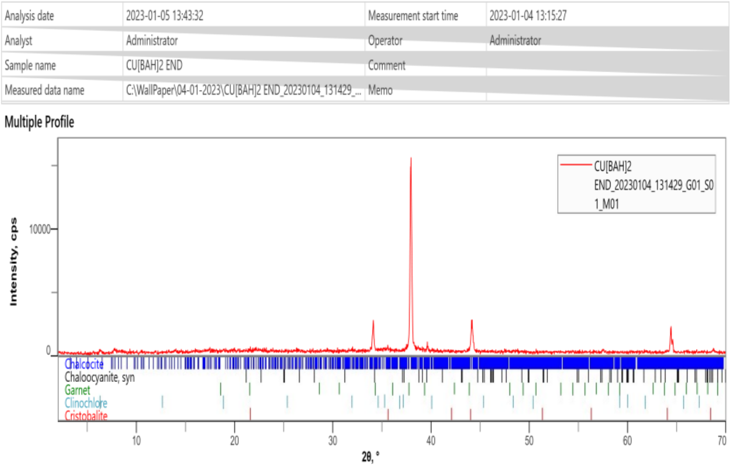


Fig. 3.8 UV-VIS result of Fe^{3+} ABAH

X-ray Diffraction for the Ligands and Complexes

X-ray diffraction (XRD) patterns of BAH and its metal complexes are shown in Figure x. It provides a detailed comparative account of the behavior of the Hydrazide ligand and its metal complexes. The pattern of BAH ligand shows the main characteristic peak and broad shoulder. In view of the relative half value width (FMWH), it may be concluded that the ligand is partially crystalline and the broad characteristic peak indicates the amorphous nature of the polymers. Therefore, the BAH complex of x,y,z have transition state between amorphous state and crystalline state, whereas x,y,z possess crystalline nature. The enhanced crystalline behavior of the BAH complexes may be due to the insertion of metal ions with their parent ligand (Ali *et al*., 2017)

2Θ degree



Analysis date	2023-01-05 13:43:32	Measurement start time	2023-01-04 13:15:27
Analyst	Administrator	Operator	Administrator
Sample name	CU[BAH]2 END	Comment	
Measured data name	C:\WallPaper\04-01-2023\CU[BAH]2 END_20230104_131429_...	Memo	

Table 6: XRD analysis result of the complexes

Compound	2θ	θ	$sin\theta$	$cos\theta$	d-spacing	FWHM	Crystalit size (D)	Phase nature
Fe$^{3+(}$ABAH)	**16**	**8**	**0.13**	**0.99**	**0.59**	**1**	**0.14**	**Crystal**
Zn$^{2+(}$ (ABAH)	**18**	**9**	**0.15**	**0.98**	**0.51**	**1**	**0.141**	**Crystal**

CONCLUSION

The synthesized acetone benzoic acid hydrazone acted as a ligand successfully to form Zn^{2+} and Fe^{3+} metal complexes, the synthesis gave a bidentate ligand function of the ligands ML2 type. The synthesized compounds were all characterized by various spectra and physical analysis. The morphological features suggest that the compounds are crystalline in nature.

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Conference Proceedings

REVIEW

AN OVERVIEW OF THE SYNERGY BETWEEN ARTIFICIAL INTELLIGENCE AND BIG DATA ANALYTICS IN REVOLUTIONIZING CHEMISTRY.

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ABSTRACT

It has been reported that 80% of scientific data becomes unavailable after 20 years. Today, with the rise of digital solutions such as artificial intelligence (AI) and big data analytics (BDA), researchers and industries have the opportunity to dust off their legacy scientific data and transform it into a new breeding ground for data-driven discoveries and innovations. The heart of revolutionizing chemistry through AI and BDA is data, and its major challenge is the curation, quality, integration, and sharing of old and new data in an open manner. The revolution of chemistry through AI and BDA is highly necessary because it leads to faster, automated, efficient, and reproducible chemical processes with sustainable and environmentally friendly approaches. This study explores the various ways in which these cutting-edge technologies (AI and BDA) have transformed traditional chemical processes, how they complement each other in advancing chemical research and development (R&D), their challenges, and their future prospects.

Keywords: Digital chemistry, Artificial intelligence, Big data analytics, Robotics, Chemoinformatics

INTRODUCTION

Artificial intelligence (AI) and big data analytics (BDA) have a symbiotic relationship. AI requires massive or large-scale datasets for greater reliability and accuracy of the model, while analysis of big data cannot be possible without implementing AI algorithms (Xu *et al.*, 2021). Since 2015, there has been an increase in the integration of AI and big data analytics in chemistry research and development, especially in analytical chemistry and biochemistry. This is evident in the number of patents and journal publications (Baum *et al.*, 2021). This tremendous revolution in chemistry research and development by AI and BDA is attributed to the availability of chemical data, high computing power, open source AI toolkits and libraries, and continuous data availability among chemists (Xu *et al.*, 2021; Baum *et al.*, 2021). Technologies such as AI and big data analytics can speed up novel, innovative, and sustainable solutions in chemistry (El-Meligi, 2023), which include molecular property prediction (Xu *et al*., 2021) such as solubility, boiling point, melting point, structuring of molecules, reactant and product prediction, predicting bioactivity of compounds, laboratory automation (Szymanski *et al*., 2023), discovering new materials, and optimizing reaction conditions. In chemical laboratories, as shown in Figure 1. AI, robotics, and BDA are rapidly transforming conventional chemical research processes through automation. This transformation is creating faster, more efficient, informative, and cost-effective research procedures, thereby paving the way for novel scientific discoveries that address global issues in the environment, health sector, energy storage industries, manufacturing, and many more (Xu *et al., 2021).*

The aim of this review is to explore the various ways in which these cutting-edge technologies (AI and BDA) have transformed traditional chemical processes, how they complement each other in advancing chemical research and development (R&D), their challenges, and their future prospects. This will enable chemists to understand the need to harness the potential of these two cutting-edge technologies in advancing R&D.

Figure 1: Robots are used to enhance research processes in Chemical laboratories

2.1 Artificial Intelligence.

Artificial intelligence (AI) is a technology that enables computers and machines to simulate/mimic human intelligence and problem-solving capabilities (Baum *et al*., 2021; El-Meligi, 2023).

2.1.1 Machine learning (ML) in chemistry

Machine learning (ML) is a subset of AI that focuses on the development of computer algorithms that improve automatically through experience and data to make decisions or predictions without being explicitly programmed (El-Meligi, 2023).

2.1.2 ML in Drug Discovery.

The major area where AI is applied is in the field of drug discovery and development (El-Meligi, 2023). The development of new drugs is not only expensive (costs greater than 2.6 billion dollars) but also takes more than 10 years, with a success rate of less than 12% (Xu *et al*., 2021). Today, AI technologies such as ML, DL, artificial neural networks (ANNs), expert systems, and ML are catalyzing the drug discovery and development stages, thereby reducing cost and equally saving time. One notable breakthrough of AI in drug discovery was the discovery of "Halicin" using an ML algorithm. Halicin is a new potent antibiotic that fights against a broad range of bacteria, even tuberculosis, and strains that are regarded as incurable (Ali, 2023). AI has been applied in various areas of drug discovery, such as druggability assessment, *de novo* molecular synthesis, and protein and ligand quantitative structure-activity relationship (QSAR) research. In January 2020, Exscienta reported that their new AI-discovered drug, DSP-1181, intended to treat obsessive-compulsive disorder, started phase I clinical trials and took less than 12 months from the initial screening to the end of preclinical testing, which, on an industry-wide scale, took approximately 4-6 years (Burki, 2020).

2.1.3 ML in Material Discovery

Materials are the cornerstone of modern industry because they have broad applications in construction, biomedicine, energy storage, information, transportation, automobiles, spaceflight, etc. (Xu *et al*., 2021). This is achievable by incorporating the material's molecular features and functionality into the training of the ML algorithm. Once trained, the machine can predict new materials and enhance material design. Various materials, such as piezocrystals with high electric strains (Yuan *et al*., 2018), molecular emitters for efficient light-emitting diodes (Paterson *et al*., 2020), and organic photovoltaics for renewable power applications (Xu *et al*., 2021), have been discovered through AI. Holistically, AI technologies (AI) have proven to be an alternative to traditional material discovery strategies that rely on the edisonian approach and theoretical simulation methods, as they are cost-effective and time-efficient.

2.2 Big Data Analytics (BDA)

Big Data Analysis (BDA) involves using advanced analytic tools and techniques for collecting, storing, examining, processing, and analyzing vast amounts of data and sharing discovered trends and insights to make informed decisions. Chemical big data are powerful digital chemical data that are too large or complex such that they cannot be handled, processed, or analyzed using conventional tools but require special technologies and methods (Batko & Ślęzak, 2022). Big data is a combination of unstructured, semi-structured, or structured data. Data are said to be big data if they are characterized by collections of V, which are volume, velocity, variety, variability, visualization, and value (Senthilkumar *et al*., 2018). Volume refers to the amount of data.

Traditional data are measured in sizes such as megabytes, gigabytes, and terabytes, but big data are very massive or large in size and are stored in petabytes and zettabytes. Velocity is the speed at which new data is created and how fast it moves. Value is the value the data provide. Variety is the heterogeneity or diversity that exists in the types of data. Veracity is the data's trustworthiness, quality, and accuracy. Variability is an inconsistency that exists in big data. Visualization is the use of visual imagery to interpret insights from data. Big data is quite challenging to visualize (Batko & Ślęzak, 2022; Senthilkumar *et al*., 2018).

2.2.1 Chemical databases

Chemical databases are places where chemical data is available. There are numerous chemical databases, which include the following: (i) ChEMBL: This is a manually curated database mined from the literature and PubChem high-throughput screening (HTS) assays. It contains more than 2.4 million compounds, >20 million activities, >15 thousand targets, >89 thousand publications, and 262 deposited datasets (Papdatos *et al*., 2015). (ii) Binding DB: Experimental protein-small molecule interaction data. As of May 2024, Binding DB's patent dataset comprises 7102 patents, 1,103,253 binding measurements, 534878 compounds, 2670 target proteins, and 10,198 assays (Gilson *et al*., 2016). (iii) PubChem: PubChem mostly contains small molecules but also larger molecules such as nucleotides, carbohydrates, lipids, peptides, and chemically modified macromolecules. It contains information on chemical structures, identifiers, chemical and physical properties, biological activities, patents, health, safety, toxicity data, and many others. (Kim *et al*., 2016). (iii) GOSTAR: This is the largest curated SAR (structural activity relationship) database. GOSTAR contains more than 9.7 million chemical structures, 31 million bioactivities, and more than 82,298 targets. (iv) OCHEM: OCHEM contains chemical and biological data and experimentally measured and published articles. The absorption, distribution, metabolism, excretion, and toxicity (ADMET) data were collected from the literature (Sushko *et al*., 2011). (v) MatWeb: This database contains material information, which includes data sheets of thermoplastic and thermoset polymers such as ABS, nylon, polycarbonate, and polyester; metals such as aluminum, cobalt, copper, lead, magnesium, nickel, steel, and superalloys; ceramics; semiconductors; fibers; and other engineering materials (Rumor & Andrade-Campos, 2022). (vi) MATDAT: MATDAT is another material property database with more than 1500 steel, aluminum, and titanium alloys, cast irons and steels, weld metals, and other relevant design materials (Rumor & Andrade-Campos, 2022). (vii) CSD: The Cambridge Structural Database, owned by the Cambridge Crystallographic Data Centre, is the world's repository for experimentally derived small-molecule organic and metal-organic crystal structures (Groom *et al*., 2016).

3.0 Synergy of AI and BDA in Revolutionizing Chemical Research & Development (R&D).

AI and BDA are two separate fields, yet they cannot function on a standalone basis; that is, both are interdependent and cannot function without the other. AI is highly dependent on data, which means that AI is data-driven; therefore, with access to a large chemical dataset, chemists can build or develop intelligent systems that can be used to solve chemical problems. It has been reported that 80% of scientific data becomes out of reach after two decades (Gibney *et al.*, 2013).

3.1 Automation to increase productivity and data consistency through Robotics.

Automated or self-driving chemical laboratories use AI and robotics to enhance laboratory processes. Robotics are revolutionizing traditional chemical processes. Today, we have named ‘RoboChem’, an autonomous chemical synthesis robot with an integrated AI-driven machine unit. This robot has been known to outperform human chemists in terms of speed and accuracy. RoboChem has been utilized to accelerate drug discovery processes and other applications (Mullin, 2021). AI trained in the scientific literature, combined with an automated chemistry laboratory, has successfully discovered and synthesized inorganic compounds. In materials science, the process of discovering energetically favorable inorganic crystals without automation is challenging and time-consuming. Google DeepMind has developed a deep learning tool called Graph Networks for Materials Exploration (Gnome) trained on a large and diverse dataset developed by Materials and used to filter candidate structures. An autonomous lab (A-Lab) has aided in the solid-state synthesis of inorganic powders. A-Lab uses computations, ML, and active learning to plan and interpret the outcomes of experiments performed using robotics and has effectively recognized 41 new compounds from a set of 58 targets. This emphasizes the effectiveness of AI in material discovery (Szymanski *et al.*, 2023).

3.2 Challenges and Limitations of Revolutionizing Chemistry Through AI and Big Data Analytics

The revolution of chemistry through AI and big data analytics has seen continued growth but has several setbacks. According to the IBM Global Adoption Index 2023s, the top five things that hinder successful AI adoption are limited AI skills, expertise, or knowledge (34%), a high price (29%), a lack of tools or platforms for developing models (25%), projects that are too complex or difficult to integrate and scale (24%), and too much data complexity (24%). This is true in chemistry research and development, as we lack AI and BDA experts and limited funding (IBM, 2024). Additionally, in BDA, data quality remains a major challenge because the data retrieved from research articles is often too noisy, which can be attributed to experimental errors, false data, unstandardized data, etc. (IBM, 2024; Zhang, 2022), and these errors can lead to robotic failure, unreliability in machine learning prediction, etc. Another challenge hindering the successful revolutionization of AI and BDA in chemistry is the lack of data sharing and data security. The sharing of data among industries and academia will foster the implementation of AI and BDA in chemistry. It is also known that AI cannot perform critical thinking or contextual comprehension, as humans and AI cannot in totality acquire human problem-solving capabilities, talent, trial and error, observation, etc. (El-Meligi, 2023).

3.3. Future Prospects of AI and Big Data Analytics in Chemistry.

As technology continues to evolve, the synergy between artificial intelligence, big data analytics, and chemistry holds the promise of unlocking new frontiers, leading to groundbreaking discoveries and innovations that will shape the future of scientific exploration. As we stand at the intersection of AI, BDA, and chemistry, the possibilities are boundless, and the journey of discovery has only begun.

4.0 Conclusion and Recommendation.

Artificial intelligence cannot stand alone without big data neither can meaningful insights be derived from big data without AI. The revolution of chemistry through AI and BDA cannot be possible without training chemists on these technologies. We recommend that both industry and academic institutions ensure that chemists undergo professional training on AI and BDA to become experts in utilizing these technologies to solve problems in chemistry and produce ground-breaking research. Additionally, to speed up this revolution in chemistry, we urge academic institutions to add the teaching of these technologies to their curricula.

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CHEMICAL SOCIETY OF NIGERIA (CSN) ABIA CHAPTER

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Conference Proceedings

Full Length Research Paper

TRACE METAL LEVELS OF IMPORTED AND LOCALLY PRODUCED RICE (*Oryza sativa*) CONSUMED IN SOUTHEASTERN NIGERIA

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ABSTRACT

Food contamination by heavy metals is a source of concern because of their potential negative impacts on consumers. The increasing use of agro-chemicals in Nigeria necessitates periodic monitoring of foodstuff. This study investigated cadmium, chromium, copper, lead, and zinc levels of imported and locally produced rice samples. Samples of locally produced and imported rice samples displayed for sale in the markets were obtained and analyzed for Zn, Pb, Cr, Cu and Cd using Atomic Absorption Spectrophotometer after mineralization using acid mixture (1:2 perchloric acid and nitric acid). Adequate quality assurance and protocols were observed. The observed metal levels were generally low and within acceptable limits of these metals in rice and other foodstuff as established by FAO/WHO. The mean metal concentrations (mg/kg; dry weight) were 1.24±1.15 (range ND-4.54) for Zn, 0.18±0.23 (ND-0.95) for Pb, 0.12±0.27 (ND-1.30) for Cr, 0.24±0.17 (ND-0.52) for Cu and 0.58±1.55 (ND-5.67). Cadmium was elevated in some samples thereby making the mean values to exceed the WHO/FAO limits of 0.2 mg/kg for rice. Mean metal concentrations were higher for locally grown rice for Zn, Pb and Cd compared to the imported rice brands with Cd being the highest - 18 times higher in local brands. This can be attributed the high Cd levels of locally produced rice from Ebonyi (1.89±3.27mg/kg). Ebonyi State has Pb-Zn mines and high Cd levels have been reported in soil and biota. Short grain rice had higher metal levels compared to long grains (mg/kg): Zn (1.59±1.20 vs 0.61±0.73), Pb (0.23±0.25 vs 0.08±0.16) and Cd (0.82±1.87 vs 0.14±0.52). Hazard quotient used to assess human health risk was calculate for the consumption of rice for adults and children and the data showed no potential noncarcinogenic and carcinogenic health risks to consumers. Regular monitoring of foodstuff to protect human health is recommended.

Key word: rice, Nigeria, heavy metals, intake, lead, monitoring

INTRODUCTION

Rice (*Oryza sativa* L.) is considered the world's third largest crop, which plays a significant role in human nutrition (Proshad *et al.*, 2019). It is an important source of energy, vitamins, minerals and amino acids for its consumers around the world (Poutanen *et al.*, 2021). Many people eat rice because of the nutritive value and it is one of the major foods eaten by half of the population in the world.

(Zhang *et al*., 2019). With the growing human population, the demand for rice in Nigeria is, however, growing faster than for any other major staples, with consumption broadening across all socio-economic classes, including the poor. Due to growing demand and lack of sufficient production, a significant proportion of this product is imported from the other countries. In the past one year the market price of rice almost quadrupled. There are evidences of smuggling of rice into the country and this can include low quality products.

In recent years food stuff contamination by heavy metals from the soil has become a serious challenge because of their potential accumulation through contaminated water and soil sources. Agricultural and industrial activities release several organic pollutants such as drugs and large quantities of inorganic pollutants as heavy metals (Malidareh *et al.*, 2014). Heavy metal contamination of the environment, which includes farm lands, is a well-known issue (Zhao *et al*., 2019). Heavy metals enter the environment from both natural and anthropogenic sources (Zazouli *et al.*, 2010). Fertilizers and pesticides are the major route of heavy metals to plants and soil (Alengebawy *et al*., 2021; Anjali *et al*., 2023). For example, phosphate fertilizers have been reported to contain high concentrations of Pb and Cd (Azzi *et al.*, 2017; Zazouli *et al.*, 2008), while pesticides contain Cu, As, Cd and Hg (Adel *et al.*, 2016). The storage of foodstuff under unfavorable conditions, including contact with water or high humidity, could result in spoilages.

Plants may absorb and bioaccumulate heavy metals from the soil; in most cases, having a detrimental effect on the plants. In addition to reduced photosynthetic activity, chlorosis, stomatal density, leaf necrosis, suppression of lateral root growth, and an unfavorable transpiration rate, rice is susceptible to Cd, just like other crops (Wang *et al*., 2014). Heavy metals are known to be harmful to both humans and plants, while the mechanism have been proposed or explained in several studies (Huybrechts *et al*., 2020; Salam *et al*., 2020; Ahmad *et al*., 2024). The main route for Cd's bioavailability-dependent entry into the human food chain is through the intake, transport, and accumulation of the metal in vegetables and cereal crops (Liu *et al*., 2022; Ahmad *et al*., 2024). Heavy metals in human body above certain thresholds result in various diseases. For example, an excess of Zn induces pH lowering and so an oxygen absorption’s decreasing coupled to increasing of heart rate (Plum *et al*., 2010; Dwivedi *et al*., 2024) while, Cd causes the Itai–Itai disease characterized by skeletal pain (Nogawa *et al.*, 2017). Cu promotes kidneys and liver's illness (Tominaga *et al*., 2023), Pb is known to be a leukemic metal but also bring to a several brain diseases, gastrointestinal colitis as well as thromboembolic venous diseases (Nutescu *et al.*, 2016).

Some studies have reported elevated levels of heavy metals, especially for cadmium, chromium, and lead, in rice grains from different countries (Rahman *et al.*, 2014; Kormoker *et al.*, 2020; Jafari *et al.*, 2018). These investigations have shown that anthropogenic activities such as industrial production, mining and transportation release a high amount of heavy metals to the water and soil sources used in the rice cultivation. The aim of this study was to determine the levels of some trace metals (Zn, Pb, Cr, Cu and Cd) in rice brands displayed for sale in the open markets in southeastern Nigeria. This includes short and long grain rice as well as locally cultivated and imported rice brands consumed in the five southeastern Nigerian states of Abia, Anambra, Enugu, Ebonyi and Imo states. The results obtained will be compared to the allowable limits set for these metals as set by FAO/WHO. Intake of these metals from rice consumption will be estimated and the likely consequences discussed. Data from this study will provide some insight into heavy metal accumulation of rice and serve as a basis for comparison to with data from other regions both in Nigeria and abroad.

MATERIALS AND METHODS

2.1 Description of the Study Area

South Eastern region of Nigeria consists of five states: Abia, Anambra, Ebonyi, Enugu and Imo states with about 29,848 square miles (77,310 km^2) of land; mainly of woodland and tall grass savannah, rainforest and fresh water swamp. The area has a tropical climate with two distinct seasons: dry (November to April) and rainy seasons (April to October) with the heaviest rains between June and July. The temperature of the region on a clear day is 30 ^{o}C (86 ^{o}F) high and 22 ^{o}C (71.6 ^{o}oF) low and the lowest rain level of 16 mm (0.63 in) and the highest 3,000 mm (118.1 in) of rain per year. The temperature at night reaches 20 °C (68 °F) and in the day has a peak temperature of 36 °C (96.8 °F) (Omaka *et al.*, 2017).

2.2 Sample collection and preparation

Thirty-six (36) different brands of rice made up of 20 imported and 16 locally produced rice samples, were purchased from different markets in the Southern part of Nigeria and used in this study. The sample were packed in a Ziploc® and properly labeled. A known weight (50 g) was ground and sieved with 2 micron-meter mesh and then stored dry in air-tight containers until further analysis.

2.3 Sample analysis

A known weight of dry powdered rice (2g) was digested with an acid mixture (10mL, 1:2 perchloric acid: nitric acid). The digestion flask was heated to boil on a hot plate until evolution of white fumes which marks the end of the digestion before heating to near dryness. Di-ionized water was added to the flask and then stirred before filtration using Whatmann No. 4 filter paper into calibrated volumetric flask. Trace metal concentrations (Zn, Pb, Cr, Cu and Cd) of the digests were measured using atomic absorption spectrometry (Varian AA 240, Agilent, USA) as described by (Braid *et al.*,2017). The range of standards required were prepared from a stock standard solution of the metal as described by the American Public health Association (APHA,1995). Blanks were included at 10% insertion rate while adequate quality control protocols were implemented. AnalaR and BDH reagents were used.

2.4 Estimation of Daily Intake of Trace Metals from Rice Consumption

The average daily intake [ADD, mg/ (kg/day)] is a parameter used to quantify the oral exposure dosage during a specific period (from food), and this is expressed as a daily dose per unit body weight. The daily metal intake dose depends on the metal concentration and the amount of food consumed. It is usually calculated using the following formula (Li *et al.*, 2013):

$$ADD = \frac{C \ X \ IR \ X \ EF \ X \ ED}{BW \ X \ AT} \qquad (1)$$

where C is the mean metal concentration (mg/kg) and *IR*, *ED*, *EF*, *BW*, and *AT* represent the ingestion rate, exposure duration, exposure frequency, reference body mass, and average time, respectively. The IR was estimated to be 0.4097 kg/day, according to the average daily rice intake of adults in Hunan Province; the BW of 60 kg and 15 kg for adult and children respectively were used according to data in related studies; EF is the exposure frequency (365/days/year). ED is the exposure duration (70 years), equivalent to the average lifetime. ATn is the average exposure time for non-carcinogens (365 days/year × ED) (WHO, 2017).

2.5. Human Health Risk Assessment

The hazard quotient (HQ), a ratio of the ADD to the RfD (Copat *et al.*, 2013) represents the health risk of noncarcinogenic adverse effects due to exposure to toxicants.

To estimate the human noncarcinogenic risk from rice consumption, the reference dose (RfD), which is the United States Environmental Protection Agency's (USEPA's) maximum acceptable oral dose for a toxic substance, was used. The HQ is estimated using the relation (Qiao *et al.*, 2011):

$$HQ = \frac{ADD}{RfD} \qquad (2)$$

Here, the RfD is an index of the estimated maximum permissible dose for humans through daily exposure. The values of HQ when less than 1 can be assumed to reflect safety, whereas HQ greater than 1 is assumed to indicate potential noncarcinogenic effects. Data were reported as mean and standard deviation (SD). One-way analysis of variance (ANOVA) was performed at a confidence level of 95%. Principal component analysis (PCA) was used to compare the pattern of trace metal concentrations in rice samples collected from different states.

3. RESULT AND DISCUSSION

3.0 Trace metal levels in Rice

A summary of the Zn, Pb, Cr, Cu and Cd contents (mg/kg) of the rice samples are presented in Table 1. The metal concentrations varied considerably and the results showed a decreasing trend of Zn > Cd > Cu > Pb > Cr (Fig. 1). Table 1 shows that mean values were below the permissible limit. Only Cd had some values above the set limit. The Cr results of the present study are comparable the reports of Rahman *et al.* (2014) which reported mean Cr in rice of 0.19, 0.14, 0.079, 0.41 and 0.07 mg/kg in Indian rice, Australian rice, Pakistani rice, Thailand rice and Vietnam rice, respectively. Presented in Figure 1 is a comparison of the mean trace metal levels of imported and locally produced rice. Data in Figure 1 showed that the Zn, Pb and Cd contents of locally produced rice were 3.6, 2 and 18 times higher than the values for imported rice. Processing methods adopted for the imported polished rice may be a factor in reducing the metal contents. The mean Zn concentrations in rice of the present study 1.24 mg/kg (range: 0.005–4.45 mg/kg). These values are below the 50 mg/kg limit set by the FAO/WHO. Zn concentration in Australian grown rice studied by Rahman et al., 2014 differ significantly with mean value of 17.1 mg/kg (range: 10.9–24.5 mg/kg). Ajah *et al*. (2022) reported mean concentration of the metals in the soil before planting, soil after harvest, and rice grain were as follows: Zn (7.28, 11.33 and24.90); Cu (3.40, 4.64 and 4.14); Fe (803.04, 735.47 and 107.78); Cd (1.14, ND and ND) and were all within FEPA and FAO/WHO limits.

3.2 Trace metal levels in Rice according to Source, Size and Sampling Location

Short rice grain samples were observed to have higher Zn (1.59±1.20 vs 0.61±0.73), Pb (0.23±0.25 vs 0.08±0.16) and Cd (0.82±1.87 vs 0.14±0.52). A comparison of the data according to the sampling locations (states) is presented in Figure 2.

Table 1: Concentration (mg/kg) of trace metals in studied rice samples

Metal	Mean±SD	Range	FAO/WHO
Zn	1.24±1.15	ND- 4.54	50
Pb	0.18±0.23	ND -0.95	0.2
Cr	0.12±0.27	ND -1.30	2.3
Cu	0.24±0.17	ND -0.52	20
Cd	0.58±1.55	ND -5.67	0.2

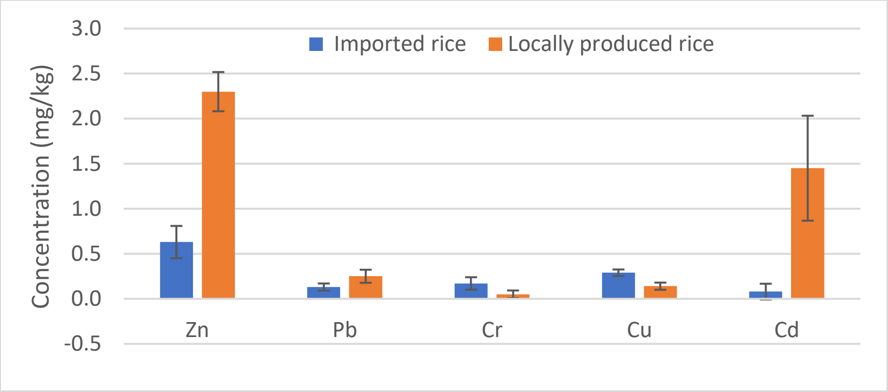

Figure 1: Comparison of trace metal contents of imported and local rice (mg/kg)

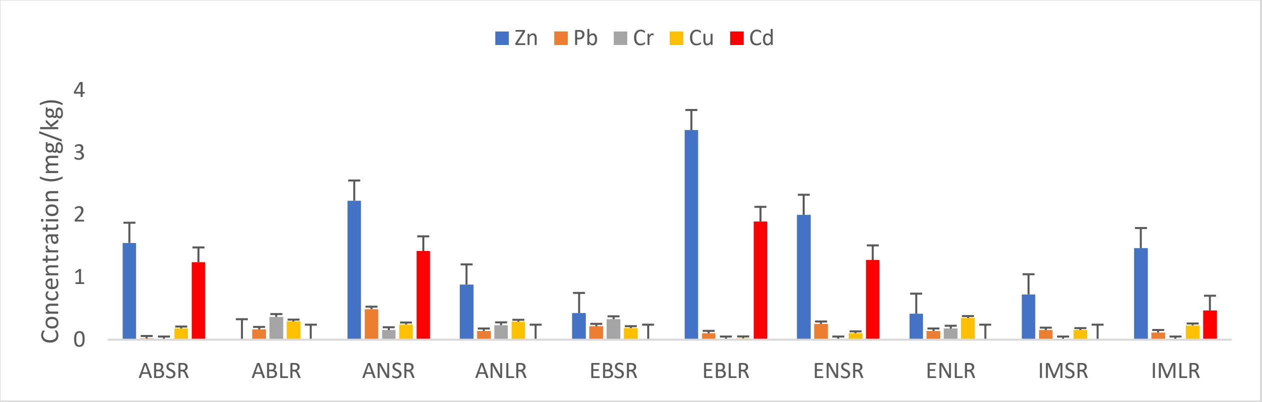

Figure 2: Trace metal contents of rice according to sampling location (mg/kg).

Note: ABSR and ABLR represent Abia State foreign and local rice respectively; for the other states, AN stand for Anambra, EB, Ebonyi, EN Enugu and IM for Imo States.

The higher metal levels in locally produced rice samples can be attributed the high levels of Cd in rice from Ebonyi (1.89±3.27 mg/kg) considering that literature abound on high Cd levels in soil and biota of Ebonyi State which has Pb-Zn mines within the Enyimgba. According to Garg *et al*. (2014), variability in metal concentrations was found among the different sampling sites because of natural characteristics, extent of anthropogenic activities, and levels of contamination. The use of different agricultural applications such as manure, fertilizer and pesticide; and extensive use of wastewater for irrigation could also bring changes in the level of heavy metals in soils which ultimately transfer and affect the metal levels of cultivated rice samples (Islam *et al*., 2018).

The lead-zinc mine communities in Ebonyi State are situated in three local government areas generally referred to as the Abakaliki lead-zinc mine area (Ogbuene *et al*., 2023). The Abakaliki lead-zinc area is primarily made up of three lodes: Enyimgba, Ameri, and Ameka in the lower Benue trough located in Ebonyi State. Ogbuene *et al*., (2023) reported cadmium in top-and-sub-soils of communities in Ebonyi to be higher that the USEPA limit value of 3.0 mg/kg with values ranging from 4.53±0.44; 3.46±0.72; 5.37±0.55; 5.04±0.23; 5.65±22 to 4.67±0.34 mg/kg (Ogbuene *et al*., 2023).

3.3 PCA Analysis of Data

Principal component analysis (PCA) was employed to compare the compositional pattern between the metals in the rice sample collected from different areas. A principal component analysis (PCA) was performed following the standard procedure to identify the hypothetical sources of the metals (natural or anthropogenic) in rice for this present study. The PCA was performed on the tabular and dimensionless standardized form of the data set and presented Figure 3. Overall, the PCA revealed two major groups of the studied five metals in rice. PC1 was strongly correlated with Pb and PC2 was also strongly correlated with Cu, Cr, Cd and Zn.

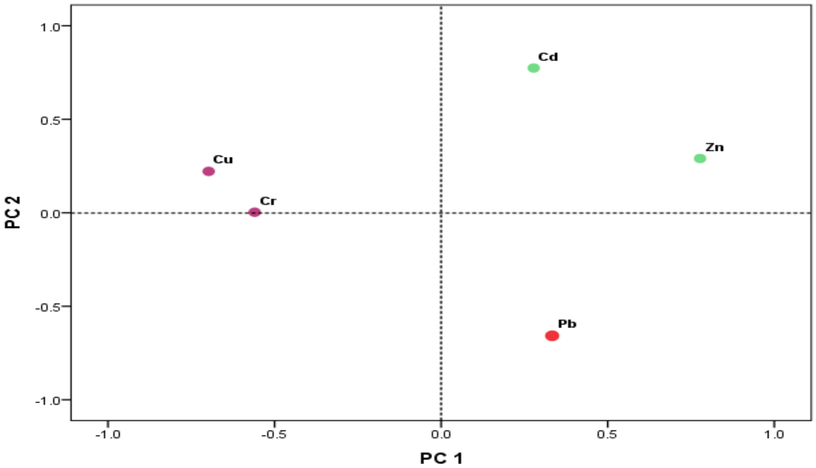

Figure 3. Principal component analysis (PCA) of results.

ANOVA for metal concentrations of the rice samples, indicated that there is no significant difference between long grains and short grain rice brand in the present study, and also that there is no significant difference between metal levels in the imported rice and locally cultivated rice brand for all metals except for Zn. Inter-relationships among the measured metal concentrations in the rice samples were investigated in terms of Pearson's correlation coefficient matrix but no strong relationships were observed. In rice samples, Zn showed significant positive correlations with Pb (r = 0.109), and Cd (r = 0.303) whereas Pb showed significant associations with Cr (r =0.035). The value of Cr showed significant positive correlation with Cu (r = 0.190), and Cd (r =0.036). Higher correlation coefficients between the metals indicated common sources, mutual dependence, and similar or nearly identical metal accumulation properties in rice (Kormoker *et al.*, 2020).

3.4 Metal Intakes from rice consumption and the Health Implications

Hazard quotient used to assess human health risk was calculate for the consumption of rice for adults and children and the data showed no potential noncarcinogenic and carcinogenic health risks to consumers. Regular monitoring of foodstuff to protect human health is recommended. The daily intake values for a 60 kg adult were Zn (0.04), Cu (0.01), and Fe (0.18) and were all below the recommended limits by Codex Alimentarius standards. The Target Hazard Quotient (THQ) for Zn, Cu, and Fe was less than one for all the metals.

One of the main routes of human exposure to the harmful metals is through food consumption including rice that could have accumulated metals. The average daily dose (ADD) of the metals determined for adults and children through rice consumption were estimated. The total daily intakes of Zn, Pb, Cr, Cu, and Cd for adult inhabitants were 1.69x10^{-05}, 2.46x10^{-06}, 1.64 x10^{-06}, 3.28 x10^{-06}, and 7.92x10^{-06} mg/day, respectively. For children, the total daily intake of Zn, Pb, Cr, Cu, and Cd were 3.63 x10^{-06}, 5.27 x10^{-07}, 3.51 x10^{-07}, 7.02 x10^{-07} and 1.7 x10^{-06}, respectively. The ADD for Zn, Pb, Cr, Cu, and Cd for both adults and children were below the provisional tolerable daily intake obtained or calculated based on standards established by Joint FAO/WHO Expert Committee on Food Additives (JECFA). This implies that the consumption of the rice samples studied would not present potential risk to the consumers. Sibuar *et al.*, (2022) in a study of Malaysian rice reported ADD for Cd, Cr, Cu, and Pb intakes through rice consumption to be 0.000011, 0.00074, 0.00048, 0.000029 mg/kg/day for adults and 0.000012, 0.00085, 0.00056, and 0.000031 mg/kg/day for children.

The estimation procedure of THQs offers an indication of the risk level due to contaminant exposure but it does not allow a quantitative estimation on the probability of an exposed population experiencing a reverse health effect. The average THQ values for both adults and children for the five metals were estimated. Among all the studied metals, the THQ value for individual metals from each sample were found to be less than 1.00. Therefore, the rice samples are considered safe for human consumption. Other studies or rice including that of Jafari *et al*. (2019) also reported HQ values of less than 1 for rice samples collected in Iran (Lorestan province). Kormoker *et al.* (2020) on the other hand reported THQ values of Cu, Cd, and Pb that were greater than 1.00 thus the consumption of rice samples was considered to be unsafe. The study concluded that the consumers are at a higher risk with respect to Cu, Cd, and Pb which can cause non-carcinogenic risks (Kormoker *et al.*, 2020).

3.4 Comparison of results with Literature

Presented in Table 2 is a comparison of the results of this study with selected data from literature. The comparison shows that the results of this study are comparable with data from literature and that the population in the study areas in Nigeria are not exposed to metal levels above established thresholds. Residents of Ebonyi State that consume locally produced rice more often may stand a rick of having elevated metals levels (especially Cd) in their system.

CONCLUSION

The results of this study revealed the presence of cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), and zinc (Zn) in rice grain samples of locally cultivated rice and imported rice sold in different markets in southeastern Nigeria. Human health risk assessment was conducted with for adult and children population, as hazard quotient (HQ) of the metals were <1 for adult and children in all rice samples assessed. The results show that potential noncarcinogenic and carcinogenic health risks does not exist for rice consumers in the region. There is a need for regular monitoring of foodstuff for contamination to protect human health.

Table 2: Comparison of metal concentration (mg/kg dry) of rice samples from different countries

Country	Cu	Zn	Cd	Pb	Cr	References
Australia	0.0029	0.0171	0.0075	0.375	0.144	Rahman *et al*. (2014)
Bangladesh	0.0016	0.0134	0.073	0.019	0.119	Rahman *et al*. (2014)
India	0.0059	0.0135	0.0275	0.267	0.19	Rahman *et al*. (2014)
India	0.0058	0.0152	0.0191	0.317	0.055	Rahman *et al*. (2014)
Pakistan	0.0026	0.0162	0.0045	0.067	0.079	Rahman *et al*. (2014)
Thailand	0.0035	0.0178	0.013	0.419	0.413	Rahman *et al*. (2014)
China	-	-	0.103	0.131	-	Fan *et al*. (2017)
China	0.0033	-	0.0345	0.355	0.199	Fang *et al*. (2014)
Iran	0.29	-	0.16	0.196	0.22	Jafari *et al*. (2018)
Iran	0.61	-	0.13	0.55	0.76	Jafari *et al*. (2018)
Bangladesh	20.54	-	0.149	1.26	5.08	Kormoker *et al* (2020)
Nigeria[a]	0.24	1.24	0.58	0.18	0.12	Present study
Nigeria[b]	0.29	0.63	0.08	0.13	0.17	Present study
Nigeria[c]	0.14	2.30	1.45	0.25	0.050	Present study

a = mean of imported and locally produced rice; b = locally grown rice c = imported rice brands

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CHEMICAL SOCIETY OF NIGERIA (CSN) ABIA CHAPTER

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Full Length Research Paper

SOME PHYSICOCHEMICAL PARAMETERS OF SOILS FROM SELECTED FARMLANDS IN THE AGRICULTURAL ZONES OF ABIA STATE

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ABSTRACT

The study investigated the physicochemical parameters of agricultural soils in Abia State, Nigeria. Soil samples were randomly collected at 0 - 30cm dept from 24 farmlands in the 3 Agricultural Zones of the State, 8 farmlands from each zone and from 2 farmlands per Local Government Area in 4 LGA in each zone. The samples were analyzed for pH, organic matter (OM), particle size and cation exchange capacity (CEC) while SPSS 23 was used for the data analysis. The correlation among these physical and chemical properties was examined. Descriptive statistics were calculated to characterize soil composition across the different locations in the study area. The mean (M) and standard deviation (SD) were computed for all variables. Results obtained showed that the agricultural zones as treatment had significant effects ($P<0.05$) on most soil properties. Predominant soil textural classes were loamy sand, sandy loam and sandy clay loam. The pH values of soils ranged from 4.80 to 6.20 in Umuahia zone which is acidic to moderately acidic level, 4.60 to 6.90 in Bende zone and 7.10 to 7.30 in Aba zone which reflected a good soil pH in the zone. The levels of OM ranged from 2.87% to 6.13%, 1.72% to 6.34% and 0.69% to 3.24% in Umuahia, Bende and Aba zones respectively. Most productive agricultural soils have been found to have between 3 and 6% organic moisture. The CEC of the soils had ranges of 4.51 - 22.34cmol/kg, 4.57 - 23.14cmol/kg and 10.81 -25.79cmol/kg in Umuahia, Bende and Aba zones respectively. A CEC value above 10cmol/kg is preferred for plant production. The results provide insights into the fertility status, composition and potential productivity of soils in the area, crucial for effective agricultural management and sustainable land use practices. Understanding these properties is essential for optimizing agricultural production, soil conservation, and environmental sustainability in Abia State.

Keywords: Abia, Agricultural zones, soil, physicochemical parameters, fertility.

INTRODUCTION

Soil is a porous, multi-phase medium consisting of a solid skeleton made of particles (sand, silt and clay), and pores filled with a fluid phase. Physicochemical parameters of soil are the physical and chemical properties that characterize the soil such as pH, soil organic matter (OM), cation exchange capacity (CEC) and particle size. These parameters play crucial roles in determining soil fertility, plant growth and overall soil health (Brady *et al.*, 2008; Lal, 2015). Cation exchange capacity (CEC), is a measure of the soil's ability to hold positively charged ions. This ability arises as a result of the presence of negative charges on soil clays and organic matter. CEC is a very important soil property influencing soil structure stability, nutrient availability, soil pH, the soil's reaction to fertilizers and other ameliorants (Hazleton *et al.,* 2007), CEC also influences the adsorption of heavy metals and organic pollutants (such as antibiotics) in soils (Dutta *et al.,* 2011).

Previous studies showed that physical and chemical properties of soil, such as OM, pH, clay content have significant effects on CEC (Wang *et al.,* 2019). Akpa *et al.,* (2016) found that clay, sand, pH and soil OM are the important influencing factors to predict topsoil CEC in Nigerian soil. Soil with more clay, organic matter and a less acidic environment can better nourish plants by holding onto essential nutrients. Soils with a higher proportion of clay, will have a greater capacity to hold and exchange cations. Particle size distribution separates the inorganic mineral portion of soil into classified grades according to particle size. It determines the proportions of these particles by weight. Only materials less than 2mm diameter is considered. The particle size limits are, sand (2.0mm to 0.05mm), silt (0.05mm to 0.002mm) and clay (less than 0.002mm).

Soils with a higher pH (more alkaline) have a higher CEC. This is because alkaline conditions increase the negative charge on clay and organic matter, allowing them to hold more cations. In acidic soils, the H^+ compete with other cations for the exchange sites, reducing the CEC. The lower the CEC of a soil, the faster the soil pH will decrease with time.

Soil OM refers to all the organic material present within the soil in various stages of decomposition and synthesis, and is variable in composition (Stevenson 1994). Its content in the soil influences CEC in that, organic matter is negatively charged like clay, and can attract and hold cations. The more organic matter a soil contains, the higher its CEC will be. Organic matter has a very high CEC ranging from 250 to 400meg/100g (Moore *et al.*, 1998). Though occurring in relatively small amounts in soils, OM has a major influence on soil aggregation, reducing concentration of toxic elements, nutrient reserve and its availability, moisture retention, and biological activity. This study aims to determine the fertility status, composition and potential productivity of soils in the area studied and inform evidence-based soil management practices tailored to the specific needs and challenges of agricultural system of the area.

MATERIALS AND METHODS

Sampling

The tested soil samples were randomly collected at the 0-30cm dept from 24 farmlands in the 3 Agricultural zones of the State, 8 farmlands from each zone and from 2 farmlands per Local Government Area in 4 LGA in each zone. The soil samples were sieved through a 2mm test sieve after air-drying. Fig. 1 shows the distribution map of soil sampling points.

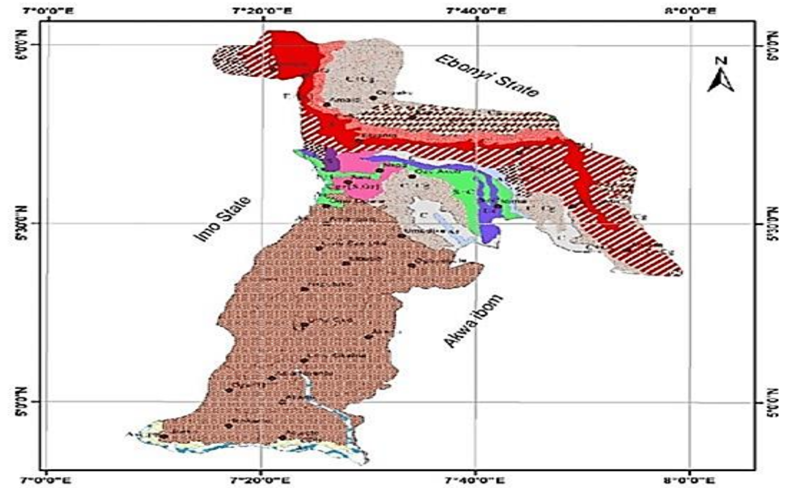

Fig 1. Distribution map of soil sampling points showing their coordinates

Table 1: Sampling Locations, Sampling Points/Areas and Coordinates

AGRIC ZONES	*LGAs*	*SAMPLING POINTS*	*Longitude/ Latitude*
UMUAHIA	Ikwuano	Umudike	5º28’21” N/7º32’55” E
		Amaoba	5º27’49” N/7º32’33” E
	Umuahia North	Umuda Isingwu	5º33’30” N/7º28’28” E
		Umukabia	5º60’22” N/7º45’84” E
	Umuahia South	Umuokpara	5º33’28” N/7º28’28” E
		Ubakala	5º28’25” N/7º25’37” E
	Isialangwa North	Amapu Ntigha	5º25’33” N/7º24’22” E
		Ama-Asa-Ohuhu	5º35’60” N/7º31’60” E
ABA	Aba North	Eziama	5º63’26” N/6º95’51” E
		Osusu	5º38’99” N/7º37’19” E
	Aba South	Eziukwu	5º10’50” N/7º37’22” E
		Ihieorji	5º36’29” N/7º37’22” E
	Osisioma Ngwa	Osisioma	5º20’49” N/7º33’01” E
		Abayi	5º12’72” N/7º33’55” E
	Ugwunago	Ntigha	5º11’40” N/7º44’66” E
		Umueke	5º13’50” N/7º50’24” E
BENDE	Ohafia	Abiriba	5º42’00” N/7º73’33” E
		Ebem	5º62’52” N/7º82’85” E
	Isiukwuato	Imenyi-Amaeke	5º66’67” N/7º55’00” E
		Ohaise	5º31’59” N/7º28’59” E
	Bende	Uzuakoli	5º63’02” N/7º56’54” E
		Itumbauzo	5º48’11” N/7º66’57” E
	Arochukwu	Amaebem	5º49’90” N/7º78’80” E
		Amodu	5º22’59” N/7º54’59” E

Test methods of soil physical and chemical properties

After air-drying and grinding, physicochemical properties were determined. The soil particle size ratio was determined by Malvin laser particle analyzer 2000, which was divided into three categories: 0 to 2 µm-clay, 2 to 20 µm-silt and 20 to 200 µm-sand. Soil texture was determined by the Bouyoucos hydrometer method (Gee and Bauder, 1986). The pH value was determined by FE-28 pH meter equipped with FE-438 glass electrode with the ratio of soil-to-water (1:2.5, W/V) mixtures of dry soil and distilled water. OM was determined by potassium dichromate volumetric method-external heating method. The acidic ($pH < 6.5$) and neutral ($6.5 < pH < 7.5$) soils were determined by ammonium acetate exchange method, and the alkaline soils ($pH > 7.5$) were tested by flame photometry method (Radojevic *et al.,* 1999). The CEC was determined by measuring the number of exchangeable cations it can hold by saturating the soil with a solution containing a known concentration of exchangeable cations (NH_4^+), and measuring the amount of remaining NH_4^+ in the solution after it has been in contact with the soil (Sumner *et al.*, 1996). The difference between the initial and final concentrations of $NH4^+$ indicated the amount of $NH4^+$ that was exchanged with the soil's cations, from which the CEC can be calculated (Brady *et al.,* 2008).

Data analysis method

Excel 16 was used as the data processing tool and SPSS 23 was used for Pearson correlation, descriptive statistics, standard deviation (SD) and mean (M) which were computed for all variables. Correlation analyses were carried out in order to understand the magnitude and nature of the relationships between various soil parameters in the different Agric soils and zones. A probability level of 0.01 was considered to be statistically significant.

RESULTS AND DISCUSSION

The Soil texture, pH, OM, and CEC levels of the collected soils showed significant differences. Figures 2-7 list the statistical distribution of four basic physical and chemical properties of the measured soils. The results showed that most soil textures are loamy sand, sandy loam and sandy clay loam. The pH values of soils ranged from 4.80 to 6.20 in Umuahia zone which is acidic to moderately acidic level, 4.60 to 6.90 in Bende zone and 7.10 to 7.30 in Aba zone which reflected a good soil pH in the zone. The level of Organic Matter ranged from 2.87% to 6.13%, 1.72% to 6.34% and 0.69% to 3.24% in Umuahia, Bende and Aba zones respectively. Most productive agricultural soils have been found to have between 3 and 6% organic moisture. The CEC of the soils ranged from 4.51cmol/kg to 22.34cmol/kg, 4.57cmol/kg to 23.14cmol/kg and 10.81cmol/kg to 25.79cmol/kg in Umuahia, Bende and Aba zones respectively. For CEC, a figure above 10cmol/kg is preferred for plant production. Generally, the soils with CEC > 20 cmol/kg, 10-20 cmol/kg, < 10 cmol/kg have relatively, high fertility, middle and low fertility respectively (Wu 2011). Soils with high levels of clay and OM can have a CEC of 30 and above. From the result it can be seen that the CEC, OM and clay minerals varied with pH. Generally, the CEC is lowest at soil pH of 3.5 to 4.0 and increases as the pH increases. Proving the fact that CEC may vary considerably with soil pH. It is therefore advisable to measure a soil's CEC at a pH of 7.0. The reduction in pH may be ascribed to increased amounts of Soil OM.

Descriptive Statistics for Soil Composition across Different Locations

Descriptive statistics were calculated to characterize soil composition across various locations in the study area as shown in Table 2. The mean (M) and standard deviation (SD) were computed for all variables. The mean sand content across all sampled locations was *M* = 80.50%, with a standard deviation of *SD* = 7.84%. Silt content had a mean of *M* = 8.42% with a standard deviation of *SD* = 3.09%, while clay content had a mean of *M* = 11.08% with a standard deviation of *SD* = 5.63%. Sand content varied considerably across locations, the lowest and highest mean sand value were found in UZUAKOLI and EZIAMA (57.40% and 92.00% respectively). Silt content ranged from 2.50% in EZIAMA to 15.00% in ITUMBUZO, indicating notable differences in fine particle content among locations. Clay content varied from 5.50% in EZIAMA to 28.60% in UZUAKOLI, demonstrating diverse soil types and textures across the studied areas.

Table 2: Descriptive Statistics for Soil Composition across Different Locations

Location		**SAND (%)**	**SILT (%)**	**CLAY (&)**	**pH (H_2O)**	**OM (%)**	**ECEC ($cmolkg^{-1}$)**
UMUDA	Mean	83.400	10.00	6.600	5.8250	5.3750	16.62800
	Std. Deviation	1.4142	.000	1.4142	.10607	.28991	.053740
UBAKALA	Mean	86.400	7.00	6.600	6.1500	5.9950	22.30000
	Std. Deviation	2.8284	1.414	1.4142	.07071	.19092	.056569
OHUHU	Mean	81.400	10.00	8.600	5.9500	2.9200	11.60500
	Std. Deviation	1.4142	.000	1.4142	.07071	.07071	.049497
NTIGHA	Mean	79.400	12.00	8.600	5.7000	3.2050	8.87000
	Std. Deviation	1.4142	2.828	1.4142	.14142	.04950	.056569
UMUKABIA	Mean	84.400	9.00	6.600	5.7500	3.5900	8.04500
	Std. Deviation	.0000	1.414	1.4142	.07071	.00000	.106066
UMUDIKE	Mean	71.400	12.00	16.600	4.8500	5.4150	7.20000
	Std. Deviation	1.4142	.000	1.4142	.07071	.04950	.056569
AMAOBA	Mean	83.400	10.00	6.600	5.5000	3.8350	10.95000
	Std. Deviation	1.4142	.000	1.4142	.14142	.03536	.113137
UMUOKPARA	Mean	84.400	8.00	7.600	5.2000	2.8900	4.51500
	Std. Deviation	.0000	.000	.0000	.00000	.01414	.007071
ABRIRIBA	Mean	90.400	3.00	6.600	4.8000	1.7550	4.60500
	Std. Deviation	.0000	1.414	1.4142	.14142	.04950	.049497
EBEM	Mean	80.400	7.00	12.600	4.5500	2.7300	6.22000
	Std. Deviation	.0000	1.414	1.4142	.07071	.04243	.056569
IMENYI	Mean	82.400	9.00	8.600	5.7500	3.1350	9.54000
	Std. Deviation	2.8284	1.414	1.4142	.07071	.04950	.056569
OHAISE	Mean	74.400	9.00	16.600	5.9250	2.4450	13.07000
	Std. Deviation	.0000	1.414	1.4142	.10607	.04950	.000000
UZUAKOLI	Mean	57.400	14.00	28.600	4.6500	3.9650	8.47000
	Std. Deviation	1.4142	.000	1.4142	.07071	.04950	.056569
ITUMBUZO	Mean	61.400	15.00	23.600	4.7500	6.3250	12.49500
	Std. Deviation	1.4142	1.414	2.8284	.07071	.02121	.049497
AMA EBEM	Mean	82.000	8. 00	10.000	6.3000	2.9150	22.43000

	Std. Deviation	1.4142	2.828	1.4142	.14142	.02121	.056569
AMA ODU	Mean	85.000	6.00	9.000	6.8250	1.8600	23.10000
	Std. Deviation	.0000	.000	.0000	.10607	.09899	.056569
EZIAMA	Mean	92.000	2.50	5.500	7.1750	.7600	14.55000
	Std. Deviation	1.4142	.707	.7071	.31820	.09899	.000000
OSUSU	Mean	74.000	10.00	16.000	7.0750	3.0050	10.85000
	Std. Deviation	1.4142	.000	1.4142	.17678	.03536	.056569
EZIUKWU	Mean	83.000	7.00	10.000	7.1000	2.5850	24.25500
	Std. Deviation	.0000	1.414	1.4142	.28284	.04950	.049497
IHIE ORJI	Mean	84.000	6.00	10.000	6.7600	2.0000	22.99000
	Std. Deviation	1.4142	2.828	1.4142	.05657	.09899	.056569
OSISIOMA	Mean	86.000	5.00	9.000	6.9250	1.4150	18.72000
	Std. Deviation	1.4142	1.414	.0000	.24749	.04950	.056569
ABAYI	Mean	83.000	7.00	10.000	6.8150	2.7250	18.11000
	Std. Deviation	.0000	1.414	1.4142	.12021	.04950	.113137
NTIGHA	Mean	83.000	7.00	10.000	7.2500	3.2750	25.78500
	Std. Deviation	.0000	1.414	1.4142	.07071	.04950	.007071
UMUEKE	Mean	77.000	8.00	15.000	6.8850	2.1050	15.88000
	Std. Deviation	.0000	.000	.0000	.12021	.04950	.056569
CONTROL	Mean	83.000	9.00	8.000	6.7100	2.2100	8.75000
	Std. Deviation	2.8284	1.414	1.4142	.01414	.00000	.000000
Total	Mean	80.504	8.42	11.076	6.0468	3.1374	13.99732
	Std. Deviation	7.8374	3.091	5.6272	.88197	1.38050	6.548090

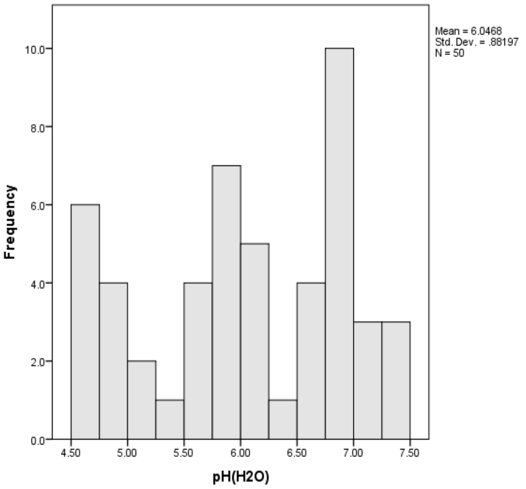

Fig.2: Distribution of soil pH

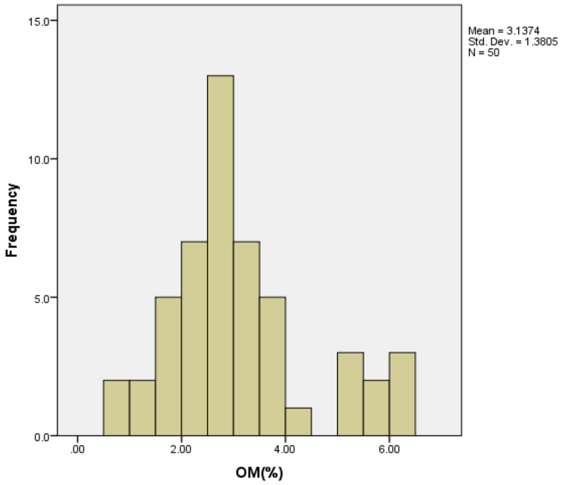

Fig.3: Distribution of soil OM

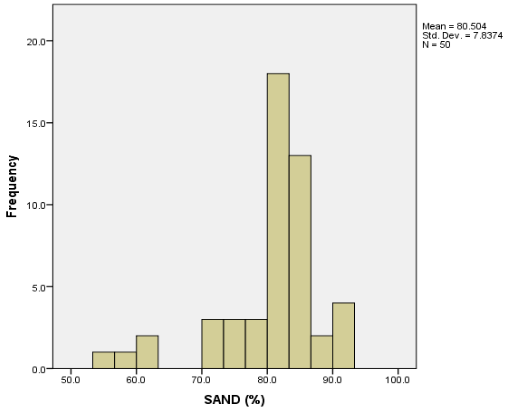

Fig. 4: Distribution of sand content

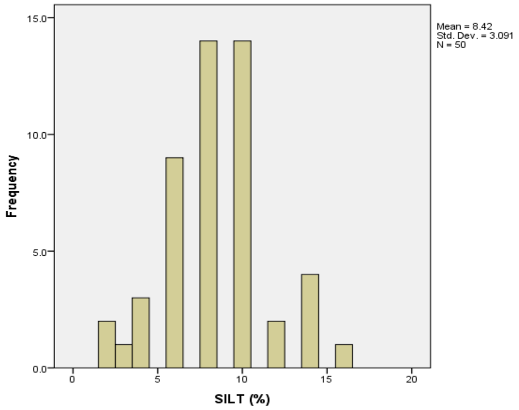

Fig. 5: Distribution of silt content

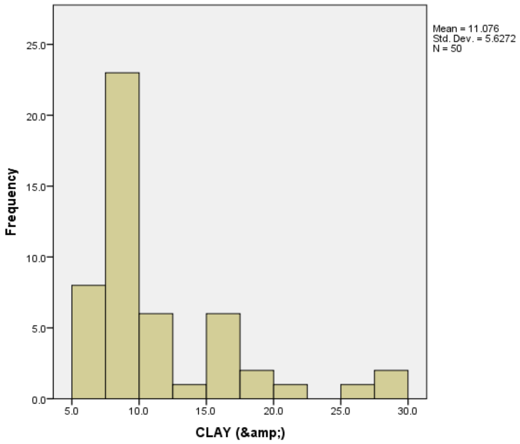

Fig. 6: Distribution of Clay content

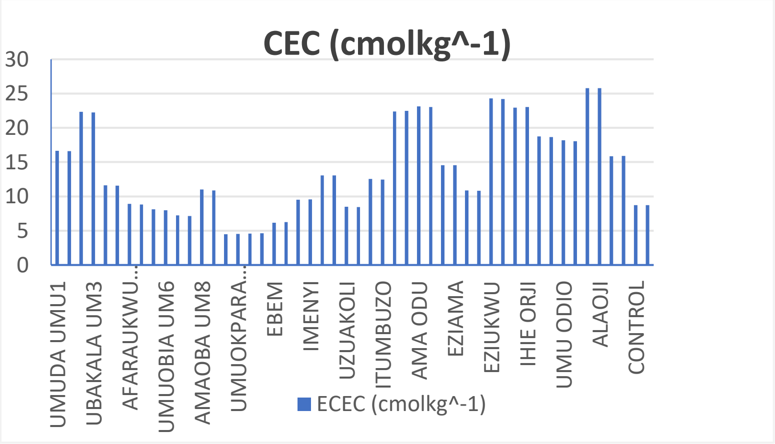

Fig. 7: Distribution of soil CEC

CORRELATIONS BETWEEN SOIL PROPERTIES

Table 3 shows the correlations between the studied variables in the entire data set considered in the study. In the different soils, Clay content showed a significant negative correlation with pH ($r = -0.357$, $p < 0.05$), indicating that higher clay content is associated with lower pH levels. Supported by the study of Helyar and Porter (1989) that highlights that soils with higher clay content typically exhibit lower pH values due to the higher CEC and the tendency of clays to retain more acidic cations. Clay content showed positive correlation with organic matter ($r = 0.328$, $p < 0.05$), suggesting that higher clay content is associated with higher levels of nutrients. A study (Hassink 1997) that supports this demonstrates that soils with higher clay content tend to have higher levels of organic matter due to the protective properties of clay particles which help in the stabilization and accumulation of organic matter. Sand content is significantly negatively correlated with silt ($r = -0.811$, $p < 0.01$) and clay ($r = -0.947$, $p < 0.01$), supported by a study (Saxton *et al*., 1986) that showed that an increase in the sand fraction typically corresponds to a decrease in the finer fractions, clay and silt. Sand content showed a positive correlation with pH ($r = 0.436$, $p < 0.01$), suggesting that higher sand content is associated with higher pH levels. Sandy soils which generally have lower OM and CEC, tend to exhibit higher pH values compared to finer-textured soils (Ahl *et al*., 2004). Sand content showed negative correlation with organic matter ($r = -0.496$, $p < 0.01$), indicating that higher sand content is associated with lower levels of these nutrients due to poorer retention and stabilization of organic materials to finer-textured soils such as those high in clay and silt (Six *et al*., 2002). Silt content showed positive correlation with clay ($r = 0.581$, $p < 0.01$), and organic matter ($r = 0.660$, $p < 0.01$), this is due to better protection and stabilization of organic materials provided by fine soil particles (Hassink *et al*., 1993). While Silt content was negatively correlated with pH ($r = -0.455$, $p < 0.01$), indicating that higher silt content is associated with lower pH levels reason being that higher OM content and different mineralogical compositions (Dao, 1994). It was found that the relationship between CEC and pH value was obvious as pH showed significant positive correlations with CEC ($r = 0.705$, $p < 0.01$), indicating that higher pH levels are associated with higher CEC. This is due to the deprotonation of functional groups on soil OM and clay minerals, which enhances their ability to hold and exchange cations (Curtin and Smillie, 1983). This finding is different from the conclusion that there is a significant negative correlation between CEC and pH in the study of Zhang et al., 2011. pH negatively correlated with organic matter ($r = -0.487$, $p < 0.01$), supported by the study (Guo, *et al*., 2023) that explains that higher OM is often associated with lower pH values. There was no significant correlation observed between CEC and clay, CEC and sand, contrary to the findings of other studies (McBratney *et al.*, 2002; Ulusoy *et al*., 2016) that found positive and negative relationships between CEC with clay and sand, respectively. Shabani and Norouzi (2015) observed that CEC had a significant negative correlation with sand content. However, this relationship is not always true. Amini *et al*. (2005) found that sand and silt did not have a significant effect in predicting CEC. Also, in this study, the correlation between CEC and OM was not significan

Table 3: Correlation between the Studied Properties.

	SAND (%)	SILT (%)	CLAY (&)	pH(H2O)	OM(%)	ECEC (cmolkg^-1)
SAND (%)	1	-.811**	-.947**	.436**	-.496**	.237
SILT (%)	-.811**	1	.581**	-.455**	.660**	-.309*
CLAY (&)	-.947**	.581**	1	-.357*	.328*	-.160
pH(H2O)	.436**	-.455**	-.357*	1	-.487**	.705**
P (Mg/kg)	-.483**	.656**	.312*	-.440**	.906**	-.067
N (%)	-.488**	.673**	.309*	-.503**	.962**	-.158
OC (%)	-.496**	.659**	.328*	-.487**	1.000**	-.073
OM(%)	-.496**	.660**	.328*	-.487**	1	-.074
ECEC (cmolkg^-1)	.237	-.309*	-.160	.705**	-.074	1
BS(%)	.220	-.088	-.258	.740**	-.077	.707**

**. Correlation is significant at the 0.01 level (2-tailed).

*. Correlation is significant at the 0.05 level (2-tailed).

CONCLUSION

This study demonstrated that there is indeed a relationship between OM, pH, CEC and soil textures and their values influence each other. It also provides significant insights into the soil health in this region. Areas with higher organic matter are likely to support better crop yields and sustain productivity over time. The pH range is generally favourable for most crops, although some areas will require lime application to mitigate acidity and improve nutrient uptake by plants. Soils with higher CEC are better equipped to hold onto nutrients, making them available to plants over time, reducing the need for frequent fertilization. The variability in the observed parameters highlights the need for regular soil testing in the region.

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CHEMICAL SOCIETY OF NIGERIA (CSN) ABIA CHAPTER
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Full Length Research Paper

EXTRACTION AND CHARACTERIZATION OF ESSENTIAL OIL IN *Citrus sinensis* (PEELS)

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ABSTRACT

The essential oils extracted from orange peels have attracted considerable attention due to their wide therapeutic properties and potential uses. Samples of orange peel were collected and prepared for oil extraction using the Soxhlet extraction method. The extracted oil underwent various physicochemical analyses to determine its properties. The results indicated that the oil yield was 2.55 ± 0.12% of the dry peel weight. The refractive index was 1.465 ± 0.003, confirming the purity and quality of the oil. With a specific gravity of 0.889 ± 0.003 g/cm^3, falling within the acceptable range for citrus peel oils, and a moisture content of 2.49 ± 0.04%, suggesting good storage stability, the oil demonstrated favorable physical properties. Additionally, the oil exhibited good thermal stability, with a smoke point of 130.6 ± 2.31°C and a flash point of 200 ± 3.46°C. The chemical properties revealed an acid value of 2.77 ± 0.07 mg KOH/g, free fatty acid content of 1.39 ± 0.03%, an iodine value of 77.71 ± 0.93 gI/100 g, peroxide value of 2.96 ± 0.23 meq O_2/kg, and a saponification value of 189.81 ± 1.24 mg KOH/g, all of which fall within the acceptable ranges for citrus peel essential oils, indicating good oxidative stability. These findings offer valuable insights into the physicochemical characteristics of orange peel essential oil. The high oil yield, favorable physical properties, and desirable chemical composition suggest that this oil could be a promising natural resource, contributing to the expanding knowledge of orange peel essential oils and their potential for sustainable utilization in the food, cosmetic, and pharmaceutical industries.

Keywords: Orange peels, Soxhlet extraction, Physicochemical properties, Essential oil

INTRODUCTION

Citrus sinensis, commonly known as sweet orange, is a fruit from an evergreen tree that grows up to 30 feet tall and belongs to the Rutaceae (citrus) family. Oranges are a good source of vitamin C (Sharma *et al*., 2017). The peels of *C. sinensis* are rich sources of essential oil. This oil is extracted from the outer colored rind or flavedo of the orange fruit (Donato *et al*., 2020; Wali *et al*., 2022). Sweet orange peel oil has a fresh, citrusy aroma that is invigorating and uplifting. It contains several beneficial compounds including limonene, linalool, and citronellal. Limonene is the major constituent, making up over 90% of the oil, and has anti-inflammatory, antioxidant, and potential chemo-preventive properties (B'chir and Arnaud, 2023).

The antioxidant activity of orange peel oil is comparable to synthetic antioxidants like BHT and vitamin E (Shehata *et al*., 2021; Darwish, 2024). This makes it a potentially valuable ingredient in skincare and cosmetic products, as antioxidants help protect the skin from oxidative damage caused by free radicals (Palmer and Kitchin, 2010). Furthermore, research has explored the chemical composition of *C. sinensis* peels and their potential applications. A study by Khan *et al*. (2012) investigated the peel oil yield, chemical composition, and antimicrobial properties of unexplored Pakistani citrus species including sweet oranges, mandarins, and grapefruits. The major compound identified in all citrus peel oils was D-limonene, and the oils exhibited antioxidant and antimicrobial activities against various bacterial and fungal strains, with orange essential oil being highly effective, particularly against *Salmonella typhi*.

Kamaliroosta *et al*. (2016) analyzed the essential oil composition of orange, tangerine, sweet lemon, and sour lemon peels, extracting oils ranging from 0.46-1.48% yield. Limonene was identified as the predominant compound in all citrus peel oils and other components like N-methyl-D3-aziridine, cytidine, xanthotoxin, and various phenolic compounds. Also, Raman microscopy has been used to analyze the distribution of essential oils, flavonoids, and carotenoids in citrus peels including *C. sinensis*, providing valuable insights into their functional components (Yang *et al*., 2017). Studies have investigated the effect of ripening stages on the chemical composition of essential oils extracted from citrus peels, revealing variations in volatile compounds and antibacterial activity (Rowshan and Najafian, 2015; Di Rauso Simeone *et al*., 2020). However, despite the growing interest in *C. sinensis* peel essential oils and their numerous applications, there is still a need for comprehensive research on optimizing the extraction processes and characterizing the chemical profiles of these valuable oils from *C. sinensis* peels. Therefore, this study aims to extract and characterize essential oils from *Citrus sinensis* peels.

MATERIALS AND METHODS

Sample Collection and Preparation

Oranges from which peels were collected were purchased from Eke-Okigwe Market and were taken to the laboratory for analysis. Samples were examined for signs of disease or spoilage. Only “healthy” ones were selected and used. The peels were removed with the aid of a sharp knife taking care to avoid the “albedo” (white fleshing mesocarp) from interfering. The obtained peels were first air dried, then oven dried at 40 ^{o}C until they became brittle enough to grind. The dried peels were ground in a laboratory mill and sieved to obtain the powder specimen that was used for oil extraction. Other reagents used were of analytical grade

Extraction of Orange Peel Oil

Oil extraction was done via the soxhlet extraction process, according to the revised method by López-Bascón and De Castro, 2020.

Determination of Physicochemical Properties of Oil Extracts

Physical parameters such as percentage yield, refractive index, specific gravity, smoke point, Fire point, and flash point were determined using a revised method by Onwuka, 2018. The moisture content was determined gravimetrically using a Vacuum Oven at 70 °C (Nielsen, 2017). chemical parameters including; acid value, free fatty acid, peroxide value, and saponification value were determined using a standard method (Onwuka, 2018).

Statistical Analysis

All analysis was done in triplicates. The data obtained were subjected to analysis of variance (ANOVA) Using the Statistical Package for Social Sciences (SPSS) version 27.

RESULTS

The results of the physical and chemical properties of orange peel oil analyzed are presented in

Table 1 and Table 2

Table 1: Physical characteristics of orange peel oil

Yield (%)	Refractive Index	Specific gravity. (g/cm^3)	Moisture content (%)	Smoke point (° C)	Flashpoint (° C)	Fire point (° C)
2.55 ± 0.12	1.465 ± 0.003	0.889 ± 0.003	2.49 ± 0.04	130.6 ± 2.31	200 ± 3.46	217.3 ± 1.15

*Values show means of duplicate analysis ± standard deviation

Table 2: Chemical characteristics of orange peel oil

Acid Value (mgKOH/g)	Free fatty acid (%)	Iodine value (gI/100g)	Peroxide value (meq/kg)	Sap. V (mgKOH/g)	Uns. V (%)
2.77 ± 0.07	1.39± 0.03	77.71 ± 0.93	2.96 ± 0.23	189.81 ± 1.24	14.7 ± 0.452

*Values show means of duplicate analysis ± standard deviation

DISCUSSION

Table 1 shows the results obtained for the physical properties of orange peel oil. The result shows an average yield of 2.55 ± 0.12% for orange peel essential oil. The obtained oil yield was higher than was reported by Kamaliroosta *et al*. (2016), with yields ranging from 0.46% to 1.48% for various citrus peels, including oranges. Pradhan *et al*. (2019) also reported a mean oil yield of 1.48% from the peel of matured orange (*Mandain* spp.). However, the result was consistent with that of Ramadan *et al*. (2018) with a yield of around 2.5% for orange peel oil. The yield of essential oils can be influenced by factors such as extraction methods, cultivar, and environmental conditions (Reazai *et al*., 2014). The refractive index of the orange peel essential oil was found to be 1.465 ± 0.003. This value is comparable to the findings of Benoudjit *et al*. (2020), who reported a refractive index of 1.475 for lemon peel essential oil, and Ramadan *et al*. (2018), who observed a refractive index of 1.499 for orange peel oil. The refractive index is an essential parameter for identifying the purity and quality of essential oils, as it reflects the density and optical properties of the oil (Liu *et al*., 2022).

The specific gravity of the orange peel

essential oil was determined to be 0.889 ± 0.003 g/cm³. This result is consistent with the findings of Benoudjit *et al*. (2020), with a specific gravity of 0.894 g/cm³ for lemon peel essential oil, and Ramadan *et al*. (2018), with a specific gravity of 0.95 g/ml for orange peel fixed oil. Additionally, Javal *et al*. (2014) and Pradhan *et al*. (2019) both recorded between 0.84g/cm^3 and 0.85g/cm^3. The specific gravity is an important parameter for determining the quality and purity of essential oils, as it reflects the density and chemical composition of the oil (Felicia *et al*., 2024). The moisture content of the orange peel essential oil was found to be 2.49 ± 0.04%. This value is relatively low, indicating that the oil has a low water content, which is desirable for prolonged shelf life and resistance to microbial contamination (Aruna *et al*., 2022). However, it is important to note that the moisture content can vary depending on the extraction method and storage conditions. The smoke point (130.6 ± 2.31 °C), flash point (200 ± 3.46 °C), and fire point (217.3 ± 1.15 °C) of the orange peel essential oil were determined. These values provide essential information for the safe handling, storage, and transportation of the oil, as well as its potential applications in cooking or industrial processes (Liu *et al*., 2022).

The chemical properties of orange peel oil are shown in **Table 2**. The acid value (2.77 ± 0.07 mg KOH/g) and free fatty acid (1.39 ± 0.03%) of the orange peel essential oil were measured. These values are similar to those reported by Benoudjit *et al*. (2020) for lemon peel essential oil (acid value of 2.10 mg KOH/g) but lower than those observed by Ramadan *et al*. (2018) for orange peel fixed oil (acid value of approximately 24 mg KOH/g). The acid value and free fatty acid content are indicators of the oil's quality and stability, with lower values generally considered desirable for longer shelf life and reduced rancidity (Mohammed *et al*., 2013; Onwuka, 2018). The iodine value of the orange peel essential oil was found to be 77.71 ± 0.93 gI/100g. This value is lower than that reported by Aruna *et al*. (2022) for lemon peel essential oil (116 gI/100g oil) and within the range observed by Liu *et al*. (2022) for various citrus seed oils (72.4% to 82.2% unsaturated fatty acids). The iodine value is a measure of the degree of unsaturation in the oil, with higher values indicating a higher proportion of unsaturated fatty acids. (Mohammed *et al*., 2013).

The peroxide value of the orange peel essential oil was found to be 2.96 ± 0.23 meq/kg which is low and confirms non-acidity. This value is higher than the range reported by Reazai *et al*. (2014) for citrus seed oils (0.54 to 0.77 meq/kg) and the value observed by Aruna *et al*. (2022) for lemon peel essential oil (1.6 meq/kg of sample). The peroxide value is an indicator of the degree of oxidative rancidity in the oil, with lower values being desirable for better quality and stability (Liu *et al*., 2022). Rancidity is an artificial factor in oil quality evaluation and is reported to set in at a peroxide value greater than 20mg/kg (Pike, 2003; Onwuka, 2018). The saponification value of the orange peel essential oil was determined to be 189.81 ± 1.24 mgKOH/g, which is considered to be low and reduces the chances of industrial utilization of the oil for things like soap making. This value is higher than that reported by Felicia *et al*. (2024) for orange peel essential oil (121.67 mg KOH/g), and also, higher than the range observed by Ramadan *et al*. (2018) for orange peel fixed oil (134 to 141 mg KOH/g). The saponification value is a measure of the average molecular weight of the fatty acids present in the oil, and it is useful for determining the suitability of the oil for various applications, such as soap and cosmetic manufacturing (Aruna *et al*., 2022).

The unsaponifiable value of the orange peel essential oil was found to be 14.7 ± 0.452%. This value represents the portion of the oil that cannot be saponified, which may include compounds such as sterols, pigments, and other minor constituents (Liu *et al*., 2022). The unsaponifiable value can provide insights into the potential presence of bioactive compounds and antioxidant properties in the oil.

CONCLUSION

The results emphasize the potential of orange peel oil as a valuable component in a wide range of applications, towing to its beneficial properties, including antioxidant and antimicrobial activities. These findings indicate that citrus peel, usually considered waste and discarded, can be sustainably repurposed to yield essential oils. This provides a natural and efficient substitute for synthetic compounds in industries like cosmetics, pharmaceuticals, and food preservation.

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CHEMICAL SOCIETY OF NIGERIA (CSN) ABIA CHAPTER

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Conference Proceedings

Full Length Research Paper

DETERMINATION OF PESTICIDE RESIDUES IN SOME FOREIGN AND LOCAL RICE BRANDS SOLD AT MAJOR MARKETS IN ABA, ABIA STATE, NIGERIA.

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ABSTRACT

Organochlorine Compounds (OCs) are among the commonly used pesticides classified as Persistent Organic Pollutants (POPs). This research work studied the concentrations of pesticides present in some commercial local and foreign rice brands sold in three major markets of Aba metropolitan city, Abia State of South Eastern Nigeria. About sixteen (16) representative samples were obtained from the three major markets including Ariaria International Market, Ahia-Ohuru and Cemetery Markets in Aba comprising of eight (8) Local rice brands and eight (8) foreign rice brands. Pesticide residues were extracted using Soxhlet by the reflux of the pulverized samples and concentrated using a rotary evaporator. The pesticide concentrates were cleaned up and analyzed qualitatively and quantitatively using Agilent 6890N GC-MS. Twenty pesticides were observed. The concentrations of each pesticide in both foreign and local rice brands were statistically reported as Mean ± standard deviation from triplicate results. The p – values of the mean concentration of each pesticide residue were obtained from two-tailed ANOVA and tested for significance at $p < 0.05$. The results for foreign rice showed that every brand had one or more pesticide residue which were compared to WHO Codex Alimentarius standards for each organochlorine in the rice grain. The range of values for benzene hexachlorides (BHCs) were from 0.00 to 0.109 ± 0.002 mg/Kg (MRL = 0.02 mg/Kg), dieldrin, aldrin and endrins ranged from 0.00 to 0.199 ± 0.002 mg/Kg (MRL = 0.01 mg/Kg), Dichloro diphenyl chloro ethylene/ethane (P', P' – DDD, P', P' – DDE, P', P' – DDT) ranged from 0.00 to 0.097 ± 0.001 mg/Kg (MRL = 0.02 mg/Kg) and so with other pesticides. Similar results were obtained for the local rice samples. The range of values for BHCs were from 0.00 to 0.109 ± 0.004 mg/Kg, aldrin ranged from 0.00 to 0.286 ± 0.002 mg/Kg while dichloro diphenyl chloro ethanes/ethylenes ranged from 0.00 to 0.224 ± 0.002 mg/Kg. Some pesticides like endrin and endosulfan II were not detected. In general, more cases of pesticides residues were seen in the foreign rice compared to the local rice brands which gives a major concern for consumption as they violate the standard limits for these pesticides. Recommendations on strict compliance to standards by farmers and merchants are therefore necessary to enhance food safety and security. This must be done in line with regulations from local and international standard organizations for the use of these pesticides.

Keywords: BHC (benzene hexachloride), P', P" – DDD (dichloro diphenyl dichloroethane), P', P" – DDE (dichloro diphenyl dichloroethylene), P', P" – DDT (dichloro diphenyl trichloroethane), MRL (Maximum Residual Limits).

INTRODUCTION

Pesticides are toxic chemicals used for the control of pests against insects, rodents, weeds, worms, mites, fungi, bacteria etc. They are generally used as insecticides, rodenticides, herbicides, fungicides, bactericides (Jayaraj *et al.,* 2016). These chemicals control pests by interrupting certain physiological activities of the target organism which may affect their propagation leading to eventual death (Lushchak *et al.,* 2018). This has immensely helped the crop outputs by farmers both for harvesting and storage. Despite their usefulness, prolonged or higher exposure of animals including humans to these chemical unleash hazardous health effects. Based on World Health Organization (WHO) studies, pesticides are classified as extremely hazardous (class I) or slightly toxic (class II) compounds and research shows that they are poisonous, hazardous, and toxic to humans (Abubakar *et al.,* 2020). Organochlorine compounds have been used as pesticides for a long time in various parts of the world (Olisah *et al.,* 2020). A wide range of organochlorine pesticides (OCPs) are used for agricultural purposes, as their chemical morphology, mechanisms of action against target / non-target species, and a number of other properties. Some of the organo chlorine pesticides include Benzene hexachloros (BHCs), polychlorinated biphenyls, endosulfan, dieldrin, methoxychlor, dieldrin, chlordane, taxophene, dicofol (Tzanetou and Karasali, 2022).

The extensive use of pesticides in crop production is essential to ensure high agricultural yields and food security (Wang *et al.,* 2022). However, improper and excessive application of these chemicals can lead to the accumulation of pesticide residues on crops, posing potential risks to human health and the environment. In Nigeria, rice is a staple food, and its cultivation relies heavily on the use of pesticides for the combation of pests and diseases (Kamai *et al.,* 2020).

Gas chromatography – Mass spectrometry (GC – MS) studies of organochlorine pesticides residues done on Nigerian grains in Borno state revealed the presence of lindane, diazinon and aldrin in pre-storage bean samples while dichlorodiphenyltrichloroethane (DDT), dichlorvos and endrin were found in both pre- and post-storage samples (Ogah *et al.,* 2012). Similarly, pesticide residues were analyzed using GC-MS in some vegetables and fruits such as spinach, lettuce, onions, cabbage and tomatoes in a study from Borno State. The study revealed that the quantity of pesticides in the vegetables were above food tolerance levels (Akan *et al.*, 2013).

There is lack of comprehensive data and risk assessment regarding the presence and levels of pesticide residues in various rice species produced and consumed in Nigeria. The potential exposure of consumers to harmful pesticide residues through the consumption of rice is a matter of serious concern, and its long-term effects on public health require thorough investigation as rice is among the most consumed stable food in Nigeria. Analyzing and identifying the types and levels of pesticide residues present in the rice samples collected from different geographic regions and species involves employing appropriate analytical methods and instrumentation to accurately detect and quantify the residues consequently, this study focused on th e determination of pesticides on rice crops including local and foreign brands sold at Aba metropolis, Abia state in south eastern Nigeria using GC-MS Spectrometer The study will contribute to the empirical literature with respect to African agriculture more generally, and Nigeria agriculture in particular towards food security.

MATERIALS AND METHODS

Study Area

This study was conducted in Aba metropolis of Abia State located in South eastern region of Nigeria. Aba is the major commercial hub of the state consisting of several large markets including Ariaria International Market, Ahia – Ohuru, Cemetery Markets. These markets serve as sources were residents and visitors buy stable foods including rice both at wholesale and retail quantities for consumption. Ariaria International market popularly acclaimed to be one of the largest markets in West Africa is reputable for a vast commercial activity beyond food stuff. There are also vast farming lands located within and around the outskirts of the city as well as a good number of small to medium scale industries and the residents are known for their artisanship and industrious nature. Aba metropolis is however located within the coordinates 5.107^{0} N longitude 7.3670 E latitude and shares boundaries with four other states (Imo, Enugu, Akwa Ibom and Rivers) in Nigeria. The location map is shown in **Figure 1.**

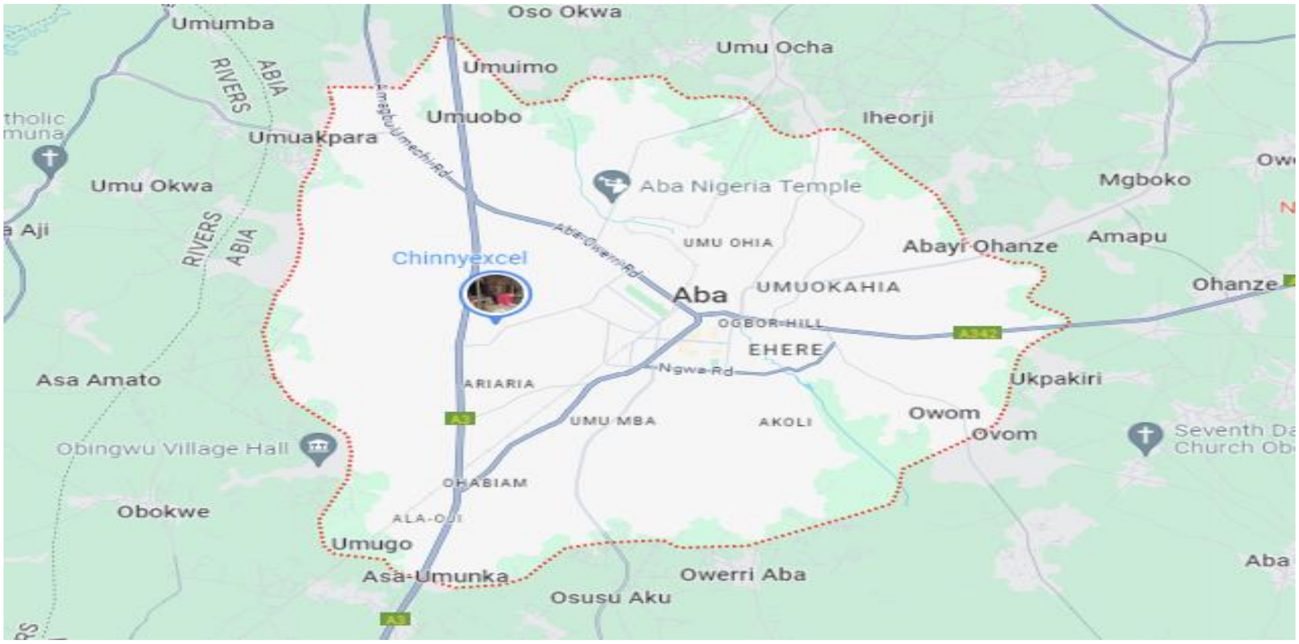

Figure 1: Map of Aba metropolis, Abia State, Nigeria.

Sample collection and preparation

Samples of dry rice (local and foreign) were purchased from the three markets (Ahia-Ohuru, Cemetery and Ariaria food markets all in Aba, Abia state, Nigeria. Eight different brands each of local and foreign rice were collected. The list of local rice brands include; Bigbull, Bigcrown, Costus rice, Local rice, Mama Rice, Pretty Lady, Warrior, White lady. The list of foreign rice include; 7/7, Habiba white, Mbenz, MasterChef, Mr. Rice, Mr. Cook, RedL and Superdelux. Eight merchants were patronized and each supplied one foreign and one local brand of the rice samples. Each brand of rice sample was supplied in three separate portions of 100 g each from randomly selected bags of a particular brand to form a representative sample of 300 g for each rice brand. The representative samples were put in black-coloured polyethylene bags, labelled and transported to the laboratory. On arrival, the samples were sorted to remove impurities including stones and shafts.

The grain samples were bought in the dried form and still further dried. They were thoroughly grounded using mortar and pestle and then pulverized into fine powder using an electric blender. Finally, each of the powdered grain sample was stored in labelled Ziploc bag and kept at 4 ºC in a refrigerator.

Determination of pesticide residues

Preparation of pesticide standard solution: The stock solutions of each of the aforementioned commercial standard pesticide compounds were prepared separately in acetone (1000 mg/L). A mixed standard solution (50 mg/L actetone) containing the standard reagents was prepared from the individual stock solution and then a lower concentration of 10 mg/L. Thereafter 0.1, 0.2, 0.5, 1.0, 2.0, 3.0, and 5.0 mg/L working standard were prepared by measuring the required volume to make up each of the concentration in a 10ml flask and making it up with the stock solution of acetone.

Extraction

Extraction was performed according to the method prescribed by Prados-Rosales *et al.*, (2003). About 10 g of the powdered rice sample was weighed with an electronic weighing balance into an extraction thimble of a soxhlet extractor. 100 mL of the solvent (dichloromethane/hexane) was poured into the round bottom flask; attached to the soxhlet extractor. This was refluxed for at least three times. The extract was transferred into the Rotary Evaporator and concentrated to about 2 mL. This was transferred further into a Teflon screw-cap vial well labeled. The extract was cleaned up with 3 g of anhydrous sodium sulfate in a well packed column for GC-MS analysis.

The prepared extract was used qualitatively and quantitatively to determine the concentration of various pesticides components. The relative percentage of each component was calculated by comparing it to average pick area to the total areas.

GC-MS Analysis

An Agilent 6890N gas chromatography equipped with an auto sampler connected to an Agilent Mass Spectrophotometric Detector was used.1 μL of sample was injected into the pulsed spitless mode onto a 30 m x 0.25 mm ID DB 5MS coated fused silica column with a film thickness of 0.15 μm. Helium gas was used as a carrier gas and the column head pressure was maintained at 20 psi to give a constant of 1 mL/min. Other operating conditions were preset. The column temperature was initially held at 55 ^{0}C for 0.4 min, increased to 200 ^{0}C at a rate of 25 ^{0}C/mins, then to 280 ^{0}C at a rate of 8 ^{0}C/mins and to a final temperature of 300 ^{0}C at a rate of 25 ^{0}C/mins, held for 2 mins. The identification time was based on retention time. Components with lower retention time elutes first before the ones of higher retention time.

Statistical Analysis

Data analyses were carried out on Excel 365, version 2307 (2023). The differences between the treatments were evaluated using Analysis of variance (ANOVA). Values were reported as the mean value ± standard deviation from the triplicate experiments done for each sample and the level of significance was calculated by one-way analysis of variance. All analyses were performed in triplicates. Differences between means were considered to be significant at $P < 0.05$.

RESULTS

The results of the GC-MS analysis done on the various foreign and local rice samples were carefully arranged and summarized into tables 1. These results showed the statistically analyzed mean concentrations of the pesticide residues in each rice brand (Foreign and Local) from the triplicate data obtained. The pesticide concentrations were reported as Mean ± standard deviation and significance at $p < 0.05$ were determined using two-way ANOVA. The maximum residue Limit (MRL) or Limit of tolerance/permissibility also known as the minimum concentration of a pesticide in rice that will pose health rice were compared with the pesticide levels in each rice brand in order to ascertain the risk potential of the pesticide in the rice brand. These MRL values were obtained from the World Health Organizations' (WHO) regulations from the Codex Alimentarius International food standards for 2019. Table 1 showed the summary of the mean concentrations of each pesticide residues for the various local and foreign rice brands and the significance of their means calculated from the ANOVA.

Table 1: Average concentrations of the pesticides for local and foreign rice samples obtained from GC-MS analysis.

S/N	PESTICIDE	CONCENTRATION (mg/Kg) Local	CONCENTRATION (mg/Kg) Foreign	p-VALUE (at p < 0.05)	MRL (mg/Kg) (WHO, 2019)
1.	ALPHA – BHC	0.0149 ± 0.001	0.00863 ± 0.0015	0.589	0.02
2.	BETA – BHC	0.00388 ± 0.0005	0.024 ± 0.0009	0.076	0.02
3.	GAMMA – BHC	0.00763 ± 0.001	0.0109 ± 0.005	0.734	0.02
4.	HEPTACHLOR	0.0085 ± 0.001	0.0498 ± 0.001	0.182	0.01
5.	DELTA – BHC	0.0226 ± 0.001	0.0306 ± 0.001	0.451	0.02
6.	ALDRIN	0.05 ± 0.002	0.0343 ± 0.038	0.823	0.01
7.	HEPTACHLOR EPOXIDE	0.0236 ± 0.0004	0.0474 ± 0.002	0.133	0.01
8.	GAMMA – CHLORDANE	0.0168 ± 0.001	0.0593 ± 0.002	0.191	0.01
9.	ALPHA – CHLORDANE	0.001 ± 0.001	0.0321 ± 0.002	**0.029**^{b}	0.01
10.	ENDOSULPFAN I	0.0163 ± 0.001	0.0339 ± 0.002	**0.042**^{c}	0.02
11.	P, P' – DDE	0.0325 ± 0.002	0.0409 ± 0.002	0.793	0.02
12.	DIELDRIN	0.0011 ± 0.001	0.0435 ± 0.002	0.14	0.01
13.	ENDRIN	N. D	0.0351 ± 0.002	0.097	0.02
14.	P,P' – DDD	0.0574 ± 0.003	0.0328 ± 0.002	0.344	0.02
15.	ENDOSULFAN II	N. D	N. D	**0**^{a}	0.02
16.	P,P' – DDT	0.0065 ± 0.001	0.0419 ± 0.002	0.3	0.02
17.	ENDRIN ALDEHYDE	0.017 ± 0.001	0.0519 ± 0.002	0.203	0.02

18.	ENDOSULFAN SULPHATE	0.0089 ± 0.001	0.0408 ± 0.002	0.05	0.02
19.	METHOXYCHLOR	0.0103 ± 0.002	0.0593 ± 0.001	0.082	0.01
20.	ENDRIN KETONE	0.0081 ± 0.001	0.0414 ± 0.001	0.201	0.02

N. D = Not Detected (Concentrations < 0.001 mg/Kg)

The high concentration (above tolerable limit) of some pesticide residues as seen in **table 1** might be as a result of the many rounds of application per time (up to 6 times). Also, the pesticides were mainly applied on a weekly basis or less across the markets which span between the storage periods of 3 – 6 months creating a substantial amount of absorbed pesticide residues (Adesuyi *et al.*, 2018). Also, the trend in the results might suggests poor knowledge and practice of the usage of pesticides and agricultural practices by the farmers. It was reported that about 70% of farmers in developing countries encounter difficulties in reading instruction manuals. Thus, resulting to the abuse in usage of highly toxic pesticides. (Oshatunberu, 2023).

DISCUSSION

All organochlorine residues were recorded both in the local and foreign rice samples. Endrin and endosulfan II were below the detection limit for local rice while endosulfan II was also below the detection limits for foreign. The detected pesticide residue concentrations for local rice samples ranged from 0.001 ± 0.001 mg for alpha – chlordane to 0.0574 ± 0.003 mg/Kg for P, P' – DDD while the range for foreign rice was from 0.00863 ± 0.0015 mg/Kg for alpha – BHC to 0.0593 ± 0.001 mg/Kg for methoxychlor. 60 % of the pesticide residue were detected below the Maximum Residual Limits (MRL) for the local rice while only about 15 % of the pesticide residues in the foreign rice samples were observed below the MRL values. **Figures 1, 2 and 3** shows the trends in the concentrations of the pesticide residues for both local and foreign rice samples.

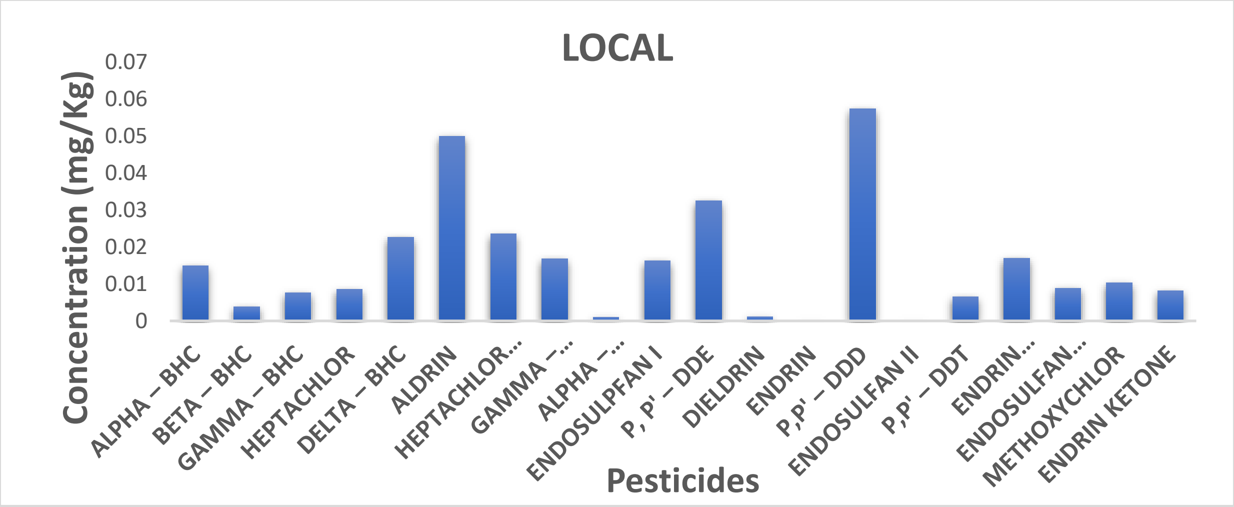

Figure 2: Pesticide residue concentrations in the local rice samples.

Very high concentrations of Aldrin pesticide residue were observed in local rice samples from 0.05 ± 0.002 mg/Kg to 0.0574 ± 0.003 mg/Kg as seen in **table 1** and **figure 2**. This result was lower with the findings of Adah *et al.*, (2020) on pesticide concentration of local rice sold in Wurukum, Modern and Wadata markets in Makurdi of Benue State, Nigeria where Aldrin was detected in concentrations of 2.003 and 2.2181 mg/kg respectively. The values determined were however higher than EU Maximum Residues Limit (MRLs) for aldrin which is 0.01 mg/kg. This suggest that the Aldrin levels are potentially toxic for consumption in the local rice samples sold at Aba, Abia state, Nigeria. P, P' – DDT were quite lower compared to the MRL value recommended by WHO and agreed with the studies from Oshatunberu, (2023). The concentration of P, P' – DDD was unusually the highest from the results as seen in figure 1 and called for concern. Most of the other pesticide residue concentrations fell below the MRL values recommended by Codex Alimentarius International food standards (Authority *et al.*, 2021).

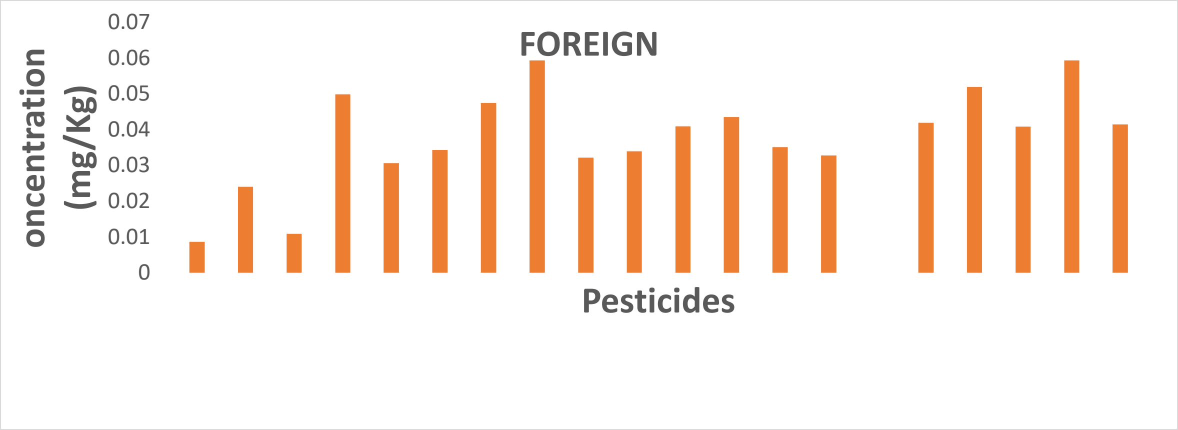

Figure 3: Pesticide concentrations in the foreign rice samples.

Table 1 and **figure 3** showed higher prevalence of organochlorine pesticides was in the foreign rice samples. About 85 % of the pesticide residues analyzed were above the recommended MRL value from WHO. The exceptions were alpha – BHC (0.00863 ± 0.0015 mg/Kg), Gamma – BHC (0.0109 ± 0.005 mg/kg) which were consistent with the findings of Chonoko *et al.*, 2024. and endosulfan II (Not Detected) MRL values for all is 0.02 mg/Kg. These higher residue concentration indicates that the foreign rice may have been subjected to high dose of these pesticides due to planting, storage and distribution at long distances (Adesuyi *et al.*, 2018).

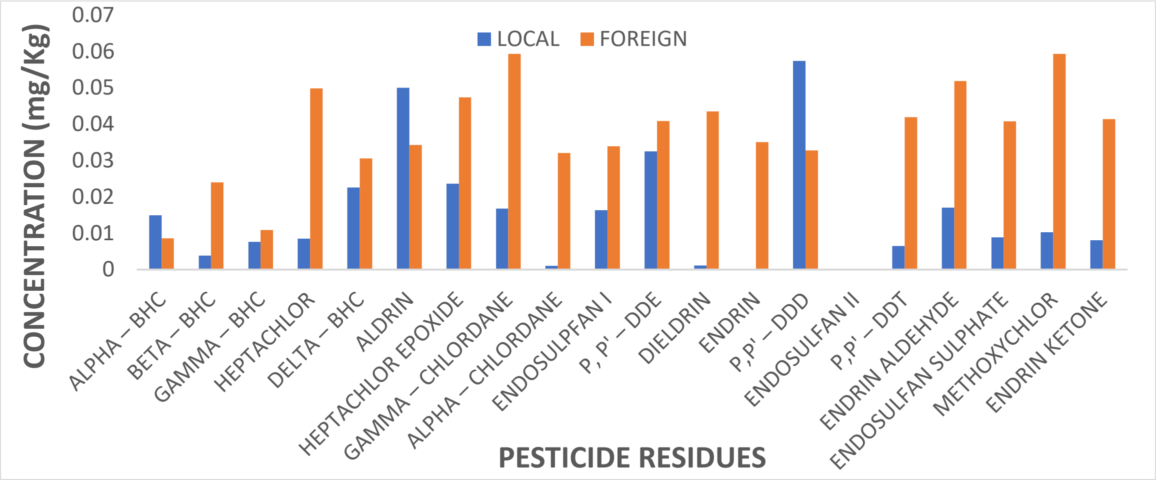

Figure 4: Comparative chart of the concentrations of pesticides in local and foreign rice.

The comparative chart as shown in **figure 4** revealed that the concentration of pesticide residues in the foreign rice samples were mostly higher when compared to the residue concentrations in the local rice samples. Thus, it is noteworthy to observe the large difference in the percentage occurrence of pesticide residues in the foreign rice samples over the domestically produced rice (over 100 %) more shows a serious concern for consumption of foreign based on the Health risk associated with high level exposures of these pesticide compounds on humans and the environment. Higher violation rates in foreign rice might be linked to import violations and differences in global tolerances for rice (Liang *et al.*, 2017).

CONCLUSION

Organochlorine pesticide residues in rice samples from local and foreign sources sold in the major markets Aba, in Abia state located in the south eastern region of Nigeria have been analyzed using GC-MS technique. About 20 organochlorine pesticides were detected across the eight rice bands. The results were analyzed statistically to obtain mean concentrations of each pesticide and then tested for statistical significance at over 95 % confidence level ($p < 0.05$).

The foreign rice samples contained higher percentages of pesticides residues when compared to the local rice samples due to series of processes involved in the movement of rice between two countries. The different regulations regarding the use of these pesticides could be seen to be a major factor responsible for the high violations of the maximum residue limit as recommended by Codex Alimentariu, WHO conference 2019.

Organochlorines are classified as persistent organic pollutants (POPs) which have been implicated in diverse health problems arising from acute, medium- and long-term exposures. Some of which are organ dysfunction, reproductive disability and nervous disorders, therefore, there is need for more stringent approach on the compliance of standard practice on pesticide usage.

RECOMMENDATION

The violation in the use of organochlorine pesticides have become a cause of serious concerns owing to the hazardous nature of these chemical contaminants in our foods. It is therefore pertinent and a serious call for the local regulating bodies such as National Agency for Food and Drugs Administration Commission (NAFDAC), Standard Organization of Nigeria (SON) and other regulatory bodies to come up with stiffer measures on the use of these pesticides by local farmers to ensure food safety to the consumers. This can be achieved by batch testing and quality assessment of these crops before they are released into the market. These bodies are also encouraged to partner with the agricultural ministries from federal, state and local government levels to make the process efficient. They also need to sensitize farmers on ways to ensure compliance in the usage of these chemicals. The government through the ministries of agriculture, education and industry should work out modalities on finding better alternatives in pest control that has limited health effect on exposures to them. International organizations should ensure that movement of processed rice must meet the international and local standards of the pesticide usage to promote health safety for the consumers.

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CHEMICAL SOCIETY OF NIGERIA (CSN) ABIA CHAPTER

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Conference Proceedings

REVIEW

AQUEOUS BIPHASIC CATALYSIS FOR SUSTAINABLE CHEMICAL PROCESSES: A REVIEW

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ABSTRACT

The increasing demand for environmentally sustainable processes has propelled the continual use of water as a solvent for chemical transformations. Its abundancy, availability and immiscibility with most organic substrates and products easily makes water a solvent of choice for biphasic catalysis. Typically, metal catalysts/ligands used in catalytic reactions are insoluble in water. Therefore, for the aqueous biphasic approach to be effective, the catalyst should be soluble in the aqueous phase and insoluble in the organic phase. This requirement brings with it the design of new water-soluble catalyst precursors or the chemical modification of known catalysts for the aqueous biphasic (liquid-liquid) system.

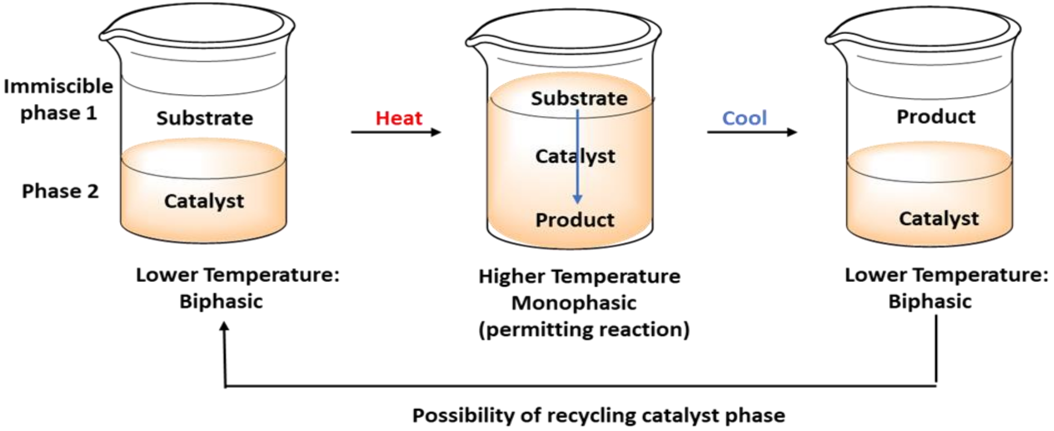


Figure 1. Liquid-liquid biphasic catalysis strategy.

The liquid-liquid biphasic approach employs the immiscible liquid separation strategy. It purports that the catalyst is immobilized in one of the liquid phases and the products/substrate is in the other phase. At elevated temperatures, the reaction is carried out under monophasic conditions or at the interface of the two phases. Post reaction, the reaction mixture is cooled to room temperature and phase separation occurs forming two immiscible liquid layers with the product and catalyst residing in different phases as depicted in Figure 1. Most importantly, the product phase is easily separated by decantation, thus enabling the recycling of the catalyst phase.

Keywords: Green chemistry, Catalysis, Homogeneous catalysis, Catalyst recycling

INTRODUCTION

Several important reactions in the bulk and fine chemical industry employ the use of homogeneous catalysts. Examples are the hydroformylation of alkenes, hydrocyanation of olefins, hydrosilylation of ketones and the

Pd-catalysed cross-coupling reactions (Zhou *et al.,* 2009) and the oligomerization of ethylene (Leeuwen, 2004). Homogeneous catalytic systems exhibit superior performance over heterogeneous catalytic systems with respect to activity and selectivity, and it is known that numerous catalytic reactions proceed favourably well in homogeneous systems under mild reaction conditions. However, the challenge of the homogeneous catalysis is the difficulty of recovery and reuse of the expensive metal catalyst (Cui *et al.*, 2018). A strategy that has been developed to address these challenges is the aqueous biphasic catalysis. It allows the feasibility of catalyst recovery and recycling by phase separation (Dyson *et al.,* 1998), therefore the design of catalysts that are soluble in water is necessary to enable the aqueous biphasic strategy to be effective. In this context, examples of catalytic reactions will be focused on the hydroformylation reaction as it constitutes the basics for bulk homogeneous catalysis on an industrial scale.

Aqueous biphasic catalysis

The idea of introducing hydrophilic substituents into electron-rich ligands and their incorporation into organometallic complexes has proven to be a successful approach (Cocq *et al.,* 2020). This strategy is in line with the Green Chemistry principles which promotes the design of environmentally friendly chemical processes. An example of a well-established industrial application of the aqueous biphasic catalysis system is the Ruhrchemie/Rhône Poulenc oxo process which makes use of the water-soluble rhodium complex based on the triphenylphosphine trisulfonate (TPPTS) ligand (Reek *et al.*, 2006). Despite the successful application of the commercialized TPPTS ligand over the years, major drawbacks of the rhodium-based TPPTS catalyst includes its instability in the presence of air/oxygen and the restricted use to only short chain olefins (<C4) due to mass transfer limitations of higher carbon chain alkenes across the interface (Sharma and Jasra, 2015). These limitations has stimulated the research towards the development of new rhodium complexes based on other water-soluble ligand systems that are air-stable and capable of being applied as catalyst precursors in the hydroformylation of longer chain olefins (>C5). The synthesis of water-soluble catalyst precursors or the chemical modification of known catalysts is usually done by introducing hydrophilic polar groups such as sulfonate, carboxylate or ammonium functionalities making them suitable for biphasic catalysis.

Water-soluble catalyst

Phosphines ligands have been widely used since the advent of organometallic homogeneous catalysis; therefore, it is not surprising that the initial attempt to synthesise/design water-soluble catalyst were based on phosphine. The first synthesis of sulfonated phosphines (triphenylphosphine mono-sulfonate (TPPMS) (Figure 2) was synthesised in 1958 (Chaudhari et al., 1995). TPPMS are synthesised *via* the direct sulfonation of phosphines. The development of parallel approaches to completely solubilise phosphine in water led to the discovery of the well-known triphenylphosphine trisulfonate (TPPTS) ligand by Kuntz in 1975 (Chaudhari *et al.,* 1995).

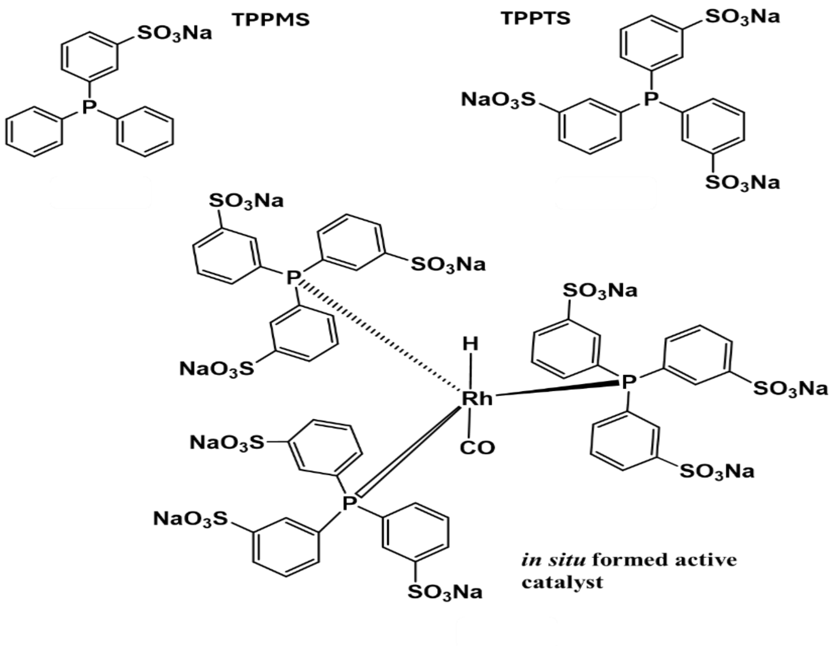


Figure 2. Structure of triphenylphosphine mono-sulfonate (TPPMS), triphenylphosphine tri-sulfonate and the proposed structure of the *in situ* formed active catalyst from TPPTS.

An important example of an industrial application of aqueous biphasic catalysis is the Rhône Poulenc/Ruhrchemie process developed in 1984 for the hydroformylation of propylene (Gonsalvi, 2018). This process uses a combination of the Rh metal and the TPPTS ligand to generate the active catalyst. this process produces about 600,000 tonnes of *n*-butyraldehyde per year (Kohlpaintner *et al.*, 2001).

A simplified flow process of the Rhône Poulenc/Ruhrchemie aqueous biphasic system is illustrated in Figure 3. Therein, the reactor contains the precatalyst (TPPTS and metal precursor), the gaseous reactants (CO, H_2), and propylene. After the reaction, the reaction mixture is transferred to a gas-liquid separator which separates the gases from the liquid product. The crude product is separated and the aqueous phase containing the catalyst is transported back into the reactor (Cents *et al.*, 2004).

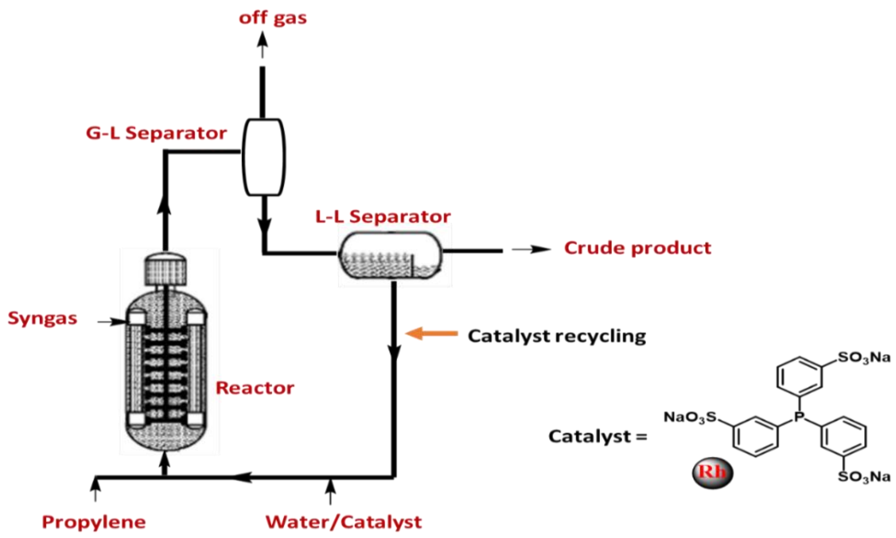


Figure 3. Simplified flow process of the Rhône Poulenc/Ruhrchemie aqueous biphasic system.

The limitation of this process is that the Rh-TPPTS catalyst biphasic system is not effective for long chain substrates (> C5). This is because, the increasing number of carbon atoms in long chain alkenes results to decreased solubility in water thus leading to mass-transfer problems (Cornils, 1998; Deshpande *et al.*, 1997). Strategies that have been employed to overcome this is the use of co-solvents, discrete water-soluble metal catalysts and mass transfer agents such as surfactants and cyclodextrins.

Surfactants in aqueous biphasic catalysis (micellar catalysis)

Surfactants are amphiphilic compounds containing hydrophilic head and hydrophobic tail. Due to their amphiphilic properties, they can mediate between the confines of two immiscible liquids by forming unique self-assembly features resulting to micelle-like aggregates.

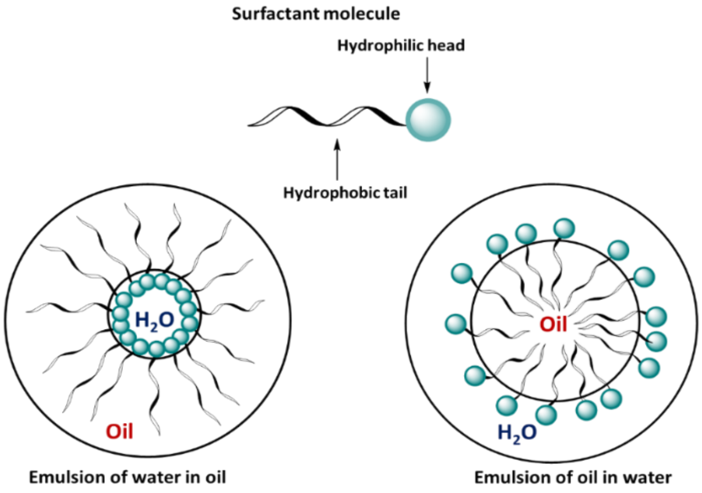


Figure 4. Schematic structure of a surfactant and self-orientation of surfactants in water/oil microemulsion (Polarz *et al.*, 2018).

In a biphasic mixture, surfactants arrange themselves with their heads pointing outwards into the aqueous phase shielding the inner hydrophobic domain of the micelle, thus lowering the interfacial tension between the two liquids as described in Figure 4 (Pogrzeba *et al.*, 2019). Surfactants are classified based on their polar head group charge. For example, anionic surfactants are surfactants possessing a negatively charged head group, cationic surfactants have a positively charged polar head group, zwitterionic surfactants have a zwitterionic head group (positive and negative charge) while non-ionic surfactants have an uncharged polar head group (Cullum, 1994). Surfactant-ligands sometimes referred to as amphiphilic ligands are functionalized ligands with an alkyl chain and a hydrophilic head group (Valls *et al.*, 2002). The design of amphiphilic ligands and their ability to form molecular micellar arrangement in water/organic solvent media has been reported in the literature. For example, Valls *et al.* reported the synthesis of surfactant containing phosphine ligands with the aim of anchoring a metal centre to obtain metallo-surfactants (Valls *et al.*, 2002). Therein, the surfactant containing ligands and their metal complexes with varying degree of ethoxylation were synthesised by reacting phenylphosphido-ethanesulfonate with the appropriate alkyl chloride and $PdCl_2(COD)$.

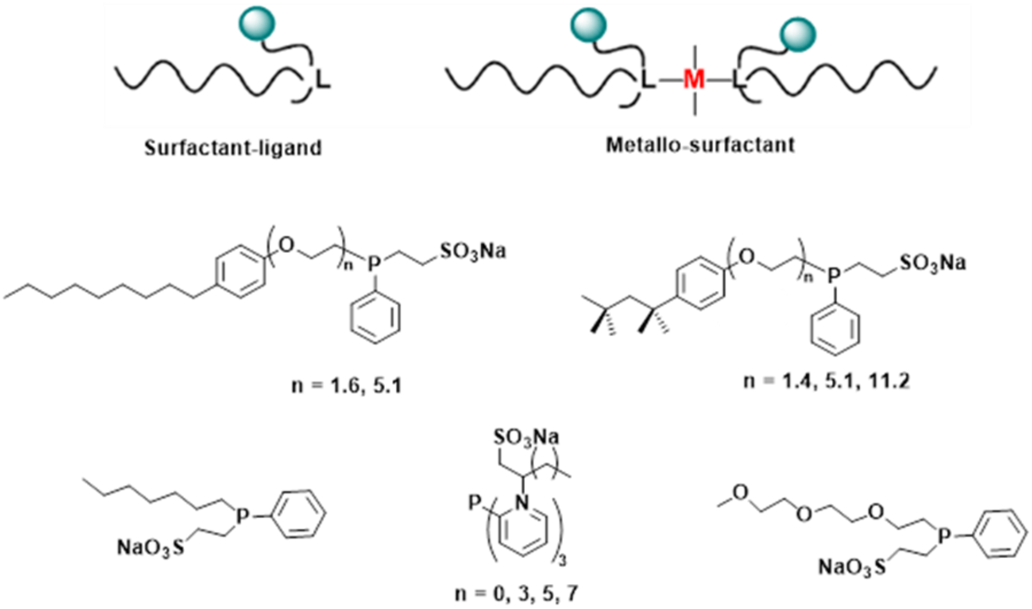


Figure 5. Illustration of surfactant-ligand, metallo-surfactant and examples of surfactant containing phosphine ligand.

Aggregation properties of these complexes in water to yield supramolecular arrangements were studied using surface tension measurements. At critical micelle concentration (CMC), a linear decrease in the surface tension was observed as the concentration of the amphiphilic ligand is increased. Unfortunately, the low solubility of the sulfonated Pd(II) complexes in water hindered investigations into their surfactant properties. More recently, Pogrzeba *et al.* investigated the phase behaviour of non-ionic surfactants in a microemulsion system for the rhodium-catalysed hydroformylation of 1-dodecane (Pogrzeba *et al.*, 2017). They reported that the degree of ethoxylation of the surfactants determines the stability and boundary conditions for reactions to occur. They also suggested that the organic−water interface (interfacial area) is where the reaction takes place as illustrated in Figure 6. In the case where no surfactant was applied, no reaction progress was observed, thus confirming that the surfactant is needed to enable the hydroformylation reaction to take place in a biphasic system.

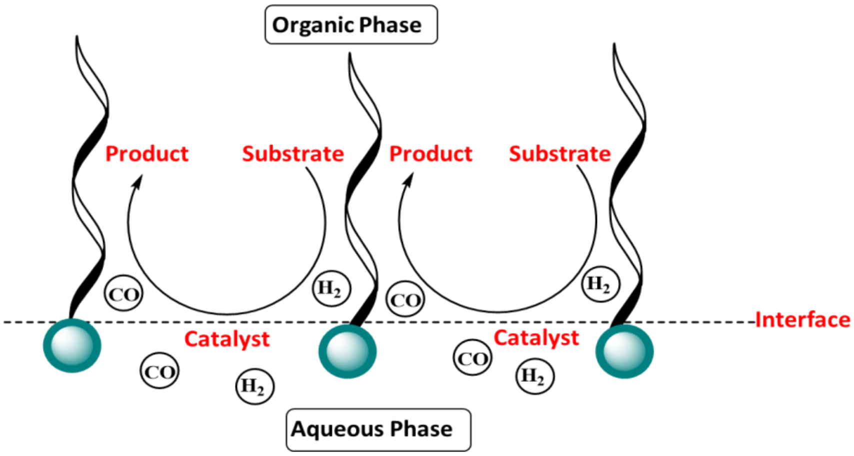
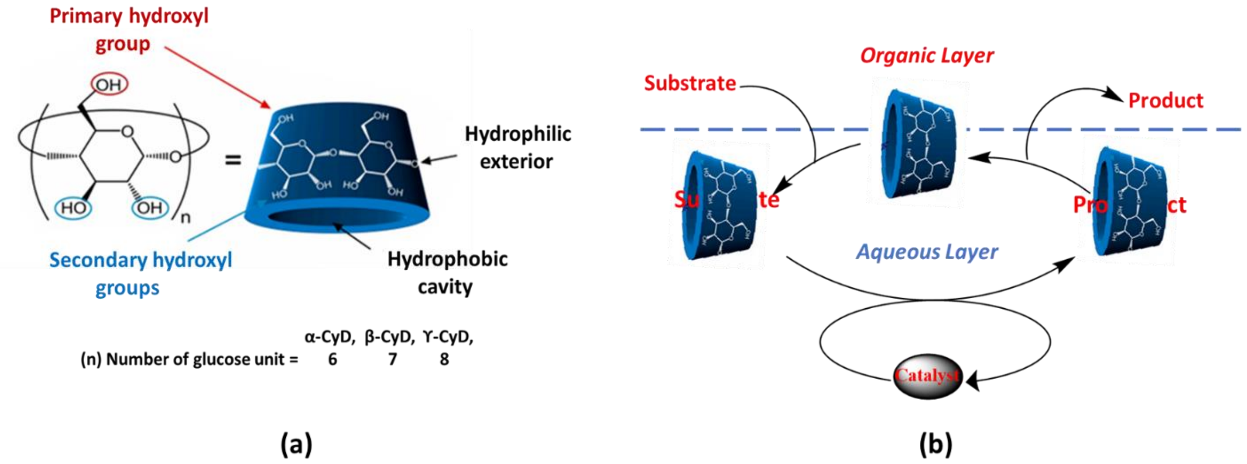


Figure 6 Illustration for the hydroformylation of long chain olefins in microemulsions.

In addition, they recommended that when considering easy product separation/catalyst recycling, high concentrations of the surfactant (not exceed 12 wt % of the entire solvent system) in microemulsions should be avoided in order to maintain good and fast switchability of the water/solvent mixture (Pogrzeba *et al.*, 2019). This described concept of micellar approach using metallo-surfactant in microemulsion systems has been explored for various catalytic reactions (Lorenzetto *et al.*, 2020). With respect catalysis, research in the use of metallo-surfactants (surfactants that are catalytically active by themselves) is yet to be explored.

Cyclodextrins in aqueous biphasic catalysis

Cyclodextrins are cyclic oligosaccharides with an inner hydrophobic surface and outer hydrophilic surface (Topuz and Uyar, 2019). The application of cyclodextrins in aqueous biphasic hydroformylation reaction was first pioneered and extensively studied by Monflier and co-workers (Elard *et al.*, 2015). It is hypothesized that the cyclodextrins operate as an inverse phase-transfer agent through host–guest complexing with hydrophobic substrates in biphasic reactions as illustrated in Figure 7. The inner cavity of cyclodextrins allows for the formation of an inclusion complex when it binds to a hydrophobic substrate thereby increasing the hydrophilicity of the substrate. This facilitates substrate migration into the aqueous phase, thus improving substrate-catalyst interaction and the overall rate of the reaction (Cocq *et al.*, 2020).



(a) (b)

Figure 7 (a) The chemical and 3D structure of cyclodextrin and (b) Illustration of cyclodextrin assisted aqueous biphasic catalysis.

Dauchy *et al*. investigated salicylaldimine and salicylhydrazone ligands based on β-cyclodextrin scaffold in the hydroformylation of 1-decene (Dauchy *et al.*, 2018). The water-soluble salicylaldimine and salicylhydrazone monosubstituted cyclodextrin were synthesised *via* condensation reactions between sulfonated salicylaldehyde or sulfonated ^{t}Bu-salicylaldehyde with β-cyclodextrin. The reaction of [Rh(COD)$_2$BF$_4$] with the ligands in Figure 8 in an alkaline solution formed the corresponding rhodium complexes *in situ*. Both complexes gave high conversions with good regioselectivity towards linear aldehydes. However, no recyclability studies were reported as a result of high catalyst leaching observed by the coloration of the organic phase, thus insinuating catalyst instability or the partial hydrolysis of the persubstituted cyclodextrin under catalytic conditions.

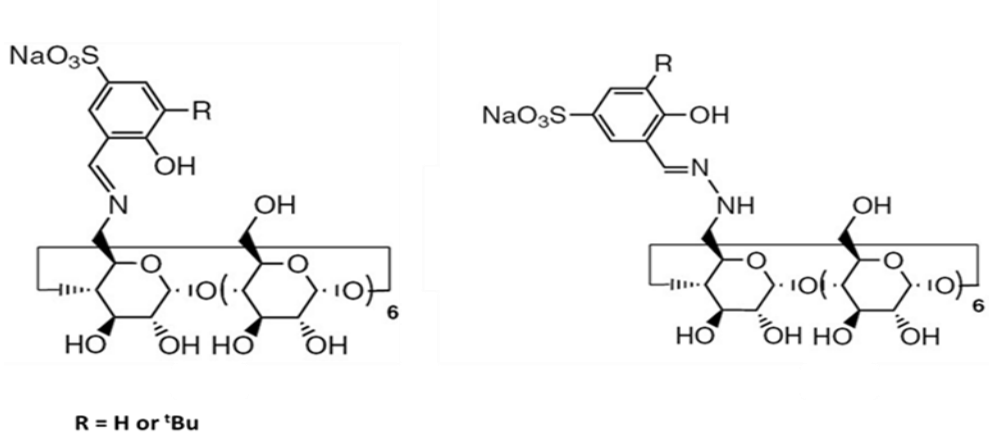


Figure 8. Structures of persubstituted salicylaldimine and salicylhydrazone cyclodextrin (Dauchy *et al.*, 2018).

Emerging water-soluble metal catalyst precursors

An elegant alternative to the classical triphenylphosphine tri-sulfonate (TPPTS) water-soluble ligands, is the use of discrete water-soluble Rh(I) catalyst precursors. The seminal work of Smith and co-workers designed various water-soluble monomeric and multimeric Schiff base metal complexes (Hager et al., 2012; Matsinha et al., 2015; Siangwata et al., 2015, 2020).

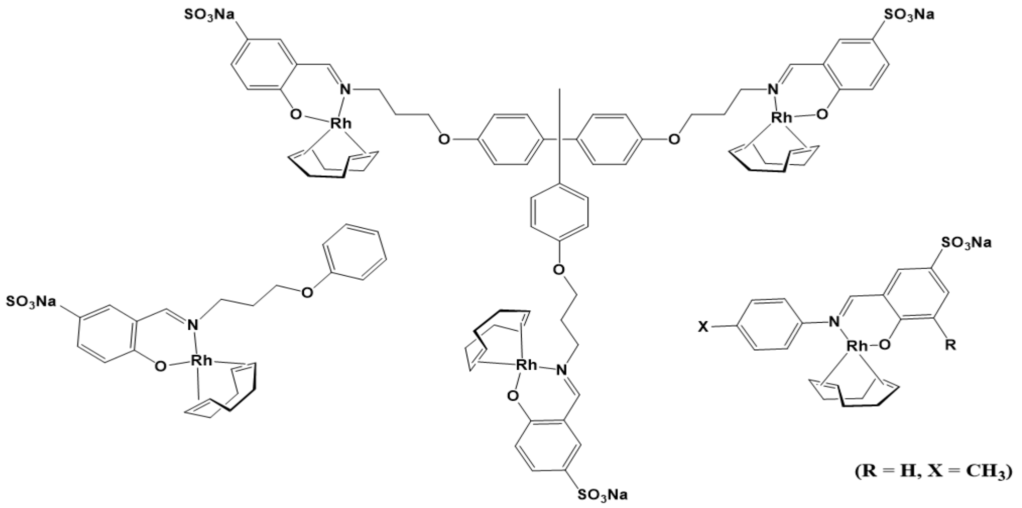


Figure 9. Sulphonated salicylaldimine Rh(I) complexes.

These water-soluble metal complexes were studied as hydroformylation catalyst for various olefinic substrates. The high polarity of the water-soluble complexes and their consequent insolubility in the organic phase could enable multiphasic reactions to be carried out with little or no leaching of the metal catalyst into the product phase.

Recently, Omosun reported the synthesis of water-soluble sulfonated imine Rh(I) complexes (Omosun and Smith 2021). The complexes were successfully evaluated in aqueous biphasic hydroformylation of 1-octene. Both catalyst precursors were highly active as hydroformylation catalysts giving near quantitative conversions and good aldehyde chemoselectivity at reaction conditions of 75 °C and 40 bar.

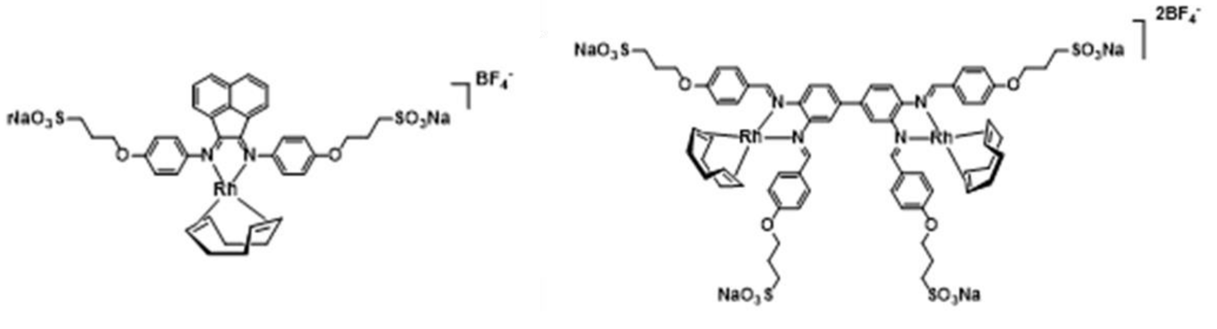


Figure 10. Water-soluble and non-water-soluble alpha-diimine Rh(I) complexes.

The catalysts were recycled up to three times in water/toluene mixtures. A decrease in catalyst performance was reported after each run, this was ascribed to the leaching of the catalyst into the organic layer alongside catalyst degradation. To circumvent leaching issues and adhere to the green chemistry integrity of the aqueous approach, the catalyst precursors were evaluated under neat conditions (in the absence of an organic solvent). Improved catalysts performance in the aqueous biphasic experiments was reported.

A water-soluble non-sulfonated strategy was reported by Ramarou *et al*. based on 1,3,5-triaza-7-phosphaadamantane (PTA) (Ramarou et al., 2018, 2019).

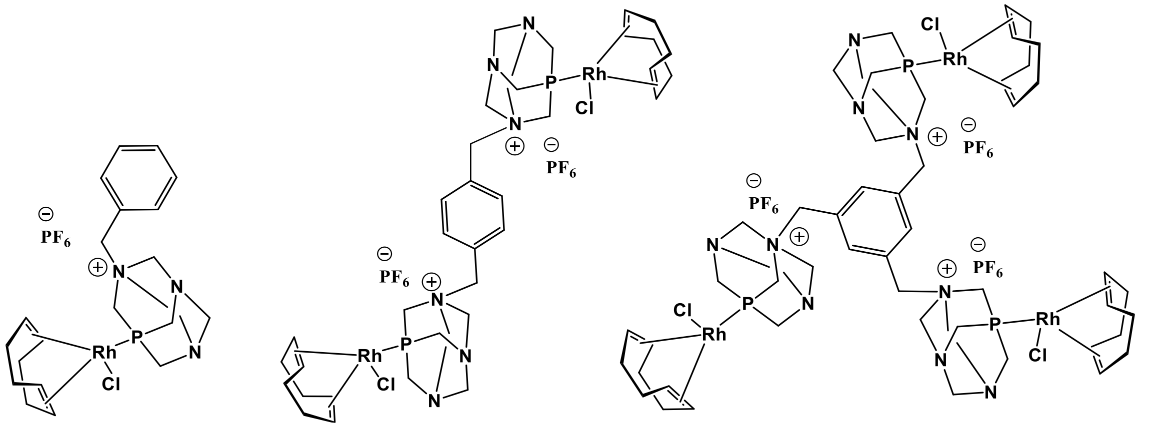


Figure 9. Structure of the Rh(I)-PTA catalyst precursors (Ramarou *et al.*, 2018)

The catalytic efficiency and recyclability of complexes were evaluated for hydroformylation of 1-octene in a water/toluene biphasic mixture at optimized conditions of 75 °C and 40 bar syngas pressures.

CONCLUSION

The demand for greener chemical processes has led to an increase in the research and development of novel recyclable homogeneous catalytic systems. The use of water for catalytic reactions is an excellent sustainable solvent alternative. However, the high polarity of water restricts the solubility of a typical metal-based catalyst in an aqueous media, this results to low catalytic activity. Therefore, designing suitable electron-rich donor ligands with sufficient hydrophilic functionalities that represses the catalytically active metal species in the aqueous phase is pivotal in enabling the aqueous biphasic recovery approach to be effective. This combats the challenge of mass transfer limitations encountered in catalytic reactions particularly the aqueous hydroformylation of long-chain olefins (1-octene) due to their poor water-solubility.

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CHEMICAL SOCIETY OF NIGERIA (CSN) ABIA CHAPTER

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Conference Proceedings

Full Length Research Paper

IN-SILICO STUDIES OF Fe (II) AND Cu (II) METAL COMPLEXES OF SULFAMETHOXAZOLE

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ABSTRACT:

Computational (*in-silico*) studies of compounds have been efficient in recent medicinal research as they carefully guide the selection of drugs and production as well as expunge the cost of the use of animals and other resources. Different routes of investigating the therapeutic effects of compounds have been developed such as *in-vitro, in-vivo* and *in-silico*. Some of which are very expensive financially to conduct. This has led to an increased use of *in-silico studies as it makes use of computer simulations in predicting if the properties of a test compound would conform to the necessary properties of a drug candidate*. The synthesis and characterization of Fe (II) and Cu (II) metal complexes of sulfamethoxazole has been reported in literature. The *in-silico* studies were done using various online tools such as Swiss ADME and Protox II. The drug likeness prediction gave an increased value for hydrogen bond acceptor and hydrogen bond donor from 4 and 2 of the sulfamethoxazole to 6 and 4 respectively for the complexes. The metal complexes also showed one violation each to the Lipinski's RO5 rule. The ADME prediction showed TPSA value of 150.51 $Å^2$ for the metal complexes, higher negative value of Log S (ESOL) indicating higher water solubility. The synthetic accessibility value also increased from 2.73 of the sulfamethoxazole to 4.04 and 3.95 for Fe(II) and Cu (II) complexes respectively. The Enzyme interaction showed no interaction with any of the P450 cytochromes. The bioavalability radar showed all test compounds had insaturation more than the expected insaturation of a potential drug. The BIOLED-Egg prediction predicted that the metal complexes can be actively effluxed by P-gp (PGP+) and are not absorbed by the human gastrointestinal tract and Blood brain barrier.The toxicity prediction showed all the test compounds to belong to a low toxicity class of 5 as a result of the predicted LD_{50} values. The *in-silico* analysis predicted that the Fe (II) and Cu (II) metal complexes have properties suitable for a potential drug candidate as they showed similar properties with sulfamethoxazole which is a known antibiotic drug. It is also recommended that these metal complexes be further examined using *in-vivo,in-vitro* pre-clinical and clinical trials to further determine its therapeutic use as a drug.

Keywords: *in-silico*, sulfamethoxazole, Fe (II), Cu (II), ADMET

INTRODUCTION

There is a constant desire for new pharmaceuticals that have improved effectiveness and lower levels of toxicity (Chang *et al.,* 2022; Otuokere *et al.,* 2019a), necessitated by the continuous abuse (misuse) of antibiotics and a gross growth in the number of bacteria (Otuokere and Okafor, 2012) that are resistant to drugs (Sirajul *et al.,* 2020; Otuokere *et al.,* 20221). Researchers have developed various routes to investigate the therapeutic effects of compounds. Some of which are very expensive financially to conduct (Otuokere *et al.,* 2019b). This has led to the increased use of *in-silico for* studies. However, the process of discovering and developing these drugs is expensive and time-consuming, and it comes with several hurdles. Setting aside the challenges of target validation and hit identification, clinical trials frequently encounter a significant rate of failure due to suboptimal pharmacokinetics, inadequate efficacy, and excessive toxicity (Chang *et al*., 2022; Otuokere *et al.,* 2021). In recent medicinal research, computational studies of compounds have been efficient because they carefully guide drug selection and production, as well as expunge the cost of animal and other resource use (Otuokere *et al.,* 2022a; Otuokere *et al.,* 2020). Many of the possible outcomes of research have been predicted with a high level of accuracy with the various algorithms used in the *in-silico* studies, which in turn helped in the modeling of research methodologies, scopes, and materials for a more effective result.

Sulfamethoxazole is a widely used antibacterial antibiotic that belongs to the class of medications known as sulfonamides. It is often combined with trimethoprim to generate a strong antibiotic known as co-trimoxazole or trimethoprim/sulfamethoxazole (Smith and Jones, 2022). This combination is often used to treat a number of bacterial diseases, including urinary tract infections, ear infections, bronchitis, and traveler's diarrhea. SMX-TMP has dominated in-vitro studies and case series as the choice treatment for *S. maltophilia* (Andelkovic *et al.,* 2019), though it has often been associated with treatment-limiting toxicities including renal and hepatic injury, fluid and electrolyte derangement, hemolysis, bone marrow suppression, and hypersensitive reactions (Giles *et al.*, 2019). The medicinal uses of sulfamethoxazole are numerous and have been shown to be useful in fighting many bacterial illnesses. One of the primary uses of sulfamethoxazole is to treat urinary tract infections (UTIs). UTIs are often caused by bacterial overgrowth in the urinary system, and sulfamethoxazole has been demonstrated to be particularly efficient in removing the germs responsible for these infections. It is typically used as a first-line treatment for uncomplicated UTIs due to its great efficacy and comparatively inexpensive cost (Prasannamedha and Kumar, 2020).

Several complexes of sulfamethoxazole have been synthesized, made possible by the presence of donor atoms like nitrogen, oxygen, and sulfur in different parts of its structure. This enables it to behave as a polydentate ligand, connecting with different metal ions to form chelates (Abdul-Hassan & Mousa, 2020). This gave the motivation to conduct *in-silico* studies on the Fe (II) and Cu (II) complexes of sulfamethoxazole to compare their possible candidacy to being an alternative antibiotic drug.

METHODOLOGY

Synthesis and Characterization

The Fe (II) and Cu (II) metal complexes has been reported by Asogwa & Otuokere (2024).

The following structures were proposed for Fe (II) and Cu (II) complexes of sulfamethoxazole:

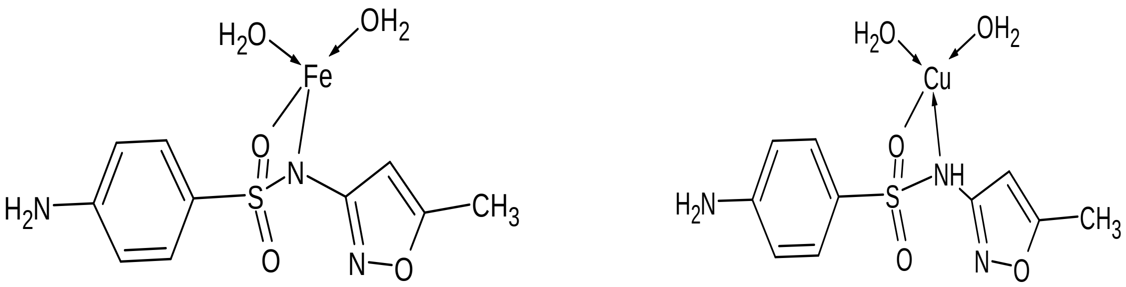

Fe (II) complex of sulfamethoxazole Cu (II) complex of sulfamethoxazole

Figure 1: Proposed structure for metal complexes of sulfamethoxazole

ADME Predictions

The ADME, drug-likeness and interactions were predicted using the Swiss ADME online tool (http://www.swissadme.ch) following the procedure by Schyman *et al.*, (2017)

Toxicity

The toxicity prediction was done using the online Protox II online tool, http://tox.charite.de/protoxII following the procedure by Arindam *et al.*, (2023).

RESULTS AND DISCUSSIONS

Drug-Likeness prediction

The prediction for the drug-likeness of the ligand and metal complexes were evaluated and presented in Table 1.

Table 1: Drug-likeness prediction of sulfamethoxazole and its metal complexes

Compounds	Mol. Weight	HB Acceptor	HB Donor	Lipophilicity LogP (g/mol)	Molar refractivity	No of violations
Sulfamethoxazole	253.28	4	2	1.03	62.99	0
Fe (II) complex	343.14	6	4	0.00	71.17	1 TPSA > 140
Cu (II) complex	350.84	6	4	0.00	71.17	1 TPSA > 140

Lipinski *et al.*, (2012) postulated a set of guidelines known as Lipinski's Rule of 5 (RO5) to determine if a compound possesses the pre-requisite physical and chemical properties of an effective oral medication. According to Lipinski's rule, a potential oral drug should normally not exceed one violation of one of the following criteria: The maximum number of hydrogen bond donors should not exceed 5. The maximum number of hydrogen bond acceptors allowed is 10. A molecular mass below 500 daltons. The Clog P value should be less than or equal to 5, indicating an octanol-water partition coefficient. The molar refractivity should vary from 40 to 130. The drug-likeness prediction of the test compounds (Table 1) showed only one violation out of five for the metal complexes and none for the ligand. These findings indicate that sulfamethoxazole and the Fe (II) and Cu (II) complexes meet RO5 standards. Predictions indicate a low attrition rate for the ligand and complexes, indicating their suitability for further drug development studies (Otuokere *et al.*, 2022b).

ADME Predictions

The ADME predictions for the ligands and metal complexes are presented in the table 2

Table 2: Some ADME Parameters prediction of sulfamethoxazole and its metal complexes

Compound	TPSA (Å^{2})	Water Solubility Log *S* (ESOL)	Bio. Avail. Score	Med. Chem. (PAIN)	Synthetic Accessibility
Sulfamethoxazole	106.60	-2.25	0.55	0	2.73
Fe (II) complex	150.51	-3.22	0.55	0	4.04
Cu (II) complex	150.51	-3.27	0.55	0	3.95

Lipinski *et al.* (2012) say that the topological polar surface area (TPSA) is a critical chemical descriptor that strongly connects to pharmacokinetic aspects. A desired medication should have a TPSA score below 140 **Å^{2}**. The TPSA values of the test compounds, as shown in Table 2, are below 140 **Å^{2}**, indicating that they are likely to be effective treatments. The availability of a soluble molecule greatly simplifies many drug development processes, particularly in terms of handling and formulation. In addition, solubility is a crucial component that impacts absorption in discovery programs focusing on oral delivery. In addition, a drug intended for parenteral administration must have high solubility in water in order to efficiently deliver a sufficient amount of the active component within the limited volume of the pharmaceutical dosage.

The water solubility profile for the test chemicals has been provided using the estimated solubility (ESOL) model (Table 2). The solubility profile indicated that all the test compounds were soluble. The test compounds also have a favorable bioavailability score of 0.55, whereas a minimum bioavailability score of 0.10 is required for a compound to be considered a therapeutic candidate (Martin, 2005), indicating that all the test substances are expected to be able to be absorbed and utilized by the body when taken orally. PAINS, or pan-assay interference compounds, are agents that exhibit high activity in assays regardless of the individual protein target. They are sometimes referred to as frequent hits or promiscuous chemicals. Our study's findings reveal that there are no substances with promiscuous properties that can potentially induce drug interference. The score for synthetic accessibility is normalized on a scale of 1 (showing easy synthesis) to 10 (representing severely difficult synthesis). The synthetic accessibility test score of the test compounds (Table 2) suggests that the test compounds can be readily synthesized.

Enzyme-Interaction prediction

The interaction between the ligand, metal complexes and isoenzymes were predicted and presented in the Tables 3.

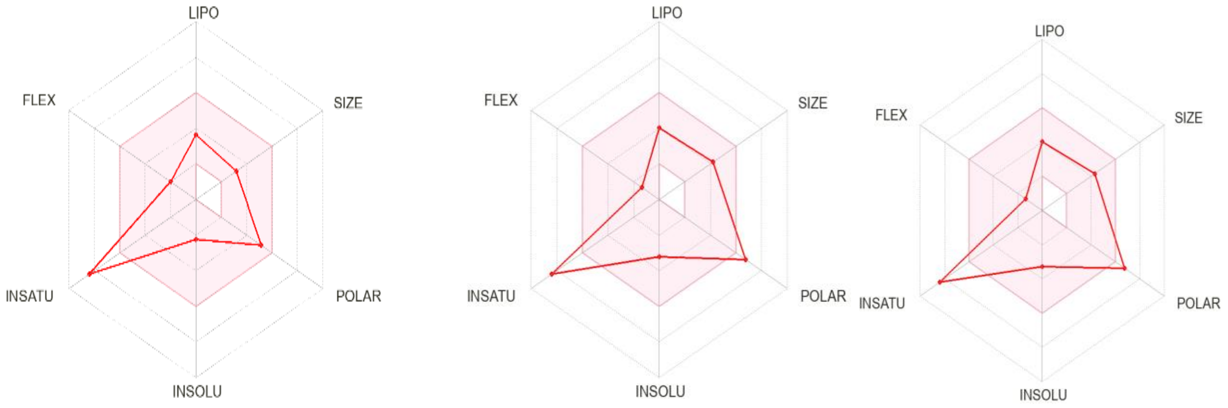
The inhibition of these isoenzymes is an important element in drug-drug interactions that impact pharmacokinetics. This inhibition might cause the medication or its metabolites to build up, resulting in harmful or unwanted side effects due to slowed clearance. Therefore, it is vital for drug development to precisely anticipate the risk of a molecule creating considerable drug interactions by inhibiting CYPs, as well as identify the specific isoforms that are impacted. The complexes and the ligand (sulfamethoxazole) revealed no inhibitory impact on any of the five isoenzymes (CYP1A2, CYP2C19, CYP2C9, CYP2D6, CYP3A4). Based on their negative log Kp values, all the test compounds were anticipated to be non-permeable to the skin. Potts & Guy (Potts and Guy, 1992) demonstrated that there is an inverse relationship between the log Kp (measured in cm/s) and the permeability of the molecule through the skin. In other words, the higher the log Kp number, the lower the molecule's permeability. All compounds have negative log Kp values. This shows that sulfamethoxazole and its Fe (II) and Cu (II) complexes do not infiltrate the skin.

Bioavailability Radar

The bioavailability radar of the ligand and metal complexes are presented in Figures 2.

Table 3: Interaction of sulfamethoxazole and its metal complexes with cytochromes P450 (CYP)

Compounds	CYP1A2	CYP2CP	CYP2D6	CYP3A4	Log K_p (skin permeation)(cm/s)
Sulfamethoxazole	No	No	No	No	-7.21
Fe (II) complex	No	No	No	No	-7.29
Cu (II) complex	No	No	No	No	-7.34



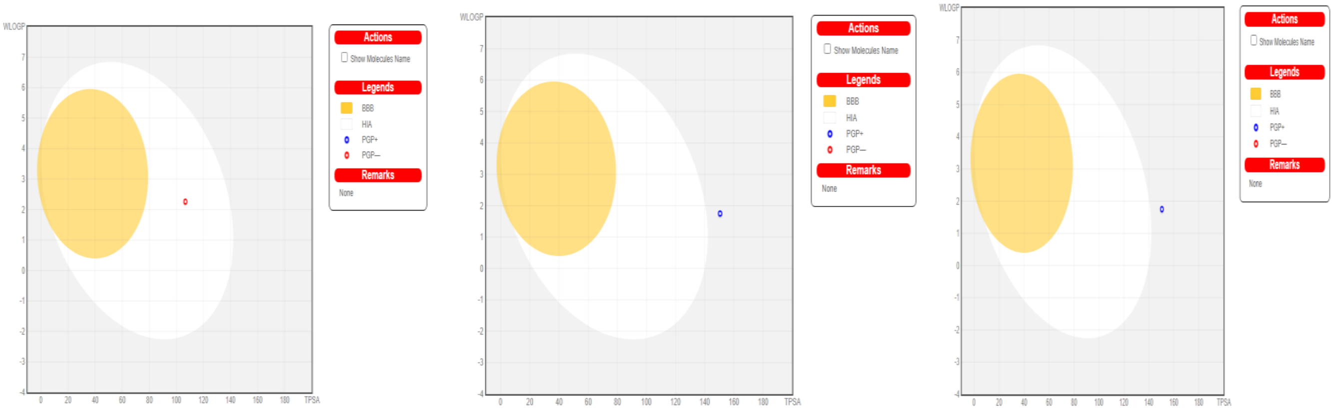
Sulfamethoxazole Fe (II) complex Cu(II) complex

Figure 2: Bioavailability radar

The Bioavailability Radar (Figure 2) is presented to quickly assess the drug-likeness of the ligand and complexes. When considering the qualities of the substances, six physicochemical factors were considered: lipophilicity, size, polarity, solubility, flexibility, and saturation. Descriptors taken from Ritchie *et al*. (2011) were used to create a physicochemical range on each axis. The molecule must completely fall within the pink area of the radar plot in order to be classified as drug-like. The bioavailability radar prediction indicated that both the ligand and the complexes possess five properties, namely lipophilicity, flexibility, size, polarity, and insolubility, which fall within the suggested range and insaturity beyond the limits for a prospective drug.

BOILED Egg

The BOILED Egg analysis on sulfamethoxazole and the metal complexes are shown in the Figure 3.



sulfamethoxazole Fe (II) complex Cu(II) complex

Figure 3: BOILED Egg analysis

The BOILED-Egg (Figure 3) provides an easy approach for assessing human gastrointestinal absorption (HIA) and blood-brain barrier (BBB) based on the molecular position in the WLOGP-versus-TPSA reference system. The white zone suggests a high possibility of passive absorption by the gastrointestinal tract, while the yellow region (yolk) indicates a high likelihood of brain penetration. The yolk and white components are not mutually exclusive, as stated in reference (Ritchie *et al.*, 2011). Furthermore, the points are highlighted in blue if they are anticipated to be actively expelled by permeability glycoprotein, P-gp (PGP+), and in red if they are projected to be non-substrates of P-gp (PGP−). The ligand (sulfamethoxazole) had a red dot within the white area, suggesting that it is not a substrate of permeability glycoprotein (PGP−). In contrast, the Fe (II) and Cu (II) complexes exhibited blue-colored dots, indicating their active efflux by P-gp (PGP+). Also, the complexes were determined to exhibit no absorption of the HIA due to their location outside the white region of the BOILED egg diagram.

Toxicity studies

The toxicity studies of the ligands and the metal complexes are presented in table 4.

ProTox-II was used to assess the *in silico* toxicity of the sulfamethoxazole, Fe (II), and Cu (II) complexes of sulfamethoxazole. Several researchers (Nwankwo *et al.*, 2022; Otuokere *et al.*, 2015) have used this server to determine toxicity. All the test compounds were predicted to be in class 5 based on their LD_{50} value ($2000 < LD_{50} \leq 5000$). This LD_{50} value is a prediction value of toxic dosage in mg/kg, giving the median lethal dose.

Table 4: Toxicity information of sulfamethoxazole and its metal complexes

Compounds	Predicted LD_{50} (mg/kg)	Predicted Toxicity Class	Average similarity: (%)	Prediction Accuracy: (%)
Sulfamethoxazole	2300	5	100	100
Fe (II) complex	3471	5	42.81	54.26
Cu (II) complex	3471	5	43.58	54.26

CONCLUSION

The *in-silico* studies on the Fe (II) and Cu (II) complexes of sulfamethoxazole were conducted. The predictions revealed that the test compounds had favorable predictions in terms of drug-likeness, TPSA value, synthetic accessibility, water solubility, skin permeability, and bioavailability score. The toxicity prediction revealed that both the ligand and the complexes are in toxicity class 5. The study's findings and conclusions show that the Fe (II) and Cu (II) complexes of sulfamethoxazole have a wide range of ADMET profiles, which means they are safe and could be used for therapeutic purposes. These findings necessitate further examination into their *in-vivo*, preclinical, and clinical trials. Future research should prioritize investigating the fundamental processes underpinning therapeutic advantages and conducting clinical trials to confirm their effectiveness and safety in humans.

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Conference Proceedings

Full Length Research Paper

UTILIZATION OF LIGNOCELLULOSIC FOR THE PRODUCTION OF BIOFERTILIZER

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ABSTRACT

The utilization of lignocellulosic biomass, which includes agricultural residues such as rice straw, wheat straw, corn stover, and sugarcane bagasse, as a renewable and abundant resource has garnered significant attention. These lignocellulosic materials comprise cellulose, hemicellulose, and lignin, which microorganisms can break down to release sugars and other compounds. These sugars and compounds can then serve as a carbon source and energy source for beneficial microbes, including nitrogen-fixing bacteria, phosphate-solubilizing bacteria, and potassium-mobilizing bacteria, to produce biofertilizers. This study investigated the potential of corn husk, fluted pumpkin vine, and goat dung as substrates for biofertilizer production. The systematic extraction method determined the lignocellulose fractions, which revealed that corn husk had the highest cellulose content (39.31%), while pumpkin vine and goat dung had 15.53% and 19.62% cellulose, respectively. Proximate analysis showed that goat dung had the highest protein (21.11%) and ash (4.06%) contents, while corn husk had the highest fiber (61.35%) and carbohydrate (25.42%) contents. The substrate had a pH of 7.57, a total nitrogen content of 1.97%, and an organic carbon content of 7.76%. After anaerobic digestion, the digestate (biofertilizer) had a slightly lower pH of 7.47 and a reduced total nitrogen content of 1.80%. However, the phosphorus, potassium, calcium, magnesium, and organic carbon contents of the digestate were higher than the substrate, indicating mineralization during digestion. The results of this study demonstrate that lignocellulosic can be utilized as suitable substrates for biofertilizer production through anaerobic digestion. The resulting digestate has an improved nutrient composition, making it a viable biofertilizer for soil amendment and plant nutrition. This study highlights the potential of waste lignocellulosic biomass as a renewable resource for sustainable biofertilizer production.

Keywords: Lignocellulose, biofertilizer, corn husk, pumpkin vine, goat dung, digestate.

INTRODUCTION

Lignocellulosic biomass is a plant biomass composed of cellulose, hemicellulose, and lignin. It is the most abundant renewable resource on Earth, with great potential to be utilized as a sustainable and renewable feedstock for producing biofuels, biochemicals, biomaterials and biofertilizers

(Dahmen *et al.*, 2019). Lignocellulosic feedstocks include agricultural residues,

such as corn stover, sugarcane bagasse, wheat straw, and rice straw, as well as dedicated energy crops like switchgrass, and forestry residues (Machado *et al.*, 2016). Using lignocellulosic

biomass for value-added products can provide environmental and economic benefits such as reducing dependence on fossil resources, reducing greenhouse gas emissions, improving soil health, and providing income opportunities for agricultural producers (Koupaie *et al.*, 2019). Biofertilizers are formulations containing living microorganisms that can increase the availability and uptake of nutrients for plants when applied to seeds, soil, or other growth media. Biofertilizers enhance soil fertility and naturally stimulate plant growth without adverse effects (Thomas and Singh, 2019). The extensive use of chemical fertilizers over time has caused soil health deterioration and environmental pollution. Chemical fertilizers are prone to losses due to leaching, run-off, volatilization, and immobilization (Rajesha and Ray, 2020). Moreover, only a small percentage of applied nitrogen and phosphorus fertilizers are absorbed by plants, leading to accumulation in soils or water bodies, resulting in eutrophication and breeding of toxin-producing aquatic organisms. The overuse of chemical fertilizers also acidifies soils, causes nutrient imbalances, and makes plants more susceptible to pests and diseases, ultimately decreasing crop yields over time (Krishnaprabu, 2020).

METHODOLOGY

Sample Collection

The Agro-waste biomass used in this work includes maize (corn) husks, fluted pumpkin vines, and Goat dung. They were obtained from homestead domestic waste dumps. Laboratory and stead domestic waste dumps. Laboratory and other facilities including rat droppings were sourced from Caslab Analytical Laboratory Umuahia.

Biogas Production Unit (Biodigester)

The biodigester (improvised) consisted of a fermentation chamber, an outlet, and inlet pipes as well as the product (gas) pipe which conducts the produced gas into an air-tight empty drip bag. The test lignocellulose (biomass) materials were mixed in a transparent plastic bucket. In this regard, the goat droppings (1.5kg), the pumpkin vine (350g), and the corn husk (350g) were mixed in the bucket and made up to 7.5 liters with water. The digester was charged with the content of the bucket and sealed up and monitored for 28 days (digestion period). During this period, the organic waste (lignocellulose) mixture was allowed to stabilize and the anaerobic fermentation continued with the degradation of the lignocellulose by the action of microorganisms (through chance inoculation) leading to the production of biogas. Meanwhile, the waste (lignocellulose) mixture was subjected to physio-chemical analysis.

Preparation of Lignocellulose (agro wastes) Material

The waste materials, corn husk, fluted pumpkin vines, and goat droppings were separately processed to increase their surface areas for effective microbial actions.

Therefore, the wastes were separately ground into a pulp (for the pumpkin vine) or powdered (for the husk). They were put in separate labeled large-mouthed screw-capped.

Determination of Lignocellulose Proportion in the Test Materials

The systematic extraction gravimetric method described by Harbone (1996) was used. The general extraction involves the separation of polysaccharides and the qualification of their respective proportions by weight.

Determination of the Proximate Composition of Lignocellulose Materials

The proximate composition was determined according to the methods described by Onwuka (2018). Protein, fat content, ash content, moisture content, fiber content, and carbohydrate composition by difference method.

Test for Biogas Production

At the end of the 28-day digestion period, as well as intervals, determined by the presence of gas in the drying bag receptacle, the gas outlet pipe was carefully reopened while a unit was kept 15cm from the nozzle. The unit's ability to attract the gas and burn with predominantly blue flame was indicative of the presence of biogas as the major component of the digestion products.

Biofertilizer By-Product of Biogas Production

At the end of the biogas production, the sludge residue in the digester unit was recovered and subjected to analysis to evaluate its content potential for use as a fertilizer of biological origin for food crop cultivations. The analytical parameters of assessment include the organic matter content, total nitrogen, phosphorus, and potassium contents as well as moisture content and pH (acidity). The following procedures were used.

Determination of pH

pH of the residual sludge was determined instrumentally using an electronic pH meter. Following the manufacturer’s directions, the machine was switched on and allowed a 10-minute equilibrium time before it was calibrated with buffered solutions of pH 4.0 and 7.0 respectively.

Determination of Total Nitrogen (N_2)

This was done using the Kjeldahl method (Onwuka, 2018).

Determination of Organic Matter

Organic matter was determined titrimetrically using the Walkey Black method.

Determination of Phosphorus and Potassium and the Residue Slurry

The dry ash acid extraction method (Onwuka, 2018) was employed.

Determination of potassium (K^+)

Potassium in the sample extract was determined photometrically in a flame photometer. In line with the manufacturers' directives, the machine was switched on and allowed to stabilize for 10 minutes before use.

RESULTS AND DISCUSSION

The results of the analysis are presented in Tables 1, 2, and 3 below.

Table 1: **Lignocellulose Fractions of Substrate Materials**

Sample	*Pectin*	*Lignin*	*Hemicellulose*	*Cellulose*
Corn husk	1.37 ± 0.06^{b}	18.88 ± 0.30^{a}	22.71 ± 0.36^{a}	39.31 ± 0.44^{a}
Pumpkin vine	2.88 ± 0.05^{a}	8.35 ± 0.33^{b}	10.61 ± 0.55^{c}	15.53 ± 0.45^{c}
Goat dung	0.41 ± 0.04^{c}	4.87 ± 0.25^{c}	13.05 ± 1.62^{b}	19.62 ± 1.25^{b}

Values show means of triplicate analysis ± standard deviation. Figures with different superscripts in the column are significantly different ($P<0.05$)

Table 2: Proximate Composition of Lignocellulose Materials Used in Biogas Production

Sample	*Moisture*	*Protein*	*Fat*	*Fiber*	*Ash*	*CHO*
Corn husk	8.55 ± 0.19^{c}	1.26 ± 0.08^{c}	0.62 ± 0.04^{c}	61.35 ± 1.51^{a}	2.92 ± 0.04^{b}	25.42 ± 1.71^{c}
Pumpkin vine	24.78 ± 0.28^{a}	9.66 ± 0.02^{b}	1.25 ± 0.02^{b}	37.77 ± 0.77^{b}	2.99 ± 0.27^{b}	28.47 ± 0.41^{b}
Goat dung	18.75 ± 0.08^{b}	21.11 ± 0.13^{a}	1.89 ± 0.07^{a}	21.25 ± 0.25^{c}	4.06 ± 0.17^{a}	36.95 ± 0.52^{a}

Values show means of triplicate analysis ± standard deviation. Figures with different superscripts in the column are significantly different ($P<0.05$).

Table 3: **Nutritional chemical composition of substrate and digestate (Biofertilizer)**

Sample	*pH*	*Total Nitrogen (N%)*	*Phosphate (P) in g/L*	*Potassium (K) in g/L*	*Ca (mg/L)*	*Mg (mg/L)*	*Organic Carbon*
Substrate	7.57 ± 0.06^{a}	1.97 ± 0.01^{a}	2.70 ± 0.03^{b}	3.97 ± 0.01^{b}	20.76 ± 1.34^{b}	72.48± 0.03^{a}	7.76 ± 0.13^{a}
Digestate (Biofertilizer)	7.47 ± 0.06^{b}	1.80 ± 0.04^{b}	2.85 ± 0.07^{a}	4.19 ± 0.01^{a}	41.18 ± 0.00^{a}	66.88± 0.06^{b}	7.24 ± 0.11^{b}

Values show means of triplicate analysis ± standard deviation. Figures with different superscripts in the column are significantly different ($P<0.05$).

DISCUSSION

The lignocellulosic fractions of corn husk, pumpkin vine, and goat dung reported in Table 1 provide useful insights into the potential of these agricultural residues as substrates for biofertilizer production. The key lignocellulosic components measured are pectin, lignin, hemicellulose, and cellulose.

The corn husk sample contained 1.37% pectin, 18.88% lignin, 22.71% hemicellulose, and 39.31% cellulose. These values align well with previous studies on the composition of corn husks. For example, Barman et al. (2018) reported a corn husk composition of 1.2% pectin, 17.3% lignin, 25.1% hemicellulose and 38.7% cellulose. The small variations can be attributed to differences in corn variety, growing conditions, and analytical methods. However, the consistency confirms corn husk is lignocellulosic biomass with substantial amounts of cellulose and hemicellulose that can be converted to biofertilizer. Another study by Mehmood et al. (2009) analyzed four different corn husk varieties grown in Pakistan. They found pectin levels ranging from 0.9-1.5%, lignin 16.4-19.2%, hemicellulose 20.1-26.3%, and cellulose 36.4-41.2%.

For pumpkin vine, results show a composition of 2.88% pectin, 8.35% lignin, 10.61% hemicellulose and 15.53% cellulose. These values differ considerably from corn husk, with pumpkin vine containing much lower lignin and particularly lower cellulose. Previous studies on pumpkin vines are limited, but Sathishkumar et al. (2008) analyzed the lignocellulosic content of vines from a pumpkin variety grown in India. They found a composition of 3.2% pectin, 10.5% lignin, 12.3% hemicellulose and 20.7% cellulose. Additional studies on pumpkin vines from diverse cultivars could help clarify the typical cellulose levels. Nonetheless, both studies show pumpkin vine is much lower in cellulose compared to corn husk, making it a less attractive substrate for biofertilizer production. The low lignin is beneficial but the low cellulose availability would limit yields.

For goat dung, results show a composition of 0.41% pectin, 4.87% lignin, 13.05% hemicellulose, and 19.62% cellulose. Very few studies have examined the detailed lignocellulosic fractions of goat dung. However, Kim et al. (2014) analyzed goat manure from Korea and found it contained 2.1% lignin, 14.7% hemicellulose and 15.3% cellulose. The lignin content matches well, confirming the low lignin concentration in goat dung compared to corn husk and pumpkin vine.

However, the lignocellulosic availability in goat dung appears significantly lower than in agricultural residues like corn husk. This is expected given goat dung contains partially digested plant materials. Consequently, it may provide fewer fermentable sugars for biofertilizer production unless supplementation is provided.

The proximate fractions of moisture, protein, fat, fiber, ash, and carbohydrates (CHO) presented in Table 2 provide useful comparison points to evaluate corn husk, pumpkin vine, and goat droppings as feedstocks for biogas production. For corn husks, the proximate fractions were 8.55% moisture, 1.26% protein, 0.62% fat, 61.35% fiber, 2.92% ash and 25.42% CHO. These align well with the literature on corn husk composition. A study by Jiang et al. (2012) on corn husks from China found a proximate makeup of 8.2% moisture, 2.1% protein, 1.1% fat, 59.8% fiber, 5.2% ash and 23.7% CHO. The moisture, fat, fiber, and CHO levels match closely with the results from this study. The higher protein and ash contents may reflect varietal and soil condition differences.

Again, good agreement is seen with the ranges overlapping the results of the present study. The consistency confirms that corn husk is low in protein and fat but high in fiber, with moderate levels of CHO and low ash. Compared to corn husk and pumpkin vine, the goat droppings appear much richer in protein, indicating good potential to provide supplemental nitrogen for anaerobic digestion. However, the lower fiber content may result in reduced biogas yields. The nutritional chemical analysis of substrate and digestate biofertilizer is presented in Table 3 provides useful insights into the impacts of anaerobic digestion on fertilizer properties. The key parameters are pH, nitrogen, phosphorus, potassium, calcium, magnesium, and organic carbon. The substrate pH was 7.57 while the biofertilizer digestate pH was 7.47. A minor reduction in pH after digestion is expected, as anaerobic fermentation processes tend to cause slight acidification. For example, Tambone et al. (2010) measured pH levels before and after the anaerobic digestion of agricultural residues and found a consistently small drop in pH from 7.8 to 7.5. This matches the pH shift seen in this study. The change is likely due to the production of organic acids like acetate and lactate during the microbial digestion process. However, the pH remains circumneutral, indicating stable and beneficial conditions for a biofertilizer product.

The total nitrogen decreased slightly from 1.97% in the substrate to 1.80% in the biofertilizer digestate according to our study. Some nitrogen loss during anaerobic digestion is expected due to volatilization and conversion to gaseous forms like ammonia. However, Tambone *et al.* (2009) reported an increase in total nitrogen from 1.3% up to 1.7% after anaerobic digestion of agricultural residues. They attributed this to the mineralization of organic nitrogen into more bioavailable ammonium and nitrate forms. The reasons for the differing response require further study but may relate to substrate properties, inoculum, and digestion parameters. However, both levels remain suitable as biofertilizers. The phosphorus content increased slightly from 2.70 g/L in the substrate to 2.85 g/L in the digestate. Increased phosphorus availability after anaerobic digestion has been widely reported and is likely due to the conversion of insoluble phosphates into more soluble and bioavailable forms. In alignment, Tambone *et al.* (2009) reported potassium levels rising from 2.8 to 3.6 g/L with anaerobic digestion. The mechanisms likely involve cell lysis, enzymatic decomposition, and acidification effects. The potassium increases demonstrate important nutrient enrichment benefits of converting residues into biofertilizers. The calcium concentration increased notably from 20.76 mg/L in the substrate to 41.18 mg/L after anaerobic digestion. This aligns with previous findings. For example, Tambone *et al.* (2010) saw calcium levels increase from 28 to 63 mg/L after crop residue digestion. The calcium increases may be due to organic acid production lowering the pH and increasing calcium solubility. Along with providing an essential macronutrient, the boosted calcium can help stabilize and flocculate colloidal particles in the digestate biofertilizer.

The reasons for these differing results need investigation but may relate to substrate properties and inoculum characteristics.

Overall, both digestate carbon levels should provide benefits.

CONCLUSION

The analysis from this study demonstrates the lignocellulosic fractions, proximate compositions, and nutritional profiles of corn husk, pumpkin vine, and goat droppings making them potential substrates for producing biofertilizers through anaerobic digestion. Corn husk appears to be the most suitable substrate due to its high cellulose, hemicellulose, and low lignin levels. These characteristics provide ample fermentable sugars for producing biogas while remaining digestible.

Additionally, the pH remained near neutral which is suitable for a biofertilizer product.

However, additional research is needed to optimize nutrient balances and enrich digestate properties for effective biofertilizers.

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Conference Proceedings

Full Length Research Paper

DETERMINATION OF HEAVY METAL CONTENTS OF PLASTIC COMPONENTS OF ELECTRONIC WASTE (E-WASTE) AND ESTIMATION OF METAL POLLUTION FROM THEIR MISMANAGEMENT IN NIGERIA

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ABSTRACT

Large quantities of both new and used electrical and electronic equipment (EEE) are imported into Nigeria annually. These products get to their end-of-life and are disposed. Scavengers are usually interested in metal fractions of electronic waste while most e-waste which have limited reuse options are disposed, mostly dumped or burned. This study examined the heavy metal levels of plastic components of some EEE categories. Data on importation of EEE into Nigeria were also obtained from UN Comtrade and used to estimate metal pollution from such imports. Plastic housing of 25 EEE products were collected from electronic hubs and repairers' shop. The levels of Pb, Cd, Cr and As were measured using AAS after digestion with an acid mixture (1:2, HNO_3 and HCl). The result (Mean±SD; all data in mg/kg) varied from 0.78±1.26 to 6.66±0.07 for Pb; 0.92±0.60 to 2.94±0.23 for Cd; 0.22±93 to 3.80±0.22 for Cr, and 0.15±0.01 to 0.32±0.00 for As. The results were below the regulatory limits of the European Union Restrictions on Hazardous substance (RoHS). The data from this study is comparable with literature. The estimated quantities of EEE imported into Nigeria between 1990 and 2022 is 4,568,043 tonnes; and this contains 1,337,310 tonnes of plastics. The purpose of this study was to determine the heavy metal levels of e-waste plastics and to estimate the amounts of these metals imported with electronics over the years. Government regulation is required, and strict enforcement is necessary to channel e-waste plastics towards proper management routes.

Keywords: Heavy metals, e-waste plastics, estimation, pollution, importation, mismanagement, Nigeria

INTRODUCTION

Plastic has become very important and useful that we cannot do without it. It comes into different forms of variety, type and different colour. Plastic has solved a lot of problems and also has created a lot of problems to our environment. The majority of different plastics are gotten from fossil-based feedstocks such as Polyethylene (PE), polypropylene (PP), polystyrene (PS), polyvinyl chloride (PVC), polyethylene terephthalate (PET) and polyurethane (PUR) are the main types of plastics used in different part of countries (Wei *et al*., 2020). The use of plastic is growing and has become a necessary component of daily living. Globally, 8.3 billion metric tons (Mt) of virgin plastics were manufactured, of which 6.3 billion Mt were wasted (Geyer *et al.*, 2017), Single use-packaging account for almost 40% of the total production. About 9% of this estimated garbage has been recycled, whereas 12 % was burned. According to Geyer *et al*. (2017), an additional 79 % of plastic trash is either immediately released into the environment or ends up in landfills. A significant amount of the plastic generated each year is lost to the ocean, where they persist and have the potential to accumulate to 250 Mt by 2025 (Jambeck *et al.*, 2015). Nigeria is the ninth-highest contributor to plastic pollution globally, producing around 2.5 million tonnes of plastic garbage each year. Regrettably, approximately 88% of Nigeria's plastic waste is not recycled (Temitope, 2022).

Some of the heavy metals that are present in plastics seep into aquatic ecosystems, depositing themselves in the environment. Individuals who reside close to where these plastic wastes are indiscriminately dumped are exposed to these harmful substances by skin contact, inhalation, or ingestion of contaminated soil and water. Once inside the body, these pollutants build up in numerous tissues and may reach critical concentrations that result in acute intoxications and health complications (Yang *et al*., 2014). The crust of the Earth naturally contains heavy metals. Heavy metals are dangerous to human health because of their tenacity, high level of toxicity, and propensity to build up in the ecosystem. Among the key metals of public health significance are arsenic, cadmium, chromium, lead, and mercury. Previous studies have invested metal levels in EEE plastics (Nnorom and Osibanjo, 2009; Narendra *et al.*, 2020; Stenvall *et al.,* 2003; Ohidul *et al*., 2019; Irada *et al.,* 2021). The adoption of inappropriate management methods for electronic waste can result in environmental pollution with toxic metals. The buildup of these hazardous metals in the food chain poses a risk to public health in addition to destabilizing the ecosystem, and their potential long-term effects on the ecosystem must be taken into consideration. The aim of this study is to determine the levels of Pb, Cd, As and Cr in waste plastic housing of EEE and estimating the amounts of these metals imported with EEE into Nigeria between 1990 and 2022.

MATERIALS AND METHODS

Sample Collection and Preparation

A total of twenty-five (25) electronic samples of the plastics samples were collected from the selected area in different markets and electronics hubs. Electronic devices studied include photocopier, mobile phones, scanners, fan, phone charger, printer and TV. The twenty-five (25) plastic samples (approx. 100–200 g) were collected using a glove and labelled properly. The samples were collected/purchased from markets in and around Aba. In the laboratory the samples were disassembled, and the plastic housing units were retrieved and prepared for digestion by crushing.

Acid Digestion of Sample

A known weight (ca. 6 g) was digested with an acid mixture (5 ml of 65 % HNO_3 and 10 ml 70 % HCl) with (up to 120 ^{o}C) for about 1 hour or on observation of disappearance of the brown fume. The digest was allowed to cool and deionized water was added and filtered into calibrated 50ml volumetric flask. The concentrations of Pb, Cd, As and Cr were determined using VARIAN Atomic Absorption Spectrometer (GBC XplorAA dual). Adequate quality control/quality assurance protocols were observed. The AAS was calibrated using a series of calibration solutions, blank was inserted at 10% rate. All reagents and distilled water used throughout this analysis were of analytical grade. Duplicate analysis was also included.

Estimation of Metal Contents of EEE imported into Nigeria (1990-2022)

The amounts of metals imported with EEE from 1990 to 2022 was estimated by obtaining data on the importation of EEE of different categories into Nigeria from the United Nations Comtrade database (UN Comtrade, https://comtradeplus.un.org). The heavy metal contents of plastics of EEE were estimated using equation 1:

$$\boldsymbol{Amount\ of\ Metal_m = Q(P)_{EEE} \times Mc} \quad .... \mathbf{1}$$

Where *Amount of Metal*$_m$ is the amount of a given metal (m) imported with a given EEE product category; $Q(P)_{EEE}$ is the quantity of plastic in a given EEE imported; and Mc is the mean metal concentration.

RESULTS AND DISCUSSION

Metal Levels in Waste Plastics of EEE

A summary of the Cd, Cr, Pb and As contents of the EEE plastics studied is presented in Table 1. The results according to product category is presented in Figure 1.

The results of this study were all below the European Union Restrictions on the use of Hazardous Substances (RoHS) in EEE (Table1). The RoHS limits the amounts of Pb and Cd in electronics to 1000 mg/kg and the amount of Cr (V) to 100 mg/kg. no significant differences were observed in the metal levels of the different product categories.

Table 1: Summary of heavy metal levels of EEE plastics (mg/kg)

	Pb	Cr	Cd	As
Mean	0.78	1.22	0.92	0.15
Standard deviation	1.26	0.93	0.60	0.08
Geometric Mean	0.50	0.90	0.76	0.11
Range	0.07 – 6.66	0.22 – 3.8	0.23 – 2.94	0.003 – 0.32
EU RoHS Limit	1000	100	1000	-

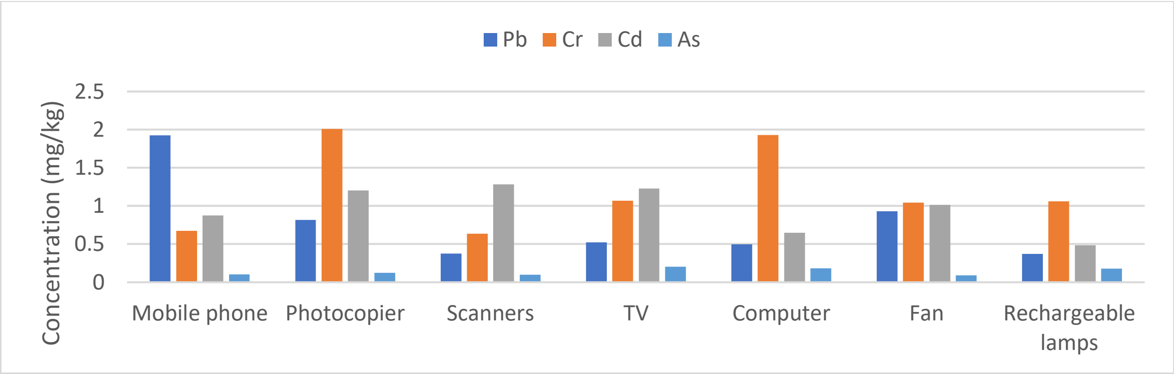

Figure 1: Comparison of metal levels in different EEE waste plastic

The results of this study were all below the European Union Restrictions on the use of Hazardous Substances (RoHS) in EEE (Table1). The RoHS limits the amounts of Pb and Cd in electronics to 1000 mg/kg and the amount of Cr (V) to 100 mg/kg. no significant differences were observed in the metal levels of the different product categories.

Comparison of Results with Literature

A comparison of the results of this study with literature is presented in Tables 2. For instance, Dimitrakakis *et al*., (2009) reported a mean of 17.4 mg/kg for Pb, 5.7 mg/kg for Cd, and 8.4 mg/kg for Cr in 51 small waste electrical and electronic equipment found in the residual household waste stream of the city of Dresden, Germany. Similarly, Ernst *et al.*, (2000) studied technical waste polymers and reported Cd in the range 80–12000 mg/kg and Pb in the range 90–700 mg/kg. Sindiku *et al*. (2015) screened 382 cathode ray tube (CRT) casings of TVs and computers produced from 1980 to 2005 in Nigeria with desktop XRF for heavy metals and bromine. She found a high variability in lead and cadmium levels in the plastics with more than 30% of CRT casings above 100 mg/kg lead with a maximum concentration of 3000 mg/kg. The results of this study are generally lower than most data in literature.

Table 2: Comparison of results of this study with literature (mg/kg)

Country	Cd	Cr	Pb	As	Reference
China	16 -474	23-75	12-71	12-43	Ohidul *et al*., (2019)
USA	-	8.18	0.36	-	Michael, (2014)
Thailand	0.10 - 0.11	0.07	0.01	-	Irada *et al*., (2021)
Nigeria	4 - 69.9	16.3	58.3 - 1750	-	Nnorom & Osibanjo (2009)
Germany	5.7	8.4	17.4	-	Dimitrakakis *et al*., (2009)
Germany	70	-	200	-	Stenvall *et al*., (2013)
Germany	80 - 12 000		90 - 700		Ernst *et al*., (2000)
EU RoHS Limit	1000	100	1000	1000	-

Environmental Implications of Metal and other Chemicals in EEE Plastics

In Nigeria, metals in waste EEE and in the EEE plastics in particular could have negatives implications in the environment considering that such are often disposed into water bodies or burned. The ash from open burning of EEE plastics will contain higher levels of these metals which may result in uptake and accumulation in the food chain. Plastics in their various applications contain a wide range of hazardous additives including several POPs listed in the Stockholm Convention, such as Hexabromocyclododecane (HBCD); HBB, PBDEs, Polychlorinated biphenyls (PCBs), Short-Chain Chlorinated Paraffins (SCCP), Dechlorane Plus, and UV-328 which although regulated are present in stocks (electronic products, vehicles, building materials, synthetic textiles) (Weber, 2022). Plastic in waste electrical and electronic equipment (WEEE or e-waste) is considered to contain the largest share of POP-PBDEs in the waste stream (Stockholm Convention 2012b). Sindiku *et al.* (2015) discovered that a high proportion of the CRT casings (61 %)

contained more than 10,000 ppm bromine from BFRs. Decabromodiphenyl ether (DecaBDE) was the major flame retardant used in TV sets and tetrabromobisphenol A (TBBPA) for computer CRTs. The average PBDE levels (of c- OctaBDE+DecaBDE) in Nigerian-stockpiled CRT casings were 1.1 % for TV and 0.13 % for PC CRTs. These are above the Restriction of Hazardous Substances (RoHS) limit and should be separated for RoHS compliant recycling. The Nigerian e-waste inventory of 237,000 t of CRT plastic would therefore contain approx. 594 t of c-OctaBDE and 1,880 t of DecaBDE. In Nigeria, as for most developing countries, there is currently no adequate e-waste management, plastic separation or destruction capacity. Five samples out of the 158 television samples analysed contained c-OctaBDE and related POP-PBDEs with concentrations ranging from 0.1 to 29.00 % (Sindiku *et al.*, 2015).

Estimation of Heavy Metal Imports with Electronics (1990 - 2022)

Data was mined from UN Comtrade for importation of EEE into Nigeria from 1990 to 2022. A summary of the data for imports from 1990 to 2023 is presented in Table 3. Considering that the amount of metals in the plastics of the various EEE categories studied did not vary much, the overall average values were used for the estimation of metals imports with EEE of all categories.

Table 3 shows that between 1990 and 2022 about 82,100 tonnes of mobile phones of various brands were imported into Nigeria; 16,801 tonnes of laptops; 30,561 tonnes of flat panel display monitor (FPDM), 229,544 tonnes of flat panel display TV (FDPT); 160,981 tonnes of cathode ray tube monitor (CRT) monitor and 2,558,043 tonnes of cathode ray tube television (CRT TV). Table 3 shows that CRT TV is the highest imported EEE product for the period under consideration. CRT screens are heavily leaded glass screens containing about 35 % of lead oxide. The presence of lead, a toxic heavy metal, with adverse effect on human health when inhaled or ingested makes CRT screens highly polluting and makes the recycling of CRT TVs and monitors very difficult. The Federal Government of Nigeria placed a ban on the importation of CRTs in 2011. Though importation of CRT TV and CRT monitor is banned, over the years, Nigeria remains one of the destination countries for illegal trans-boundary shipment of end-of-life EEE.

To estimate the heavy metal imports with EEE plastics, the plastic fractions of the individual EEEs was estimated (Table 3) based on data from literature. Literature shows that plastics constitute about 24% of mobile phone weight, 30% for Professional Heating and Ventilation (PHV), Household Heating and Ventilation (HHV), CRT Monitors and CRT TVs, 25% for washing machines, HAC, fridge and freezers (FF), 42% for laptops, notebooks and tablets (LNT), 37% for flat display panel monitor (FDPM), and 37% for flat display panel TV (FDPT) (UNEP, 2021a,b; Union of Concerned Scientists, 2022; Weber, 2022).

Table 3: Estimated metal content of EEE plastic fraction imported into Nigeria (1990-2022)

EEE	Quantity imported (t)	Plastic fraction	Plastics content (t)	Estimated Quantity of metal (kg) imported with plastics			
				Cd	Cr	Pb	As
Cameras	280	0.24	67	0.06	0.08	0.05	0.01
Hot Water equipment	1437	0.3	431	0.40	0.53	0.34	0.06
Vacuum Cleaners	2536	0.73	1851	1.70	2.26	1.44	0.28
Dishwashers	2761	0.24	663	0.61	0.81	0.52	0.10
Washing machines	5196	0.25	1,299	1.20	1.58	1.01	0.19
Food processing equipment	3118	0.3	935	0.86	1.14	0.73	0.14
Dryers	3744	0.3	1123	1.03	1.37	0.88	0.17
Small Consumer Electronics	5068	0.24	1216	1.12	1.48	0.95	0.18
Other Cooling	8011	0.25	2002	1.84	2.44	1.56	0.30
Desktop PCs	8387	0.42	3523	3.24	4.30	2.75	0.53
Household Heating & Ventilation	7,435	0.3	2,231	2.05	2.72	1.74	0.33
Microwaves	19,895	0.3	5969	5.49	7.28	4.66	0.90
Household Tools	21,664	0.24	5199	4.78	6.34	4.06	0.78
Professional IT	21,988	0.42	9235	8.50	11.27	7.20	1.39
Flat display panel monitor	30,561	0.37	11,308	10.40	13.80	8.82	1.70
Laptop, notebooks and tablets	16,801	0.42	7,056	6.49	8.61	5.50	1.06
Small IT	35,707	0.42	14997	13.80	18.30	11.70	2.25
Printers	53,795	0.26	13987	12.87	17.06	10.91	2.10
Kitchen Equipment	67,707	0.37	25052	23.05	30.56	19.54	3.76
Photovoltaic Panels	71,312	0.1	7131	6.56	8.70	5.56	1.07
Mobile phones	82,100	0.24	19,704	18.13	24.04	15.37	2.96
Professional heating & ventilation	31,495	0.3	9,448	8.69	11.53	7.37	1.42
Other Small Household	105,573	0.37	39062	35.94	47.66	30.47	5.86
CRT Monitors	160,114	0.3	48034	44.19	58.60	37.47	7.21
Flat display panel TV	229,544	0.37	84,931	78.14	103.62	66.25	12.74
Household air conditioner	508,339	0.25	127,085	116.92	155.04	99.13	19.06
Fridge & Freezers	505,432	0.25	126,358	116.25	154.16	98.56	18.95
CRT TVs	2,558,043	0.3	767413	706.02	936.24	598.58	115.11
Total	**4,568,043**		**1,337,310**	**1230**	**1632**	**1043**	**201.6**

From Table 3, the highest quantity of EEE imported was from CRT TVs which is 2,558,043 tonnes and is about half of the total quantity of EEE imported from the period of 32 years (1990-2022). The importation of about 2.5M tonnes of CRT TVs from 1990 to 2022 saw the importation of 767,413t of plastics that contain 598 kg of Pb, 936 kg of Cr, 115 kg of As and 706 kg of Cd (Table 3). Overall, the period 1990 to 2022 witnessed the importation of about 4,568,043 t of EEE of different categories. These huge amounts of

EEE contained about 1,337,310 t of plastics. This is really huge considering the absence of e-waste plastic management policy in Nigeria.

Environmental Concerns

Heavy metals have become a public health concern due to their toxicity and bioaccumulation in the food chain. In as much as none of the results exceed any of the RoHS limits, long term disposal of waste plastics especially open burning can result in the accumulation of metals at the dump sites which can contaminate the soil as well as affect plants and ground water. Lead, chromium and cadmium have high toxicity and their effects on human health (e.g. neurological, respiratory, urinary and cardiovascular diseases etc.) are well documented (Joseph *et al.*, 2005). Households also burn e-waste plastics while others dump then along the street or at open dumps. The heavy metals and flame retardants can seep directly from the plastic into the soil, causing contamination of underlying groundwater or contamination of crops that may be planted nearby or in such a place in the future. They are hazardous to both the environment and human health.

CONCLUSION

Waste plastics from twenty-five different electronic products including mobile phones, printers, scanners, rechargeable fans, and televisions were examined for their metal levels. The results show relatively low metal levels and none of the samples studied exceeded the European Union RoHS limit for the metals analyzed. Although the metal levels were generally low, the amount of metals imported over the years shows that effort should be made to ensure environmentally sound management of e-waste plastics to protect man and the environment. There is concern over pollution and human exposure to toxins from the improper management of e-waste plastics especially by informal operators using open burning. Regulatory bodies should ensure that individuals and businesses engaged in e-waste management are properly trained to adhere to existing standards. Waste plastic that contain flame retardants should be separated and managed in environmentally sound manner. Open burning of e-waste which is prohibited should be enforced by the relevant agencies.

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Full Length Research Paper

TRACE METAL CONTAMINATION OF WASTE PLASTIC DEBRIS GENERATED BY INFORMAL PLASTIC RECYCLERS USED FOR COOKING BY VILLAGERS: IMPLICATIONS FOR HUMAN HEALTH AND ENVIRONMENTAL SAFETY IN NIGERIA

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ABSTRACT

Informal recycling of waste plastics is common in Nigeria. Such facilities recycling waste plastics from diverse products (e.g. buckets, e-waste plastics) but have no safety measures and operate within inhabited villages to hide from regulatory agencies. Workers sort waste plastic into plastic types and then crush and sieve (without PPEs) before recycling directly into non-food contact products without producing pellets. Sieved out tiny plastic fractions are not recycled but dumped around the facilities and villagers use such to cook. This study analyzed trace metal levels of the sieved out plastic debris dumped by recyclers and assessed human exposure risks. Six (6) composite samples of the plastics debris were collected from informal recyclers and analyzed for Mn, Cd, Cr, Cu, Pb and Zn using AAS after acid mineralization. Adequate quality assurance protocols were followed. The metal levels (mg/kg) are 51.37±21.39 (34.21 – 88.68) for Mn; 1.36±1.79 (0.06 – 4.96) for Cd; 15.58±15.28 (2.39 - 45.47) for Cu; 4.80±3.74 (1.43 - 11.67) for Cr; 49.87±25.09 (4.74 – 77.76) for Pb and 113.06±102.56 (0.01 – 294.05) for Zn. The results show that the inhalation of the dust particles, by operators and residents, apart from depositing microplastics into the operators' lungs, would also expose them to metals. Cooking with the plastic debris would make inhalation more likely. Target Hazard Quotient (THQ), a risk factor applied to noncarcinogens, a ratio of potential exposure to a contaminant to the level at which no adverse effects are likely to occur, was also evaluated and found to be elevated (>1) for most metals indicate potential health risks from prolonged exposure for dermal and oral exposures. To protect public health and the environment, there is need for strict implementation of safety measures in such facilities and monitoring by regulatory agencies for sound management of waste plastics.

Key Words: trace metals, plastic, recycling, human exposure, Nigeria.

INTRODUCTION

Nigeria's economy heavily relies on the plastics sector, which offers opportunities for innovation, foreign direct investments and job creation. However, the country faces environmental challenges from plastic waste management. Due to its durability, affordability, and simplicity, plastic is widely used, leading to plastic waste management issues. Nigeria is one of Africa's top importers of plastics, with a 62.5% increase in imports between 2008 and 2015; while per capita plastic consumption increased from 4.0 kg in 2007 to 7.5 kg by 2020 (Federal Ministry of Environment, 2020).

Nigeria's plastic waste recycling is primarily carried out by informal recyclers who prioritize profit over regulation and oversight. They recycle shredded plastic directly into finished products instead of pellets. They employ migrant laborers to manually sift the plastics based on polymer type before grinding and recycling, and dispose waste without considering environmental implication. Few informal recyclers use personal protective equipment and maintain operational logs.

Plastics contain various additives like plasticizers, flame retardants, antioxidants, acid scavengers, light and heat stabilizers, lubricants, pigments, antistatic agents, slip compounds, and thermal stabilizers. These chemicals are used for various purposes, but some are hazardous, including endocrine-disrupting chemicals (EDCs) like bisphenol A and Di(2-ethylhexyl) phthalate (DEHP), and persistent organic pollutants (POPs) like Perfluorooctanoic acid (PFOA), Short-Chain chlorinated Paraffins (SCCPs), Hexabromobiphenyl (HBB), Hexabromocyclododecane (HBCD), and Polybrominated diphenyl ethers (PBDEs) (GESAMP, 2015; Aurisano *et al.,* 2021; UNEP, 2023).

Improper use and disposal of waste plastics, such as plastics from e-waste and vehicles, can release toxic compounds by leaching and open burning (Nnorom and Osibanjo, 2008). Open burning of plastics can release persistent additives like PBDEs and form Dioxins accumulating in soils and in the food chain such as eggs, milk and meat (Weber *et al.,* 2018; Oloruntoba *et al.,* 2019, Oloruntoba *et al.,* 2021; Petrlik *et al.,* 2022). Toys made partially of recycled plastic or soft PVC used in toys or medical devices can release hazardous chemicals when they come into direct contact with humans. Industrialized nations regulate additives in water bottles and polymers used in food packaging, but lax regulations exist in Africa (Weber *et al.*, 2018; United Nations Economic and Social Council, 2009). Most polymers are resistant to breaking down, making plastic waste resistant to degradation and able to travel long distances from their source (Webb *et al.,* 2012). The international waste management agenda prioritizes plastic, with UNEP (2019) encouraging Basel and Stockholm Convention regional centers to work on the impact of plastic waste, microplastics, and marine plastic litter, as well as prevention and environmentally sound management measures. The Basel Convention Annexes include an inventory of hazardous waste for international trade (IISD, 2019). In 2022, the UN Environment Assembly (UNEA) adopted a historic resolution to develop an international legally binding instrument on plastic pollution (UNEP 2022). The fifth session of the Intergovernmental Negotiating Committee to develop an international legally binding instrument on plastic pollution (INC-5), is scheduled to take place end of November 2024 at in Korea to establish a Plastic Treaty (UNEP 2024a).

Presented here is the results of a preliminary study carried out after sampling activities of plastic recyclates in Nigeria in 2023 for a GEF-funded UNEP POPs Global Monitoring Plan (GMP) project where pellets from recycled plastics where samples in selected countries were in Africa, Asia, and the Latin America for analysis. While sampling for the UNEP GMP POP project, it was observed that residents used the sieved out plastic debris (dumped around informal recycling facilities) as cheap fuel for cooking. Due to the exposure risk for recyclers and the surrounding, the decision was made to determine the metals levels to assess the risk of metal exposure considering that some plastics can contain heavy metals as additives (Sindiku *et al.,* 2015a; Aurisano *et al.*, 2021; UNEP, 2023). This study reports on the trace metal levels of the sieved out plastic debris dumped by informal recyclers and assesses the potential risks from human exposure.

2. Material and Methods

2.1 Sample Collection and Chemical Analysis

Six (6) composite samples of a varieties of plastic waste dumped by informal recyclers around their recycling facilities were collected. Though the samples can best be described as a mix of waste plastics of different types, physical inspection and interview of the informal operators enabled grouping of the waste polymers (Table 1).

Table 1: Overview of the plastic samples collected and analyzed in the present work.

Sample Code	Type	Color	Feedstock Material
S1	Low Density Polyethylene	Black	End of Life Vehicle
S2	High Density Polyethylene	Black	Water Tank
S3	High Density Polyethylene	Red	Tables, Chairs, Crates
S4	Low Density Polyethylene	Multiple	Disposable Food Containers
S5	Polyvinyl Chloride	Lemon-Green	PVC Pipes
S6	Polyethylene Terephthalate	Multiple	Labels and Nylons

The samples were stored in Ziploc® bags and properly labelled. Other relevant information such as the sample ID, sample location/industry sampled, date of collection, type of polymer, and potential feedstock materials were documented. Sub-samples were taken from the samples collected for the UNEP POPs GMP project (ca 100g) after homogenization.

The plastic waste samples were digested (5.0 g) with an acid mixture (3:1 of $HCl:HNO_3$) and the concentrations of Cu, Cr, Mn, Pb, Zn and Cd were determined using Agilent AA55 Atomic Absorption Spectrometer. Adequate quality assurance and quality control measures were included. The AAS was calibrated while blanks (20%) were included.

2.2 Risk Assessment

Risk assessment identifies and analyses potential (future) events that may negatively impact individuals, assets, and/or the environment (i.e. hazard analysis). It also makes judgments "*on the tolerability of the risk on the basis of a risk analysis*" while considering influencing factors (i.e. risk evaluation) (Rausand, 2013).

The US EPA human health risk assessment method was adopted in this study. The US EPA model (2002) was designed to assess the nature and probability of adverse health effects to humans who may be exposed to trace metals in the environment. The US EPA model is designed to address the likely adverse health outcomes from exposure, the probabilities of people experiencing the adverse health effects and whether the current exposure levels pose a health risk to humans. The Australian Exposure Factor Guidance Document recommends the use of daily plastic ingestion rates of 50 mg/d (milligram per day) for children (1–2 years) and 25 mg/d for adults in exposure assessment (DHS, 2011). The Chronic Daily Intake (CDI) for ingestion, inhalation and dermal exposure routes was estimated using equations (1)-(3) while hazard quotient was estimated using equation (4):

$$\mathrm{CDI}_{\mathrm{ingestion}} = C \times \frac{IngR \times EF \times ED}{\mathrm{BW} \times \mathrm{AT}} \times CF \qquad (1)$$

$$\mathrm{CDI}_{\mathrm{inhalation}} = C \times \frac{IngR \times EF \times ET \times ED}{\mathrm{PEF} \times \mathrm{BW} \times \mathrm{AT}} \qquad (2)$$

$$\mathrm{CDI}_{\mathrm{dermal}} = C \times \frac{SA \times SL \times ABS \times EF \times ED}{\mathrm{BW} \times \mathrm{AT}} \times CF \qquad (3)$$

$$\mathrm{HQ} = \frac{PDI}{RfD} \qquad (4)$$

All statistical analysis and computations were performed using the computer program of Microsoft Office Excel 2021.

3. RESULTS

3.1 Metal Concentrations in the Waste Plastics

A summary of the analytical results (Table 2) shows a wide variability in metal concentrations with ranges spanning multiple orders of magnitude.

Table 2: Summary of metal concentrations in waste plastic debris

Metal	Mean±Standard Deviation	Geometric Mean	Range
Cu	15.58±15.29	10.84	2.39 - 45.47
Cr	4.80±3.74	3.83	1.43 - 11.67
Mn	51.37±21.38	48.54	34.21 - 88.68
Cd	1.36±1.79	0.67	0.06 - 4.96
Pb	49.87±25.09	38.03	4.74 - 77.76
Zn	113±102	23.13	0.01 - 294

The observed metals levels could be from two sources: from the plastic matrix added as additives or from external contamination from usage and contact with waste materials at waste dumps. The observed elevated Zn contents of this study could be from the use of plastic additive such as zinc stearate as a stabilizer, lubricant or slip agent (Rizzotto, 2012). Zinc can also be employed in the production stage: the use of Zn-containing catalysts and Zn-containing additives such as pigments, fillers etc. (Prunier, 2019) As heat stabilizers, Pb, Cd, Zn-dicarboxylates and various organotin compounds have been found widely used in thermoplastic, polyvinyl chloride (Rizzotto, 2012; Lui *et al.*, 2007). These materials decompose at a temperature lower than their processing temperature (Lui *et al.*, 2007). Metals, such as Cd, Zn and Pb, are used as stabilizers in PE materials (Hansen *et al.*, 2013). For example, Cu is used in the form of copper oxides and chromates and cadmium sulphoselenide is used as orange colorants (Maier and Calafut, 1998). Fillers are typically made of calcium carbonate or zinc oxide and can be incorporated at up to 50% w/w (Lazzeri *et al.*, 2005). Some metal-based compounds are used as antimicrobial agents; Cu, Mn, Co, Ni, Zn, Ag and Cd are used in sulfonamides, and organotin compounds are used as biocides in plastic (Rizzoto, 2012). Sindiku *et al.*, (2015a) screened 382 cathode ray tube (CRT) casings of TVs and computers produced 1980 to 2005 in Nigeria with desktop XRF for heavy metals and bromine. She found a high variability in lead and cadmium levels in the plastics with more than 30% of CRT casings above 100 mg/kg lead with a maximum concentration of 3000 mg/kg lead documenting the use of lead additives as colorants and stabilizer. If CRT casings which have been shown to contain high concentrations of lead and some other toxic chemicals are mixed with the feedstock by the informal operators, it will contaminate the recycled batch and the finished products. This will expose user of such plastic products to potential harm. Informal operators will also be exposed to a cocktail of toxins considering that they hardly use personal protective equipment (PPEs). In Europe, Pb has been phased out as a plastic additive and Cd use is still under discussion; according to the Restriction of Hazardous Substances (RoHS) Directive for any new or recycled product, the concentration limits for Cd are set at 100 µg/g (RoHS, 2006). Apart from exposing users and other residents to metals, the waste plastic debris can also contaminate soil and impact plant growth, soil microbial activity, and overall soil health. This can reduce agricultural productivity and biodiversity. The disruption of soil and water ecosystems can impair essential ecosystem services such as nutrient cycling, water purification, and habitat provision, affecting overall environmental health and human well-being.

As researchers examine a wider variety of marine organisms, the number of reports of plastic debris ingestion is growing. Some of the earliest reports showed that plastic debris was consumed by seabirds, sea turtles, manatees, and cetaceans (Ryan, 2015). The consuming creature may experience several negative effects from ingested debris. Large amounts of debris have been shown to cause gut obstruction and feed digestibility in fish species and other aquatic life in the marine ecosystem, according to McCauley and Bjorndal (1999). They have also been hypothesized to reduce stomach storage capacity and cause false satiation, which leads to a decreased appetite (Day *et al.*, 1985).

3.2 Risk Assessment of Human Exposure to Metal from the Use of the Waste Plastics

Presented in Table 3 is a summary of chronic daily intake (CDI) and the Total hazard quotient (THQ) for adult for various routes of exposure. The exposures for an adult from inhalation, ingestion, and dermal contact for the metals determined were observed to be low. The oral THQ were observed to be low (<1) for Cr and Mn. For Cu, Zn and Cd, the residents may be exposed to harm considering that the THQ estimations for the higher values of these metals determined in the plastic waste were >1. THQ for Pb was >1 indicating that Pb present a more potential risk to residents that that ingest the waste plastic dust. For dermal contact, users of the waste plastic debris may be exposed to risks from Cu, Cr, Mn and Zn considering that the THQ estimations for the higher values of these metals were >1. THQ estimates for the lower concentrations were <1. Residents will be exposed to more risk of harm from Pb and Cd through dermal contact considering that they have the highest THQ values.

Table 3: Summary of CDI and Target Hazard Quotients for Adult

		Chronic Daily Intake (CDI)			Target Hazard Quotients	
Element		Inhalation	Ingestion	Dermal	Adult Oral	Adult Dermal
Cu	(Minimum)	6.5 x10^{-9}	1.1 x10^{-5}	9.8 x10^{-8}	8.3x10^{-2}	2.x10^{-1}
	(Maximum)	1.2 x10^{-7}	2.1 x10^{-4}	1.8 x10^{-6}	1.6	5.3
Cr	(Minimum)	3.9 x10^{-9}	6.6 x10^{-6}	5.8 x10^{-8}	1.3x10^{-3}	2.6x10^{-1}
	(Maximum)	3.2 x10^{-8}	5.4 x10^{-5}	4.8 x10^{-7}	1.0x10^{-2}	2.2
Mn	(Minimum)	2.7 x10^{-11}	4.6 x10^{-8}	4.1 x10^{-10}	9.9x10^{-5}	2.5x10^{-3}
	(Maximum)	2.4 x10^{-7}	4.1 x10^{-4}	3.6 x10^{-6}	8.8x10^{-1}	22.0
Pb	(Minimum)	1.3 x10^{-8}	2.2 x10^{-5}	1.9 x10^{-7}	1.7	658
	(Maximum)	2.1 x10^{-7}	3.6 x10^{-4}	3.2 x10^{-6}	27.0	1080
Zn	(Minimum)	2.7 x10^{-11}	4.6 x10^{-8}	4.1 x10^{-10}	4.6 x10^{-5}	2.3x10^{-4}
	(Maximum)	8.0 x10^{-7}	1.4 x10^{-3}	1.2 x10^{-5}	1.3	6.8
Cd	(Minimum)	1.6 x10^{-10}	2.8 x10^{-7}	2.4 x10^{-9}	8.3 x10^{-2}	8.3
	(Maximum)	1.4 x10^{-8}	2.3 x10^{-5}	2.0 x10^{-7}	6.9	689

Key: **CDI:** Chronic daily intake**; THQ:** Total hazard quotient

From the data of this study Pb and Cd presents the most health risk potential based on their THQ data values (Table 3) especially dermal exposure. There is significant variability in the concentrations across different samples also dermal exposure constantly show higher values. The Chronic Daily Intake (CDI) via inhalation for these elements generally indicates lower immediate risk compared to ingestion and dermal exposure, but long-term exposure can still pose significant health risks, particularly for elements like lead and cadmium. The ingestion CDI values suggest that consuming water or food contaminated with the waste plastics, which is very likely in the informal industry setting, could lead to significant health issues, especially for lead and cadmium, which have very low safe intake thresholds.

3.3 Risk of exposure when plastics is used as fuel for cooking

As mentioned above, waste plastics was partly sold as fuel for cooking which will release heavy metals which contaminate indoor environment and when resulting ashes are disposed also soils with risk of accumulation by chicken/eggs (Petrlik *et al.,* 2022) frequently present at poor households. In addition to the heavy metal exposure, cooking with waste plastics result in exposure of products of incomplete combustion like polycyclic aromatic hydrocarbons (PAHs), benzene, toluene, xylene (BTX) and styrene most considered as carcinogens (Green *et al.,* 1976; Wu *et al.,* 2021; Xu *et al.,* 2022). Also, small particles are released from open burning of plastics (Wu *et al.,* 2021). Furthermore, if part of plastics contains brominated flame retardants and PVC, they can release PBDEs, tetrabromobisphenol A (TBBPA) and highly toxic brominated and brominated-chlorinated dioxins and furans (Weber and Kuch 2003; Ortuño *et al.*, 2014; Sindiku *et al.*, 2015b) which have recently been proposed as POPs for the Stockholm Convention (UNEP 2024b). The exposure risk from using plastic as a fuel for cooking is likely very high and needs dedicated sampling and assessment of exposure risk.

4. CONCLUSION

This study showed a wide-ranging concentration of metals in waste plastic debris. The results demonstrated that there are likely two main sources of metals in the plastic debris: (1) the additives initially incorporated in the plastic and, (2) exogenous contaminations. The waste plastics pose health and environmental risks from heavy metals. There are a wide range of other hazardous plastic additives which need to be considered for overall exposure risk. To protect public health and the environment, there is need for strict implementation of safety measures in such facilities and monitoring by regulatory agencies for sound management of waste plastics. Furthermore, the exposure from the practice of using plastic as fuel for cooking need urgent attention and assessment and the sales and practice of using waste plastics for cooking should be prohibited.

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CHEMICAL SOCIETY OF NIGERIA (CSN) ABIA CHAPTER

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REVIEW

HEAVY METAL CONTAMINATION IN THE ENVIRONMENT: A REVIEW

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ABSTRACT

Heavy metal in the environment is a global problem and is found to increase due to man's activity which results from increase in industrialization, agricultural processes, incineration, domestic waste, industrial and domestic effluents. Due to the connectivity of the lithosphere, hydrosphere, atmosphere and biosphere, what affects one affects the other. Heavy metals become toxic when in excess of its required concentration. The Bioaccumulation, Bio magnification and non-degradable property of heavy metals makes it possible for heavy metals to accumulate and biomagnify to higher concentration, contaminating the water, soil, air which gives plants life and transcend from one trophic level to the other causing diverse effect. Contamination of the soil, water, air and food produced therein result in environmental issues capable of destroying humanity if not well managed. This review is to explore the consequences of heavy metals in the environment, enlighten the Nigeria Populace, to create environmental consciousness on the heavy metal sources and route of entry so the populace can be guided to be protected from harm while the Environmental Protection Agencies do more to protect the people.

KEY WORDS: Heavy Metal, Contamination, Bioaccumulation, Toxic, Environment.

INTRODUCTION

Heavy metals include some metalloids, transition metals, basic metals, lanthanides and actinides. The main elements that are considered as heavy metal are chromium (Cr), manganese (Mn), cobalt (Co), copper (Cu), zinc (Zn), molybdenum (Mo), mercury (Hg), nickel (Ni), tin (Sn), lead (Pb), cadmium (Cd), antimony (Sb), etc. (Sandeep *et al* 2019). Heavy metals are defined as metallic elements with a density of 5g/cm^3 (Briffa *et al*, 2019). Heavy metals are naturally occurring elements with a large atomic weight and at least five times the density of water (Sharma and Agrawal, 2005). Heavy metals also include metalloids, such as arsenic (As) that can induce toxicity at low exposure levels. Various heavy metals, such as chromium (Cr), cadmium (Cd), nickel (Ni), copper (Cu), zinc (Zn), lead (Pb), mercury (Hg), and As, are recognized as biologically dispensable and detrimental to the aquatic ecosystem (Kilaru *et al*, 2019; Manar *et al*, 2023). Majority of heavy metals are found in the biosphere, in water, soils, and rocks, and are also released into the surroundings from anthropogenic resources, mostly commercial and industrial (Saikat *et al*, 2022).

A heavy metal is toxic when relatively a dense metal or metalloid that is noted for its potential toxicity, especially in environmental contexts, Heavy metal toxicity means excess of required concentration or it is unwanted where found naturally on the earth (Tchonou *et al*, 2014). Metal (or metalloid) species may be considered a “contaminant” if it occurs where it is unwanted, or in a form or concentration that causes a detrimental human or environmental effect. These metals/metalloids include lead (Pb), cadmium (Cd), mercury (Hg), arsenic (As), chromium (Cr), copper (Cu), selenium (Se), nickel (Ni), silver (Ag), and zinc (Zn). Other less common metallic contaminants include aluminium (Al), cesium (Cs), cobalt (Co), manganese (Mn), molybdenum (Mo), strontium (Sr), and uranium (U) (Reena *et al*, 2011) Living organisms require varying amounts of heavy metals for their metabolic processes. Iron, cobalt, copper, manganese, molybdenum, and zinc are required by humans. All metals are toxic at higher concentrations (Saikat *et al*, 2000). Excessive levels can be damaging to the organism. Other heavy metals such as mercury, plutonium, and lead are toxic metals that have no known vital or beneficial effect on organisms, and their accumulation over time in the bodies of animals can cause serious illness. Certain elements that are normally toxic are for certain organisms or under certain conditions, beneficial. Examples include vanadium, tungsten, and even cadmium. (Singh *et al*, 2011).

Heavy metal contamination is a global phenomenon disrupting the ecosystem and creating serious risks for human health. The main challenges include increased urbanization, property transition, and industrial development, particularly in highly populated and emerging countries (Naveed *et al*, 2022). Heavy metals enter rivers and lakes from a variety of sources such as rock and soil directly exposed to surface water, in addition to the discharge of treated and untreated liquid wastes into water bodies. These harmful wastes and other dangerous industrial by-products constitute major sources of environmental contaminants/pollutants (Olaniyi *et al*, 2019)

Water pollution has become a global problem (Obasohan *et al*, 2008; Nachana’a and Williams, 2019). Heavy metals have long been recognized as a serious contaminant of the aquatic environment and are natural trace components of the aquatic environment, but background levels in the environment have increased especially in areas where industrial, agricultural and mining activities are widespread. (Obasohan *et al*, 2008). He also recorded that heavy metals released into the environment find their way into aquatic systems as a result of direct input, atmospheric deposition and surface runoffs. Heavy metal contamination of water is one of the most serious environmental concerns affecting plants, animals, and humans. Heavy metals are hazardous even in low concentrations because they are not biodegradable (Zaynab *et al* 2022). In the food chain, metals constitute a core group of aquatic pollutants. Thus, in view of the quality of public food supplies, their levels in aquatic environment should be monitored regularly to check water quality and effects of the contamination on human health (Authman *et al*, 2013). Most industrial pollutants discharged into the environment contain organic and inorganic contamination in dissolved, suspended and insoluble forms. Effluents discharged into the water bodies may affect fish and other aquatic organisms, either directly or indirectly (Olaniyi *et al,* 2019). Most rivers and freshwater streams are seriously polluted by industrial waste water discharged from factories. A large amount of water used in industry turns into wastewater that pollutes surface and groundwater. According to (Sandeep *et al,* 2019; Saikat *et al,* 2022), Heavy metals can be divided into two groups based on their health importance

(1) Essential metals such as Cu, Fe, Mn, Co, Zn, and Ni

(2) Non essential Heavy Metals As, Cd, Pb, Hg, Cr, and Al

Naturally found vital heavy metals penetrate into the body via food, air, and water, where they regulate numerous biological activities (Saikat *et al,* 2022)

SOURCES OF HEAVY METAL CONTAMINATION

Heavy metal Pollutants/contaminants enter the ecosystem in various ways and enter into the hydrosphere, lithosphere and atmosphere (Briffa *et al,* 2020). Heavy metal contamination originates from both natural and anthropogenic sources (Sandeep *et al,* 2019; Briffa *et al,* 2020)

NATURAL SOURCES OF HEAVY METALS:

The most important natural source of heavy metals is weathering of geologic parent material or rock outcroppings (Kilaru *et al,* 2019). The composition and concentration of heavy metals depend on the rock type and environmental conditions, activating the weathering process. The geologic plant materials generally have high concentrations of Cr, Mn, Co, Ni, Cu, In, Cd, Sn, Hg and Pb. However, class wise the heavy metal concentrations vary within the rocks. Soil formation takes place mostly from sedimentary rock, but is only a small source of heavy metals, since it is not generally or easily weathered. However, many igneous rocks such as olivine, augite and hornblende contribute considerable amounts of Mn, Co, Ni, Cu and In to the soils, within the class of sedimentary rocks, shale has highest concentrations of Cr, Mn, Co, Ni, Cu, In, Cd, Sn, Hg and Pb followed by limestone and then sandstone. Volcanoes have been reported to emit high levels of AI, In, Mn, Pb, Ni, Cu and Hg along with toxic and harmful gases (Sandeep *et al,* 2019). Airborne emissions of heavy metals originate from forest and prairie fires. Volatile heavy metals such Hg and Se are part of carbonaceous matter produced during the fire. Wind dust, which arises from desert region such as Sahara, has high levels of Fe and lesser amounts of Mn, In, Cr, Ni and Pb. Natural vegetation emits heavy metals into the soil and atmosphere through leaching from leaves and stems, decomposition and volatilization. Many heavy metals have been detected in inland coastal areas due to seasprays and aerosols produced in oceanic activities. (Rajesh *et al,* 2005; Asad *et al,* 2020). Occurrence of heavy metal in water by natural sources depends on the local geology, hydrogeology and geochemical characteristics of the aquifer (Priti and Biswajit, 2016).

ANTHROPOGENIC ACTIVITIES: These are man-made sources of heavy metal in the ecosystem. They include activities such as agricultural practices, mining, smelting operation, rubber and plastics, metal finishing, tanneries, organic chemicals, pesticides, pharmaceuticals, electroplating, and so forth (Sandeep, 2019).

Agricultural sources of heavy metals: Agriculture have locally increased the levels of heavy metals such as Cd, Co, Cr, Pb, As and Ni in soil up to dangerous levels. Heavy metals are persistent in nature, get accumulated in soils and plants (Sharma *et al*,2005) (Elnabi *et al*, 2023). The application of farmyard and chemical fertilizer is a pathway through which some heavy metals migrated into the soil. (Nkwunonw *et al* 2020). The inorganic and organic fertilizers are the most important sources of heavy metals to agricultural soil which include liming, sewage sludge, irrigation waters, fungicides and pesticides (Sandeep *et al*, 2019). Inorganic fertilizers, particularly phosphate fertilizers have variable levels of Cd, Cr, Ni, Pb and In depending on their sources. (Rajesh *et al*,2005; Nkwunonwo *et al*, 2020). Industrialization and urbanization have increased the anthropogenic contribution of heavy metals contamination in biosphere (Sharma *et al*, 2005). The soil getscontaminated due to the heavy metals because of the entry of the industrial wastewater, sewage sludge, fertilizers, utilization of treated wastewater in land application (Kilaru *et al*, 2019).

Industrial sources of heavy metals: Most of the toxic heavy metals including lead, thallium, cadmium and antimony, are common in industrial operations and are substantial contaminants of the environment (Saikat *et al*, 2022). They include mining, refinement (spoil heaps and tailings, transport of ores, smelting and metal finishing and recycling of metals). Mining operation emits different heavy metals depending on the type of mining. For example, coal mines are sources of As, Cd, Fe, etc, which enrich the soil around the coalfield directly or indirectly (Kumar and Agrawal, 2005). High temperature processing of metals such as smelting and castings emit metals in particulate and vapor forms. Vapor form of heavy metals such as As, Cd, Cu, Pb, Sn and In combine with water in the atmosphere to form aerosols which can be dispersed as by wind or precipitated by rainfall (Kumar and Agrawal, 2005; Sandeep *et al*, 2019). Energy supplying power stations such as coal burning power plants, petroleum combustion, nuclear power stations and high-tension lines contribute many heavy metals such as Se, B, Cd, Cu, In, Cs and Ni to the environment. Other industrial sources include processing of plastics, textiles, microelectronics, wood preservation and paper processing (Kumar and Agrawal, 2005). In Nigeria, mining of ore deposits, oil and gas exploration and exploitation, and agriculture, besides manufacturing, construction, and production activities are among the several commercial and artisanal extractions of natural resources, capable of influencing the disruption, dispersion, and distribution of naturally placed heavy metals and metalloid to the environment These metals and metalloid are further influenced by the conditions of the environment of deposition such as acidity, alkalinity, pH, adsorption, speciation, and temperature which inform their solubility, mobility, availability, and accessibility. They make their way into the different environmental media such as soil, water, rock, and sediment from which we grow most of our food. (Nkwunonwo *et al,* 2020).

Domestic effluent and Domestic Waste Incineration: Domestic wastewaters contain fairly high concentrations of metals, where these metals are derived from household products such as cleaning materials (detergents), toothpaste, cosmetic and human feces. (Nkwunonwo *et al,* 2020). Burning of waste derived from domestic use release heavy metals into the atmosphere.

Other sources of heavy metals include refuse incineration, landfills and transportation automobiles, diesel powered vehicles and aircraft (Kumar and Agrawal *2005*; Sandeep et al, 2019; Nkwunonwo *et al*, 2020). Metal emission during the transportation of vehicles includes Ni and In from tires, Al from catalyst, Cd and Cu primarily from diesel engines and Ni and In from aerosol emissions. Lubricants, which are antiwear protectants for vehicles emit Cd, Cr, Hg, Ni, Pb and In, particularly in case of inefficient engines. The burning of leaded gasoline has been an important source of Pb in the environment. Incinerations of municipal wastes generate significant concentrations of In, Pb, AI, Sn, Fe and Cu (Sharma *et al*, 2005)

ENVIRONMENTAL IMPACT OF HEAVY METAL CONTAMINATION:

IMPACT ON SOIL AND WATER QUALITY

The problem of water contamination due to toxic metals is a cause of concern in most metropolitan cities. The toxic heavy metals entering the ecosystem lead to geoaccumulation, bioaccumulation and biomagnifications. Food chain contamination by heavy metals is a burning issue because of their potential accumulation in biosystems through contaminated water, soil and air. The main sources of heavy metals to vegetable crops are their growth media (soil, air, nutrient solutions) from which these are taken up by the roots or foliage (Prabue *et al*, 2009). The heavy metals released into the aquatic environment may enter into the food chain through bio-magnification which may cause various health problems in humans. The leachate that contains a high concentration of heavy metals migrating away from landfill boundaries and to the environment is a serious environmental concern (Rafil *et al*, 2020). The concentration level of Hg in water increases mostly due to agricultural activities, human activities such as tillage, logging, domestic sewage discharge, atmospheric deposition from solid waste incineration, coal and oil combustion, pyrometallurgical processes (Fe, Pb and Zn) and mining activities. The anthropogenic source of Ni is from corroded metal pipes and containers. Lead in aquatic environment comes from compounds like paints and petrol additives and precipitation of aerosols formed from high temperature industrial process such as coal combustion, smelting and cement production. Cd enters into water system through industrial discharge and galvanized pipe. Cadmium is also present in phosphate fertilizers. Cu normally occurs in drinking water from copper pipes, industrial waste, and from additives designed to control algal growth. Fe and Mn in water come from industrial effluent, acid-mine drainage, sewage and landfill leachate (Priti *et al,* 2014). Polluting heavy metals – copper, zinc and manganese especially have negative impact on soil characteristics, its composition and soil-formation processes, which results in deterioration of hydro-physical potential of the soil. Balanced correlation between solid, liquid and air phases in the soil is disturbed as a result of heavy metal presence. (Lia *et al*, 2014)

BIO-ACCUMULATION OF HEAVY METALS IN PLANTS AND ANIMALS

Environmental contamination caused by heavy metals is persistent, covert, and long-term because metals are non-biodegradable and have a lengthy half-life; biological species are unable to decompose them, and they remain in their body parts and surroundings, posing health risks (Saikat *et al,* 2022). Heavy metals not only cause soil pollution, it also influences food generation and food quality. Some heavy metals are poisonous to plants even at a very low concentration, while other heavy metals may accumulate in plant tissues to moderately abnormal states with no obvious side effects or decrease in yield. The growing of plants in heavy metal-contaminated areas, bring change in their metabolism, physiological and biochemical means which results in metal accumulation, lower biomass generation and reduction in the biomass growth (Kilaru *et al*, 2019). Heavy metals may affect organisms directly by accumulating in their body or indirectly by transferring to the next trophic level of the food chain (Obasohan *et al*, 2008). The plants are consumed by the animals in a higher tropic level passing these heavy metals into them. Metals accumulate in ecological food chain through uptake at primary producer level and then through consumption at consumer levels and plants roots are the primary contact site for heavy metal ions. (Tchonwou *et al*, 2014) In the aquatic environment, heavy metals in dissolved form are easily taken up by aquatic organisms and accumulate in their tissues and may become toxic when accumulation reaches a substantially high level. Heavy metals may affect organisms directly by accumulating in their body or indirectly by transferring to the next trophic level of the food chain (Authman *et al*, 2013) Heavy metal ions do not degrade into harmless end products and are toxic to humans and the surrounding environment (Olaniyi *et al*, 2019). Accumulation is usually much higher during the dry season and relatively low during the peak of the rainy season. (Zaynab *et al*, 2022). Heavy metal bioaccumulation in the body causes biological and physiological complications (Briffa *et al*, 2019)

REDUCTION OF FERTILITY

The human body has no biochemical pathways to detoxify heavy metal, its exposition leads to an accumulation in the body, a risks to health and development derived from the exposure to heavy metals have become a matter of interest. In particular, the aforementioned chemical species can affect male fertility by lowering the seminal quality, thereby causing infertility. For example, copper (Cu) and chromium (Cr) were found in the semen samples of a father and his son from the “Land of Fires”, in Italy. The results showed alterations in the content of sperm nuclear basic proteins (SNBP) and a low DNA binding affinity, the son’s proteins showed unstable DNA binding, thus able to produce DNA damage (Andrea *et al*, 2021). Females are more affected because of fixed and non-renewable pool of germ cells in the ovary. Deleterious effects can be observed at several stages of reproductive life in females, from fetal life to puberty and maturity. Data indicate that HMs can influence gene expression by modulating epigenetic mechanisms and the expression of non-coding RNAs, especially microRNAs. Moreover, chronic exposure causes steroidogenic dysfunction, fetal abnormalities and embryotoxicity because many HMs, such as Cd and Ni, act as endocrine disruptors (EDs), capable of manipulating the production and activity of hormones and their receptors HMs have also been reported to enhance oxidative stress (OS), thereby affecting a range of physiological processes involved in hormonal homeostasis and germ cell and embryo quality. All these negative effects may ultimately contribute to infertility. It has been shown that involuntary exposure to HMs during pregnancy is directly related to preterm birth due to excess reactive oxygen species (ROS), particularly the significant increase in OS in the trophoblastic placental tissue (Canipari *et al,* 2020). Heavy metals are found to be more toxic to plants and human beings, as they mix with soil, they cause retardation in plant growth, reduce the nutritive value, affect photosynthesis, and also pose a harmful effect on human beings who consume plants generated from these soil (Kiran *et al,* 2022).

CONTAMINATION OF GROUND AND SURFACE WATER RESOURCES.

Water of optimum quality is essential to human life, and water of acceptable quality is essential for agricultural, industrial, domestic, and commercial uses; in addition, water is also used for recreational activities. Therefore, major activities having potential effects on surface water are certain to be of appreciable concern. Contamination of freshwater sources can be caused by both anthropogenic and natural processes (Govinde *et al,* 2022). Heavy metals is a contaminant that are continuously introduced into the aquatic environment mainly due to direct atmospheric precipitation (Vinod *et al*, 2019) increased industrialization, technological development, growing human population and exploitation of natural resources, agricultural and domestic wastes run-off (Mahipal *et al,* 2016). Toxic metals and metalloids are a risk factor for the health of both human populations and for the natural environment. Chemical elements widely detected in groundwater include metals, such as zinc (Zn), lead (Pb), mercury (Hg), chromium (Cr), and cadmium (Cd), and metalloids, such as selenium (Se) and arsenic (As). Exposures at high concentrations of these heavy metals can lead to severe poisoning (Peiyei *et al,* 2021). Some dissolved metals are readily taken up by aquatic species and may enter the human body via drinking water, skin absorption, and ingestion of products, posing a health risk. (Govinde *et al,* 2022).

ROUTE OF ENTRY OF HEAVY METALS

Heavy metals may enter a human in four ways from; ingestion of contaminated food; inhalation from the atmosphere, drinking contaminated water; and due to skin contact from agriculture, pharmaceutical, manufacturing, residential and industrial areas (Briffa *et al*, 2020). Our food chain is constantly being replenished with essential and non-essential materials as a result of the excessive use of agrochemicals, municipal wastewater, industrial effluents, and raw sewage for irrigation (Saikat *et al,* 2022).

Food chain is perceived as one of the major pathways for human exposure to heavy metal pollution. The generation of heavy metals in the food chain is of great concern because of the variously related wellbeing dangers in humans and animals. (Kilaru *et al,* 2019). These heavy metals accumulate in the environment and over time contaminate the food chain, and become a major source of environmental and human health risk (Nkwunonwo *et al,* 2020).

The aim of this work is to enlighten the average Nigerian populace on heavy metal and the environment. We live with them because there sources are so close to us especially since industrialization and agricultural practices have increased drastically. Enlightenment is key and will reduce contamination ensuring the safety of the environment.

CONCLUSION:

Man is exposed every day to contaminated food, water and air emanating from the heavy metals accumulated in the environment. Awareness is key to reducing heavy metal contamination and pollution. Environmental consciousness is important in navigating this environmental threat. It is highly commended that the Environmental Protection Agency should do more to protect the Nigerian populace.

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Full Length Research Paper

COMPARATIVE ANALYSIS OF PALM OIL SAMPLES COLLECTED FROM BOLOU-ORUA LOCAL OIL MILL, AKENFA MARKET AND SWALI MARKET IN BAYELSA STATE, NIGERIA

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ABSTRACT

Palm oil (*Elaeis guineensis*) is important for its nutritional, culinary, industrial, and economic benefits. This study presents a comparative analysis of palm oil samples collected from Bolou-Orua local oil mill (sample A), Akenfa market (sample B) and Swali market (sample C) within Yenagoa Metropolis, Nigeria. Proximate results of the three oil (samples A, B and C) showed 3.00 %, 1.00 % and 0.00 % moisture contents, 13.02 %, 20.06 % and 20.06 %, ash contents, 5.80%, 7.40%, and 6.40%, protein contents, 34.0 %, 20.0 %, and 47.00 %, fat contents, 2.00 %, 2.00 % and 4.00 %, carbohydrate contents, respectively. Proximate results indicate that sample A, contained more moisture. Residual water in oils significantly affects their appearance and shelf-life. Sample A, had the lowest ash content, indicating it contained less organic matter. The fat contents of the three oil samples were significantly low compared with values reported in the literature. Potassium concentrations of 8.61 %, 5.63 %, 10.9 %, Iron concentrations (0.19 mg, 0.18 mg, 0.19 mg), Sodium concentration (106.3 mg, 106.3 mg, 107.1 mg), Cupper concentration (10.00 mg, 39.00 mg, 20.00 mg), Magnesium concentrations (0.10 mg, 0.03 mg, 0.01 mg), Zinc concentration (0.435 mg, 0.302 mg, 388 mg) and Phosphorus concentrations (0.30 mg, 0.50 mg, 0.53 mg), were recorded, respectively. GC-MS results of hexane extracts of oil samples A, B and C recorded 50, 70 and 34 chemical components, respectively. Sample A (Bolou-Orua local oil mill) showed 5 natural components of palm oil: Squalene (80.1 %), Behenic acid (98.3 %), Stearic acid (93.3 %), Oleic acid (71.1 %) and Palmitic acid (94.3 %). Sample B (Akenfa market) recorded 5 natural components of palm oil: Methyl oleate, 44.1 %, Oleic acid (61.0 %), Stearic acid (93.3%), hexadeecanoic acid methyl ester (92.1 %) and Myristic acid, 92.0 %. Sample C (Swali market) recorded 6 natural components of palm oil: Methyl palmitate (92.1 %), Palmitic acid (94.3 %), Methyl oleate (44.6 %), Methyl stearate (90.5 %), Oleic acid (62.8 %) and Stearic acid (93.3 %). The GC-MS results clearly indicate that all three palm oil samples (A, B, and C) contained substantial amounts of essential fatty acids, making them suitable for both cooking and industrial applications. However, all the samples (A, B and C) recorded 50, 65 and 28 residual solvents (contaminants) including: hexane, benzene and toluene, in substantial amounts. Hexane can negatively affect the central nervous system, benzene is a known carcinogen linked to leukemia, and toluene can cause reproductive harm and developmental issues in pregnant women. To mitigate these risks, it's crucial to ensure that palm oil is processed in a way that minimizes or eliminates residual solvents.

Keywords: Palm oil, residual solvents, health implications

INTRODUCTION

Edible oils, also known as cooking oils are mostly extracted from plants and animals. Edible oil is a substance of food gotten from fat or oil (Tuei, 2023). Edible oils contain a high level of fatty acids such as saturated fatty acids, mono and polyunsaturated fatty acids. Edible oils are essential ingredients of daily diet, for they serve as transporters of fat-soluble vitamins for and provide essential energy to human health (Uddin *et al.*, 2020). Edible oil is considered to be one of the natural sources of carotenoids. The human body uses carotenoids as Vitamin A. Carotenoids enhance immune function and can improve cardiovascular health. Carotenoids also act as biological antioxidants, protecting cells and tissues from the damaging effect of free radicals (Kulczyński *et al.* 2017).

Oil palm (*Elaeis guineensis*) is a monocotyledonous plant that belongs to the palm family *Arecaceae*, it produces male and female inflorescences in an alternating cycle (Adams *et al.*, 2011). The fruit produces two distinct types of oil: orange-red crude palm oil which is extracted from the mesocarp and brownish yellow crude palm kernel oil extracted from the seeds (kernel). Orange-red crude palm oil, commonly known as palm oil, has been used in food preparation for over 5,000 years (Imoisi *et al.*, 2015). Palm oil is the most widely produced edible vegetable oil in the world and it's nutritional and health attributes have been well documented.

The beta-carotene in palm oil helps balance the body hormonal levels (Imoisi *et al.*, 2015). Palm oil contains tocopherols, very powerful antioxidants that target and eliminate cancerous cells (Nazaimoon *et al.*, 1996). The oil is effective in the treatment of thrombosis in rats (Pereira *et al.*, 1991). When used in moderation palm oil helps balance the cholesterol levels in the body (Ong and Goh, 2002). Palm oil contains a small amount of omega 3 fatty acids that support the health cardiovascular and endocrine systems (Cleveland Clinic). Vitamin E in palm oil exhibits anti-inflammatory as well as antioxidant characteristics (Zainal *et al.*, 2022). Palm oil is a good source of vitamin D enabling the body maintain healthy joints and bone density. It also contains ubiquinone (energy booster) and a small amount of squalene, that possesses cholesterol lowering and anti-cancer properties (Kalogeropoulos & Andrikopoulos, 2004). Red palm oil is also rich in co-enzyme Q10 (Loganathan *et al.*, 2017).

During the extraction of palm oil, solvent extraction is the most efficient means of recovering the most oil possible (Anderson International Corp). Solvents used in extracting palm oil include: Hexane, Petroleum Ether, Ethanol, Isopropanol and Acetone.

Despite the high nutritional value of palm oil, research shows that palm oil can contain microbial contaminants, including: Bacillus cereus, Bacillus subtilis, Escherichia coli, Klebsiella sp., Serratia marcescens, Pseudomonas aeruginosa, Staphylococcus aureus and Staphylococcus epidermidi (Akinola *et al.*, 2020). Aromatic hydrocarbons and **3-monochloropropane-1, 2-diol esters (3-MCPDE) and glycidyl esters (GE)** contaminants have also been reported (Alfalaval.com.; Eze *et al.*, 2015). Incomplete purification or recovery of extraction solvents can leave traces of aromatic hydrocarbons in the oil (Palade *et al*., 2023).

Additionally, industrial activities near palm plantations can release benzene, toluene, and other volatile organic compounds (VOCs) into the air, which can then settle on the palm fruits. Contaminated water sources used for irrigation or polluted soil can introduce these chemicals into the palm trees, and subsequently, into the extracted oil. The use of certain industrial lubricants and cleaning agents containing benzene, toluene, or their derivatives in processing equipment can also lead to contamination (Abdullahi *et al.,* 2023). Moreover, packaging materials derived from or coming into contact with substances harboring these contaminants have the potential to seep into the oil. Palm plantations sometimes employ pesticides and herbicides containing impurities like benzene, toluene, or related compounds, which can contaminate palm oil. Accidental spills or leaks of industrial chemicals near processing facilities or during transportation can introduce contaminants. These contaminants in palm oil pose significant health hazards. Hexane exposure, for instance, may result in peripheral neuropathy, characterized by numbness, tingling, and muscle weakness. Similarly, the presence of acetone in food can lead to respiratory tract irritation, dizziness, headaches, and in severe instances, central nervous system depression (Very Well Health).

Although ethanol is generally less toxic than other solvents, high levels can cause liver damage and central nervous system effects. Benzene is a known human carcinogen (American Cancer Society). Chronic exposure to toluene has been associated with developmental delays and congenital malformations.

This study aims to analyze the proximate, elemental and chemical content of three (3) palm oil samples collected from Bolou-orua local oil mill, Akenfa market and Swali market, in Bayelsa State, Nigeria, and assess their potential impacts on public health and food safety within the area.

EXPERIMENTALS

Three palm oil (*Elaeis guineensis*) samples were collected from Yenagoa metropolis. Palm oil sample A, was purchased from a local oil mill in Bolou-Orua, sample B and C were purchased from Akenfa and Swali markets, in Bayelsa State, Nigeria. The oils, shown in Figure 1, were accurately identified at the Biotechnology Department of the University of Africa, Toru-Orua. The samples were then transferred into three reagent bottles, properly labeled, and stored in a cupboard for further analysis.

Proximate Analysis

The moisture (water content), fat, ash, carbohydrates, protein, and non-fat nutrients levels were assessed employing the established methodologies outlined by the Association of Official Analytical Chemists (AOAC, 2005).

Elemental Results

The elemental composition of magnesium, iron, copper, phosphorus, sodium, potassium, and zinc was analyzed using the techniques recommended by the Association of Official Analytical Chemists (AOAC, 2005).

Figure 1: Palm oil samples collected from Bolou-Orua (A), Akenfa market (B), and Swali market (C)

Gas Chromatography-Mass Spectroscopy (GC-MS) analysis of bioactive components

An analysis of the hexane extract from air-dried D. bulbifera bubils was performed using an Agilent 6890 gas chromatograph (GC) connected to an Agilent 5973N Mass Spectrometer (MS), both from Agilent Technology in Palo Alto, CA, USA. The GC-MS system featured an Agilent 7683 Series Automatic Liquid Sampler injector. A META X5 coated fused capillary column (30 meters long, 0.25 mm in diameter, with a film thickness of 0.25 µm) was used, with a maximum column temperature of 325°C.

The oven temperature program started at 70°C, held for 2 minutes, then increased to 300°C at a rate of 20°C/min. Ultra-high purity helium (99.99%) was used as the carrier gas at a flow rate of 1.0 mL/min. A 1 µL sample volume was injected in split mode with a split ratio of 20:1. The MS source and MS Quad temperatures were set at 230°C and 150°C, respectively. The injection port, transfer line, and ion source temperatures were maintained at 280°C. Mass spectra were recorded over a scan range of 50-550 atomic mass units (amu), with an ionizing energy of 70 electronvolts (eV). The electron multiplier voltage was determined through the autotune process.

Identification of Components

The identification and characterization of chemical compounds in the sample extracts were based on the retention times obtained through gas chromatography. Mass spectra were matched against a known spectra library using computer algorithms. For interpreting the gas chromatography-mass spectroscopy (GC-MS) mass spectrum, we referenced the extensive database maintained by the National Institute of Standards and Technology (NIST), which includes over 590,000 patterns. To understand the properties of the components in the sample extract, the mass spectra of unidentified compounds were compared with the spectra of established components stored in the NIST library (version 2014). This process facilitated the determination of the names, molecular weights, molecular formulas, structures, and fragmentation patterns of the compounds.

RESULTS

The findings from the analyses conducted on the three palm oil samples A, B and C are outlined below:

Proximate and elemental analyses results

Proximate and elemental analyses of the three (3) palm oil (*Elaeis guineensis*) samples A, B and C were performed in triplicate, and the results are as shown in Table 1.

GC-MS Results

GC-MS results of hexane extracts of three (3) Palm oil samples A, B and C, are shown in Tables 2-4.

Table 1: Proximate and mineral composition of three (3) Palm oil (*Elaeis guineensis*) samples collected from Yenagoa Metropolis

Oil Samples	**Proximate composition**	**Mean ± SD (%)**	**Elemental composition**	**Mean ± SD (mg)**
Sample A Sample B Sample C	Moisture	3.00 ± 0.1 1.00 ± 0.3 0.00	Potassium (K)	8.61 ± 0.2 5.63 ± 0.1 10.9 ± 0.1
Sample A Sample B Sample C	Protein	5.80 ± 0.1 7.40 ± 0.3 6.40 ± 0.2	Iron (Fe)	0.19 ± 0.1 0.18 ± 0.2 0.19 ± 0.2
Sample A Sample B Sample C	Carbohydrate	2.00 ± 0.1 2.00 ± 0.2 4.00 ± 0.2	Sodium (Na)	106.3 ± 0.1 106.3 ± 0.1 107.1 ± 0.1
Sample A Sample B Sample B	Ash	13.2 ± 0.2 20.6 ± 0.1 20.6 ± 0.2	Copper (Cu)	10.00 ± 0.2 39.00 ± 0.1 20.00 ± 0.2
Sample A Sample B Sample C	Fat/Oil	34.0 ± 0.01 20.0 ± 0.2 47.0 ± 0.2	Magnesium (Mg)	0.10 ± 0.1 0.03 ± 0.2 0.10 ± 0.1
Sample A Sample B Sample C			Zinc	0.435 ± 0.1 0.302 ± 0.1 0.388 ± 0.1
Sample A Sample B Sample C			Phosphorus	0.30 ± 0.1 0.50 ± 0.1 0.30 ± 0.2

Table 2: Identified compounds from the hexane extract of palm oil sample A by gas chromatography-mass spectrometry (GC-MS)

S/N	**Retention Time (min)**	**Name of compound**	**Area**	**Probability (%)**	**Molecular formula**	**Molecular weight**
1.	1.303	Borane, compd. with dimethylamine (1:1)	6633	93.5	$C_2H_{10}BN$	59
2.	1.370	Trimethylamine, compd. with borane	1343	88.9	$C_3H_{12}BN$	73
3.	1.394	Diaziridine,3,3-dimethyl	6986	95.2	$C_3H_8N_2$	72
4.	1.441	Butane, 2,2-dimethyl	3989	76.3	C_6H_{14}	86
6.	1.542	Isobutylene glycol	1313	89.1	$C_5H_{10}O$	86

7.	1.585	Ethyl tert-butyl ether	1668	91.9	$C_5H_{10}O$	86
8.	1.707	Furan, 2,5-dihydro-3-methyl	2733	94.1	C_5H_8O	84
9.	1.824	Pentane, 3,3-dimethyl	5126	84.0	C_7H_{16}	100
10.	1.880	Benzene	3236	81.9	C_6H_6	78
11.	1.939	Cyclopentane, 1,1-dimethyl	2154	70.9	C_7H_{14}	98
12.	2.042	Cycloheptane	3210	76.8	C_7H_{14}	98
13.	2.103	Heptane, 3-4-dimethyl	1919	82.3	C_9H_2O	128
14.	2.340	Cyclopentane,1-ethyl-1-methyl	6069	84.2	C_8H_{16}	112
15.	2.403	Cyclopentane, ethyl1-	2227	88.5	C_7H_{14}	98
16.	2.444	Cyclopentane, 1,2,4-trimethyl	2840	70.9	C_8H_{16}	112
17.	2.509	Cyclopentane, 1,2,3-trimethyl-	2331	66.6	C_8H_{16}	112
18.	2.604	Pentane, 3-ethyl-2-methyl	5564	79.1	C_8H_{18}	114
19.	2.677	Heptane, 2-methyl-	5865	80.3	C_8H_{18}	114
20.	2.752	Toluene	3917	80.5	C_7H_8	92
21.	2.844	Cyclohexane, 1,3-dimethy-	1368	72.7	C_8H_{16}	112
22.	2.864	Cyclohexane, 1,4-dimethyl	5447	60.5	C_8H_{16}	112
23.	2.910	Cyclohexane, 1,1-dimethyl-	2406	81.4	C_8H_{16}	112
24.	2.932	Cyclopentane, 1-ethyl-2-methyl-	1146	58.4	C_8H_{16}	112
25	3.012	Octane	1018	74.5	C_8H_{18}	114
26.	3.038	Cyclohexane, 1,2-dimethyl-	4419	69.5	C_8H_{16}	112
27.	3.085	Cyclohexane, 1,3-dimethyl-	2428	59.4	C_8H_{16}	112
28.	3.261	Heptane, 2,6-dimethyl	8019	81.4	C_9H_{20}	128
29.	3.326	1-Nonene	1635	44.0	C_9H_{18}	126
30.	3.361	Cyclohexane, ethyl-	4250	88.3	C_8H_{16}	112
31.	3.389	Cyclohexane, 1,1,3-trimethyl-	1952	83.0	C_9H_{18}	126
32.	3.421	1,1,4-Trimethylcyclohexane	5782	81.6	C_9H_{18}	126
33.	3.536	Cyclohexane, 1,2,4-trimethyl-	1247	72.8	C_9H_{18}	126
34.	3.627	Benzene, 1,3-dimethyl	2721	62.4	C_8H_{10}	106

35.	3.820	Cyclopentane, butyl-	7914	73.7	C_9H_{18}	126
37.	3.853	1-Ethyl-3-methylcyclohexane	8401	66.1	C_9H_{18}	126
37.	3.889	Cyclohexane, 1-ethyl-4-methyl-	4661	73.6	C_9H_{18}	126
38.	3.931	Nonane	5497	74.3	C_9H_{20}	128
39.	4.020	Cyclohexane, 1-ethyl-2-methyl	6895	61.6	C_9H_{18}	126
40.	4.132	Bicyclo[3.2.1]octane	5919	59.9	C_8H_{14}	110
41.	4.210	Cyclohexane, propyl	1058	85.8	C_9H_{18}	126
42.	4.442	Dichloroacetic acid, heptadecyl ester	4869	40.5	$C_{19}H_{36}Cl_2O_2$	366
43.	4.473	Mesitylene	7773	68.6	C_9H_{12}	120
44.	4.530	Benzene, 1,2,3-trimethyl-	1046	61.4	C_9H_{12}	120
45.	4.703	Decane	1252	77.7	$C_{10}H_{22}$	142
46.	9.196	palmitic acid	3056	94.3	$C_{16}H_{32}O_2$	256
47.	9.784	oleic acid	4255	71.1	$C_{18}H_{34}O_2$	282
48.	9.819	stearic acid	4780	93.3	$C_{18}H_{36}O_2$	284
49.	10.948	Behenic acid	3276	98.3	$C_{22}H_{44}O_2$	340
50.	11.773	Squalene	5359	80.1	$C_{30}H_{50}$	410

Table 3: Identified compounds from the hexane extract of palm oil sample B by gas chromatography-mass spectrometry (GC-MS)

S/N	**Retention Time (min)**	**Name of compound**	**Area X 10^6**	**Probability** (%)	**Molecular formula**	**Molecular weight**
1.	1.316	(Methylenecyclopropyl)sulfonylbenzene	1039	96.5	$C_{10}H_{10}O_2S$	194
2.	1.354	3-Methoxypropene	2020	93.4	C_4H_8O	72
3.	1.401	4-Methyl-5-oxazolecarbonitrile	1092	97.9	$C_5H_4N_2O$	108
4.	1.432	2-Hexynyl alcohol	1842	86.3	$C_6H_{10}O$	98
5.	1.475	2-Ethyl-2-methyloxirane	1399	91.9	$C_5H_{10}O$	86
6.	1.519	4-Cyclopentene-1,3-diol, trans	2709	94.1	$C_5H_8O_2$	100
7.	1.542	octyl but-3-yn-1-yl carbonate	2623	93.5	$C_{13}H_{22}O_3$	226
8.	1.586	3-Methyltetrahydrofuran	2180	94.1	C_5H_8O	84
9.	1.663	1,3-Cyclobutanedicarbonitrile	3806	71.3	$C_6H_6N_2$	106
10.	1.696	2-Undecyne	3359	63.4	$C_{11}H_{20}$	152
11.	1.816	2-Pyridinecarbonitrile, 6-chloro	7930	98.6	$C_6H_3CIN_2$	138
12.	1.873	Benzene	5718	81.9	C_6H_6	78
13.	1.900	2,4-Hexadiyne	2712	86.5	C_6H_6	78

14.	1.971	1,3-Cyclobutanedicarbonitrile	1504	71.3	$C_6H_6N_2$	106
15.	2.238	4-Cyclopentene-1,3-diol, trans-	1332	94.1	$C_5H_8O_2$	100
16.	2.327	2-Hexene, 5-methyl-	1496	69.0	C_7H_{14}	98
17.	2.363	Heptane, 3-methylene	1627	78.5	C_8H_{16}	112
18.	2.423	3-Octene	1599	64.1	C_8H_{16}	112
19.	2.619	N-(4-Carboxymethyl)-N'-phenyl-urea	1331	97.7	$C_{15}H_{14}N_2O_3$	270
20.	2.668	2-Penten-4-yne, 2-methyl-	4811	84.8	C_6H_8	80
21.	2.757	Cyclopropanecarboxylic acid, 2-methylene-, methyl ester	5232	97.6	$C_6H_8O_2$	112
22.	2.774	7,8-Dioxabicyclo[3.2.1]oct-2-ene	2183	94.7	$C_6H_8O_2$	112
23.	2.816	Cyclooctane	2366	63.7	C_8H_{16}	112
24.	2.922	Carbonic acid, but-2-yn-1-yl hexadecyl este	5332	74.5	$C_{21}H_{38}O_3$	338
25.	2.946	2-Cyclopenten-1-one, 4-methoxy	2068	95.3	$C_6H_8O_2$	112
26	2.992	2,4-Dimethyl-3-hexene(c,t)	1421	52.8	C_8H_{16}	112
27.	3.049	Dodecane, 2,2,11,11-tetramethyl-	1852	86.8	$C_{16}H_{34}$	226
28.	3.079	Heptane, 2,4-dimethyl-	1361	69.3	C_9H_{20}	128
29.	3.160	Heptane, 2,6-dimethyl	5205	81.4	C_9H_{20}	128
30.	3.230	Cyclooctane, methyl	1099	59.7	C_9H_{18}	126
31.	3.270	trans-4,4-Dimethyl-2-hexene	2125	51.0	C_8H_{16}	112
32.	3.298	3-Hexene, 2,3-dimethyl-	1105	65.7	C_8H_{16}	112
33.	3.328	1,1,4-Trimethylcyclohexane	3571	81.6	C_9H_{18}	126
34.	3.380	5-Eicosene	1026	36.5	$C_{20}H_{40}$	280
35.	3.445	Cyclohexane, 1,2,4-trimethyl	7919	75.9	C_9H_{18}	126
36.	3.534	1,5-Hexadien-3-yne, 2-methyl	2105	91.5	C_7H_8	92
37.	3.653	Benzisoxazole-2-acetic acid, hydrazide	9255	95.6	$C_9H_9N_3O_2$	191
38.	3.713	Bicyclo[3.2.1]octane	1210	59.9	C_8H_{14}	110
39.	3.738	Cyclohexane, 1,2,4-trimethyl-	2531	75.9	C_9H_{18}	126
40.	3.775	cis-1-Ethyl-3-methyl-cyclohexane	4745	67.1	C_9H_{18}	126
41.	3.814	Cyclohexane, 1-ethyl-4-methyl-, trans-	2173	61.1	C_9H_{18}	126
42.	3.844	1,5-Hexadien-3-yne, 2-methyl-	3600	91.5	C_7H_8	92
43.	3.950	Cyclohexane, 1-ethyl-2-	3910	61.6	C_9H_{18}	126

		methyl-				
44.	3.984	trans-1,2-Diethyl cyclopentane	1402	80.3	C_9H_{18}	126
45.	4.063	Hexenyl angelate, 4z-	3469	76.9	$C_{11}H_{18}O_2$	182
46.	4.101	Benzene, (1-methylethyl)-	1011	74.1	C_9H_{12}	120
47.	4.144	Propylcyclohexane	5971	85.8	C_9H_{18}	126
48.	4.182	Heptane, 3-ethyl-2-methyl-	7562	79.6	$C_{10}H_{22}$	142
49.	4.215	1-Methyl-2-methylenecyclohexane	9532	52.9	C_8H_{14}	110
50.	4.303	Cyclohexane, 1,3-dimethyl-2-methylene-, trans-	9660	68.8	C_9H_{16}	124
51.	4.362	Benzene, propyl-	1345	89.4	C_9H_{12}	120
52.	4.386	Nonane, 2-methyl-	1950	72.5	$C_{10}H_{22}$	142
53.	4.413	Benzene, 1-ethyl-3-methyl-	4267	61.7	C_9H_{12}	120
54.	4.442	Benzene, 1-ethyl-2-methyl-	2337	63.3	C_9H_{12}	120
55.	4.478	1,3,5-Trimethylbenzene	6328	68.6	C_9H_{12}	120
56.	4.570	Cyclohexane, 1-ethyl-1-methyl-	2046	72.5	C_9H_{18}	126
57.	4.790	4,5-Dihydro-4,4-undecamethylene-2-phenyl-1,3-oxazin-6-one	8876	97.6	$C_{21}H_{29}NO_2$	327
58.	4.815	Decane, 4-methyl-	5374	62.3	$C_{11}H_{24}$	156
59.	4.887	Benzene, 1,2,3-trimethyl-	9812	61.4	C_9H_{12}	120
60.	4.931	Cyclohexane, (2-methylpropyl)-	6455	93.6	$C_{10}H_{20}$	140
61.	5.117	Benzene, 1,3-diethyl-	4628	70.1	$C_{10}H_{14}$	134
62.	5.144	Naphthalene, decahydro-	5730	66.8	$C_{10}H_{18}$	138
63.	5.338	Undecane	7635	55.0	$C_{11}H_{24}$	156
64.	8.460	Myristic acid	7083	92.0	$C_{14}H_{28}O_2$	228
65.	9.020	Hexadecanoic acid, methyl ester	2078	92.1	$C_{17}H_{34}O_2$	270
66.	9.268	1-(3-Methylbutoxy)-1-methyl-1-silacyclohexane	1379	95.3	$C_{11}H_{24}OSi$	200
67.	9.614	Methyl oleate	3755	44.1	$C_{19}H_{36}O_2$	296
68.	9.842	Oleic acid	1577	61.0	$C_{18}H_{34}O_2$	282
69.	9.877	Stearic acid	1466	93.3	$C_{18}H_{36}O_2$	284
70.	11.867	Supraene	1145	91.3	$C_{30}H_{50}$	410

Table 4: Identified compounds from the hexane extract of palm oil sample C, by gas chromatography-mass spectrometry (GC-MS)

S/N	**Retention Time (min)**	**Name of compound**	**Area 10^6**	**Probability** (%)	**Molecular formula**	**Molecular weight**
1.	1.325	isoamyl chloride	4468	92.3	$C_5H_{11}Cl$	106
2.	1.388	Butane,2,2-dimethyl-	7110	76.3	C_6H_{14}	86

3.	1.455	Pentane, 2-methyl-	1848	91.8	C_6H_{14}	86
4.	1.490	Pentane, 3-methyl-	1867	74.3	C_6H_{14}	86
5.	1.531	n-Hexane	2245	90.2	C_6H_{14}	86
6.	1.641	1-Hexyl trifluoroacetate	5553	92.5	$C_8H_{13}F_3O_2$	198
7.	1.805	1,3-Hexadien-5-yne	2314	84.9	C_6H_6	78
8.	1.931	Cyclopentane, 1,2-dimethyl-, cis-	6011	54.8	C_7H_{14}	98
9.	1.971	Heptane	3518	83.7	C_7H_{16}	100
10.	2.194	Cycloheptane	2621	76.8	C_7H_{14}	98
11.	2.305	Hexane, 2-methyl-4-methylene-	9910	79.7	C_8H_{16}	112
12.	2.370	Cyclopentane, 1,2,3-trimethyl-	8517	66.6	C_8H_{16}	112
13.	2.502	Heptane, 2-methyl-	1666	80.3	C_8H_{18}	114
14.	2.591	Toluene	2572	80.5	C_7H_8	92
15.	2.678	Cyclohexane, 1,3-dimethyl-	7560	67.2	C_8H_{16}	112
16.	2.839	Octane	1457	74.5	C_8H_{18}	114
17.	2.874	Cyclohexane, 1,2-dimethyl-, trans-	2474	69.5	C_8H_{16}	112
18.	2.938	Cyclohexane, 1,3-dimethyl-	1011	67.2	C_8H_{16}	112
19.	3.190	Cyclooctane, methyl-	4903	59.7	C_9H_{18}	126
20.	3.223	Ethylcyclohexane	1268	83.3	C_8H_{16}	112
21.	3.251	3-Hexene, 2,3-dimethyl-	1686	65.7	C_8H_{16}	112
22.	3.533	Ethylbenzene	1980	74.8	C_8H_{10}	106
23.	3.615	1,4-Dimethylbenzene	1468	69.6	C_8H_{10}	106
24.	3.830	1,2-Dimethylbenzene	3405	65.8	C_8H_{10}	106
25.	4.129	Cyclohexane, 2-propenyl-	7809	88.7	C_9H_{16}	124
26	4.420	Benzene, 1-ethyl-2-methyl-	7263	63.3	C_9H_{12}	120
27.	4.480	Hemimelitene	9805	61.4	C_9H_{12}	120
28.	4.658	Decane	2839	77.7	$C_{10}H_{22}$	142
29.	9.030	methyl palmitate	2497	92.1	$C_{17}H_{34}O_2$	270
30.	9.222	palmitic acid	2996	94.3	$C_{16}H_{32}O_2$	256
31.	9.624	methyl oleate	3540	44.6	$C_{19}H_{36}O_2$	296
32.	9.685	Methyl stearate	2330	90.5	$C_{19}H_{38}O_2$	298
33.	9.808	oleic acid	4977	62.8	$C_{18}H_{34}O_2$	282
34.	9.849	stearic acid	6087	93.3	$C_{18}H_{36}O_2$	284

DISCUSSION

Table 1 shows the proximate contents of oil samples, A, B, and C, collected from Yenagoa metropolis. The moisture content of sample A, B and C were 3.00 %, 1.00 % and 0.00 % respectively. Ajiboye *et al.* (2013) recorded a moisture content of 2.11 %. The variations observed could be attributed to differences in palm fruit species. However, exceedingly low moisture levels can be detrimental to oil and fat products. Residual water in oils significantly affects their appearance and shelf-life (Raji *et al.* 2022),

The ash content of sample A, B and C were 13.02 %, 20.06 % and 20.06 %, indicating that, sample A, contained fewer organic matter than samples B and C. Raji and colleagues (2022) reported a lower value. The variations in ash content could be attributed to soil conditions in different geographic locations. The protein content of samples A, B, and C were 5.80 %, 7.40 %, and 6.40 %, respectively. Ajiboye and colleagues (2013) reported a similar value, 5.43 %.

The fat content of samples A, B, and C were 34.0 %, 20.0 %, and 47.0 %, respectively. These results indicated that sample C had a higher fat content than sample A and sample B. Notably, sample C contained more fat content than sample A and B. Ajiboye and others (2013) reported a higher value, 78.19 %. The variance of the fat composition of the palm oil samples was attributed to genetic variations, geographical location, agricultural practices, and harvesting time and storage conditions.

The carbohydrate content of sample A, B and C were 2.00 %, 2.00 % and 4.00 %, respectively. Raji and others (2022) reported 0.01756 % of carbohydrate content in palm oil collected from Bayelsa State.

Table 2 shows the mineral content of samples A, B, and C. The potassium concentrations were 8.61 % in sample A, 5.63 % in sample B, and 10.9 % in sample C. Sample C had the highest potassium content. Potassium is the most crucial nutrient in oil palm production, playing a key role in converting light into biochemical energy during photosynthesis and facilitating the rapid transport of assimilates from the leaves to other plant organs. (K-Pius-S.com). The iron (Fe) concentration in samples A, B, and C were 0.19 %, 0.18 %, and 0.19 %, respectively. These low levels of iron suggested that palm oil is not a significant source of this mineral. The magnesium (Mg) concentrations were 0.10 % in sample A, 0.03 % in sample B, and 0.01 % in sample C. Phosphorus (P) levels in samples A, B, and C were 0.30 %, 0.50 %, and 0.53 %, respectively, with sample C having the highest phosphorus concentration. Phosphorus is essential for ATP synthesis and bone mineralization (Serna and Bergwitz, 2020; Bennett and Tiewei, 2022).

This comparative study indicated that palm oil samples A, B, and C contained essential proximate and mineral nutrients necessary for various body functions. The Gas Chromatography-Mass Spectrometry (GC-MS) analyses of hexane extracts from palm oil samples A, B, and C are detailed in Tables 3 through 5. Table 3, which presents the data for oil sample A, lists fifty (50) phytochemicals along with their retention time, molecular weight, molecular formula, and peak area percentages. Bioactive components with peak area percentages below 5 % were considered insignificant. Notable phytochemicals included Squalene (80.1 %), Behenic acid (98.3 %), Stearic acid (93.3 %), Oleic acid (71.1 %), and Palmitic acid (94.3 %).

Squalene possesses antioxidant and moisturizing properties (Huang *et al.*, 2009). Stearic acid is mainly used in the production of detergents, soaps, and cosmetics (PubChem, 2023). Oleic acid commonly known as 9-octadecanoic acid possesses antiflammatory properties (Santamarina *et al.*, 2021). Palmitic acid provides texture, stability, and flavor to food. However, excessive consumption of palmitic acid has been associated with negative health effects, such as increasing low density lipoprotein (LDL), bad cholesterol levels, which can contribute to cardiovascular diseases (Odia *et al.* 2015). ,

Forty-five (45) compounds not naturally found in crude palm oil were detected in sample A, at varying concentrations. These compounds included Isobutylene glycol at 89.1 %, Oxirane 2-ethyl-2-methyl at 91.9 %, Furan 2,5-dihydro-3-methyl at 94.1 %, Benzene at 81.9 %, Trimethylamine compound with borane at 88.9 %, Diaziridine 3,3-dimethyl at 95.2 %, Cyclopentane 1-ethyl-1-methyl at 82.2 %, Cyclopentane 1,2,4-trimethyl at 70.9 %, Pentane 3-ethyl-2-methyl at 79.1 %, Heptane 2-methyl at 80.3 %, Toluene at 80.5 %, Cyclohexane 1,1-dimethyl at 81.4 %, 1,1,4-Trimethylcyclohexane at 81.6 %, Cyclohexane propyl at 85.8 %, and Mesitylene at 68.6 %.

Isobutylene glycol, also known as 3-Methyl-2-buten-1-ol, is a synthetic compound commonly utilized as solvents, fuel additives, and chemical intermediates. It possesses toxicity towards aquatic life (TCI America). Trimethylamine, compd. with borane and Diaziridine,3,3-dimethyl are compounds not found in palm oil. Trimethylamine borane can cause lungs irritation and shortness of breath (New Jersey).

Seventy (70) phytochemicals were analysed from sample B, Table 4. These include: Methyl oleate, 44.1 %, Oleic acid, 61.0 %, Stearic acid, 93.3 %, hexadeecanoic acid methyl ester, 92.1 % and Myristic acid, 92.0 %

Sixty-five (65) compounds not naturally found in crude palm oil were detected in oil Sample B. These included octyl but-3-yn-1-yl carbonate (93.5 %), (Methylenecyclopropyl)sulfonylbenzene (96.5 %), 3-Methoxypropene (93.4 %), 4-Methyl-5-oxazolecarbonitrile (97.9 %), 2-Hexynyl alcohol (86.3 %), 2-Ethyl-2-methyloxirane (91.9 %), 3-Methyltetrahydrofuran (94.1 %), Benzene (81.9 %), Propylcyclohexane (85.8 %), and 1,3,5-Trimethylbenzene (68.6 %). The presence of these contaminants, as detailed in Table 3, poses a potential threat to human health. (ECHA, 2023; Jamall and Willhite, 2008).

Thirty-five (34) phytochemicals were analyzed from Sample C, as detailed in Table 4. These include Methyl palmitate (92.1 %), Palmitic acid (94.3 %), Methyl oleate (44.6 %), Methyl stearate (90.5 %), Oleic acid (62.8 %), and Stearic acid (93.3 %). Methyl oleate and Methyl stearate are utilized in biodiesel production, lubrication, and cosmetic formulations. (Interfat; Tankov *et al.*, 2022; Said and El-Sayed, 2018; Naik *et al.*, 2011).

Twenty-eight (28) compounds not naturally found in crude palm oil were detected in oil sample C. These included isoamyl chloride (92.3 %), n-hexane (90.2 %), toluene (80.5 %), 1-hexyl trifluoroacetate (92 %), ethylcyclohexane (83.3 %), 2-hexyn-1-ol (86.3 %), ethylbenzene (74.8 %), 1,4-dimethylbenzene (69.9 %), 1,2-dimethylbenzene (65.8 %), benzene, 1-ethyl-2-methyl (63.3 %), and hemimellitene (61.4 %). Isoamyl chloride, 1-hexyl trifluoroacetate, ethylcyclohexane, 1,4-dimethylbenzene, 1,2-dimethylbenzene, n-hexane, toluene, and hemimellitene are not inherent constituents of palm oil. Some of these pollutants are hazardous to human health (Kim *et al.*, 2021; ThermoFisher Scientific, 2024). Their presence in sample C was linked to processing methods and storage conditions.

CONCLUSION

A comparative study was conducted on the proximate, mineral, and bioactive composition of palm oil (Elaeis guineensis) collected from three locations in Yenagoa metropolis: Bolou-Orua (sample A), Akenfa market (sample B), and Swali market (sample C). The moisture content was 3 % in sample A, 1 % in sample B, and 0 % in sample C. Residual water in oils significantly affects their appearance and shelf-life. Sample A had the lowest ash content, indicating it contained less organic matter compared to samples B and C, a variation likely due to differing soil conditions at each location. Sample B had the highest protein content, while sample C had the highest fat content. These differences were attributed to geographic location, agricultural practices, and harvesting times. All three samples contained significant amounts of sodium and moderate amounts of potassium and copper.

The GC-MS analysis of the hexane extracts from oil samples A, B, and C revealed the presence of 50, 70, and 34 bioactive compounds, respectively. Sample A contained five natural components of palm oil: squalene, behenic acid, stearic acid, oleic acid, and palmitic acid. Sample B also contained five natural palm oil components: methyl oleate, oleic acid, stearic acid, hexadecanoic acid methyl ester, and myristic acid. Sample C contained six natural components: methyl palmitate, palmitic acid, methyl oleate, methyl stearate, oleic acid, and stearic acid. These results clearly indicated that all three palm oil samples (A, B, and C) contained significant amounts of essential fatty acids, making them suitable for both cooking and industrial applications.

However, samples A, B, and C recorded 45, 65, and 28 compounds not naturally found in crude palm oil (residual solvents) respectively. Residual solvents are pollutants, and some of these solvents are harmful to health. Hexane can affect the central nervous system, benzene is highly toxic and a known carcinogen linked to leukemia, and toluene can cause reproductive harm and developmental issues in pregnant women. The presence of residual solvents in the three samples was attributed to incomplete processing methods and contaminated storage facilities.

RECOMMENDATION

To mitigate the health risks associated with consumption of contaminated palm oil, it's crucial to ensure that palm oil is processed in a way that minimizes or eliminates residual solvents. Manufacturers should adhere to regulatory guidelines and consumers should be aware of the potential risks associated with solvent residues in palm oil and other food products.

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CHEMICAL SOCIETY OF NIGERIA (CSN) ABIA CHAPTER
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Conference Proceedings

Full Length Research Paper

DETERMINATION OF CO, LI, MN AND NI LEVELS OF WASTE LI-ION, LI-POLYMER AND NIMH RECHARGEABLE BATTERIES AND ESTIMATION OF RECOVERABLE METALS FROM BATTERY CONSUMPTION IN NIGERIA

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ABSTRACT

The consumption of portable rechargeable batteries has increased since the introduction of mobile telecommunication and other portable electronics. This study assessed the levels of Co, Li, Mn and Ni in rechargeable batteries, and estimated recoverable metals from battery importation in Nigeria and the financial benefits of locally recycling them. Metal levels in the electrode materials of spent batteries were determined using AAS after digestion using acid mixture (2:1 HCl and HNO_3). For Li-ion batteries, the results of Co, Li, Mn and Ni in the battery electrodes (mean ± standard deviation) are 28899±5277 mg/kg (range 33397-14706 mg/kg), 65961±8490 mg/kg (81159-47132 mg/kg), 18310±4961 mg/kg (32549-8821 mg/kg) and 24329±12271 mg/kg (35857-3808 mg/kg) respectively. Results for Li-polymer batteries are 29753±4649 mg/kg (range 33555-17743 mg/kg) for Co, 65477±5293 mg/kg (73284-55494 mg/kg) for Li, 21287±6628 mg/kg (30260-8461 mg/kg) for Mn and 20159±10120 mg/kg (32706-2766 mg/kg) for Ni. Corresponding values for NiMH are 66287±7487 mg/kg (71581-60993 mg/kg) for Co, 13851±2455 mg/kg (15587-12115 mg/kg) for Li, 32899±30689 mg/kg (54605-11192 mg/kg) for Mn and 82735±2610 mg/kg (84580-80889 mg/kg) for Ni. All Co, Mn and Ni exceeded the toxicity threshold limit concentration values (Co: 8000 mg/kg and Ni; 2000 mg/kg) indicating that these batteries should be treated as hazardous wastes. Import data from UN Comtrade showed that 2.6 million tonnes of lithium-ion and 4351 tonnes of mobile phone batteries were imported into Nigeria between 1999 and 2022. If the waste batteries are collected and recycled, the recoverable metals are worth US$6 Million and US$9914 respectively. This shows that much forex can be obtained from waste batteries if collected, recycled and sold in the mineral market. If disposed with municipal waste, they will contaminate the environment; endangering the lives of plants, animals and humans.

Key Words: heavy metals, lithium, batteries, Nigeria, recycling

INTRODUCTION

In an era dominated by portable electronics, the proliferation of rechargeable batteries has led to a surge in electronic waste (e-waste) due to their limited lifespan and improper disposal practices (Liang *et al.,* 2019; Meshiram *et al.,* 2020). Electronic waste, commonly referred to as e-waste, is used to describe discarded electronic devices that have reached the end of their useful life. They include a wide range of items such as computers, laptops, smartphones, tablets, digital cameras and other electronic appliances. They are mostly generated when older electronic devices become outdated and are replaced by newer, more advanced models. Some electronic devices have relatively short lifecycle due to rapid technological advancements or built – in-obsolescence, some may become non – functional due to technical issues, damages, or wear and tears. Also, upgrade of these electronic devices may necessitate a change and disposal of older ones. E-waste poses environmental and health risks if not managed properly (Mrozik *et al*., 2021).

While rechargeable batteries are designed to be reusable through multiple charging cycles, they eventually reach a point where their capacity diminishes and they need to be replaced. Waste rechargeable batteries become a part of e-waste at their end-of-life; when they are thrown into the regular trash, they may end up in landfills, where they can pose environmental risks. Also, these rechargeable batteries contain toxic substances that can leach into soil and water, leading to environmental contamination. E-waste not only poses environmental and health risks but also represents a potential loss of valuable resources contained within these discarded batteries (Sambarmurthy *et al.*, 2021; Saha *et al*., 2021).

Among the key components of lithium-ion, lithium-polymer and nickel-metal hydride rechargeable batteries are valuable metals such as lithium, cobalt, nickel, and rare earth elements (Roy *et al.*, 2021). These metals play a pivotal role in the functionality and performance of batteries, making them indispensable for various applications (Mrozik *et al.*, 2021). However, the conventional disposal methods of e-waste, often characterized by incineration and landfilling, not only squander these precious resources but also contribute to environmental pollution and resource scarcity (Sambarmurthy *et al.*, 2021; Melchor-Martinez *et al*., 2021). As society moves towards more sustainable practices, there is a pressing need to develop efficient and environmentally sound methods for the recovery of valuable metals from waste rechargeable batteries (Roy *et al.*, 2021).

2.0 MATERIALS AND METHODS

2.1. Sample Collection

Spent rechargeable batteries were collected from mobile phone and laptop repairers and users from a major repair hub located at Hospital Road and St Michaels Road by Asa Road, both in Aba and some from phone users, photographers, microphone users and repairers also within Aba. The batteries that were collected were lithium – ion, lithium-polymer and nickel - metal hydride batteries and were of different brands. A representative sample of 53 Li-ion, 30 Li-polymer and 8 Ni-MH batteries were selected. They were produced between 2013 and 2023 and used laptops, MP3, microphones and mobile phones.

2.2. Sample Preparation

The individual weights of the batteries were taken. Other data that were collected on the individual batteries were their types, years of production, countries of production, disposability, recyclability etc. They were finally grouped into 34 samples of which 22 were Li-ion, 10 were Li-polymer and 2 were NiMH (all comprising of 22 single and 12 pooled samples). The batteries were soaked in salt solution (NaCl solution) for 24 hours to ensure a complete discharge (Du *et al*., 2022). Then they were washed thoroughly with clean distilled water and heated at 60 ^{o}C in a hot air oven (Yamato Scientific DGS400 Oven) for 2 hours to dry (Bae and Kim, 2021; Zhou *et al.*, 2021). Using a pair of scissors and pliers, the batteries were disassembled. Plastic and metal casings were removed to separate the electrode materials (cathode and anode materials) and the separators (Zhou *et al.*, 2021; Sambarmurthy *et al.*, 2021).

2.3. Sample Digestion

The digestion flasks were each soaked with 10 % HNO_3 solution. Then they were rinsed with deionized water and dried in hot air oven at 60 ^{0}C for 90 mins. Oher glass wares were washed thoroughly with soap and tap water and left to dry.

A known weight (2.0 g) of the cut electrode materials was weighed into the digestion flask. Also, 5 ml of 65 % nitric acid and 10 ml of 70 % hydrochloric acid was added into the digestion flask and placed on the heating mantle/digester in a fume hood at 120 ^{0}C. On addition of acid, some of the samples changed color to greenish blue and then to maroon red when distilled water was added and allowed to boil. Brown fumes started to appear and escaped through the mouth of the digestion flask as heating began which completely disappeared after about an hour. Thereafter, 20ml of distilled water was added and allowed to boil for 10 minutes. It was brought down and allowed to cool. It was then filtered into a 50 ml flask using a Whatmann filter paper (the filtrate was about 25 ml). The filtrate was then marked up to 50 ml with distilled water and subjected to an Atomic Absorption Spectroscopy.

2.4 Measurement of Metals in the Digests

Valuable metals namely; Co, Li, Mn and Ni were detected and their concentrations determined by atomic absorption spectroscopy. Standard solutions with known concentrations of the studied metals were prepared. The AAS was turned on to warm up for a few minutes. The acetylene gas and the compressor were turned on. After venting the air, then the flow valve was turned on. The computer was turned on and the software launched and allowed to warm up for 30 minutes to stabilize the light source for optimal performance. The instrument status was checked to know if the lamp was properly positioned and if the current was good for use. Distilled water was first aspirated for 5 minutes to allow the system to warm up. The metal of interest was selected, the flame was turned on and the calibration blank was aspirated. The prepared standards were aspirated and the absorbance of each standard solution was measured. A calibration curve was plotted by plotting Absorbance value against the known Concentrations of the standards. Sample blank was aspirated after the calibration. The sample digests were aspirated using a nebulizer and the absorbance was measured at the absorption wavelengths of the metals.

2.5. Quality Control and Data Analysis

Adequate quality control measures were included in the study. Instruments were calibrated using standards while all glass and plastic-wares were cleaned properly and soaked in 10% HNO_3 overnight, then rinsed with distilled water before use. ANALAR grade reagents and deionized water were used. SPSS 10 was used for data analysis. Blanks were also employed.

3.0. RESULTS AND DISCUSSION

*3.1. **Comparison of Metal Contents of Studied Li-Ion, Li-Polymer and NiMH Batteries***

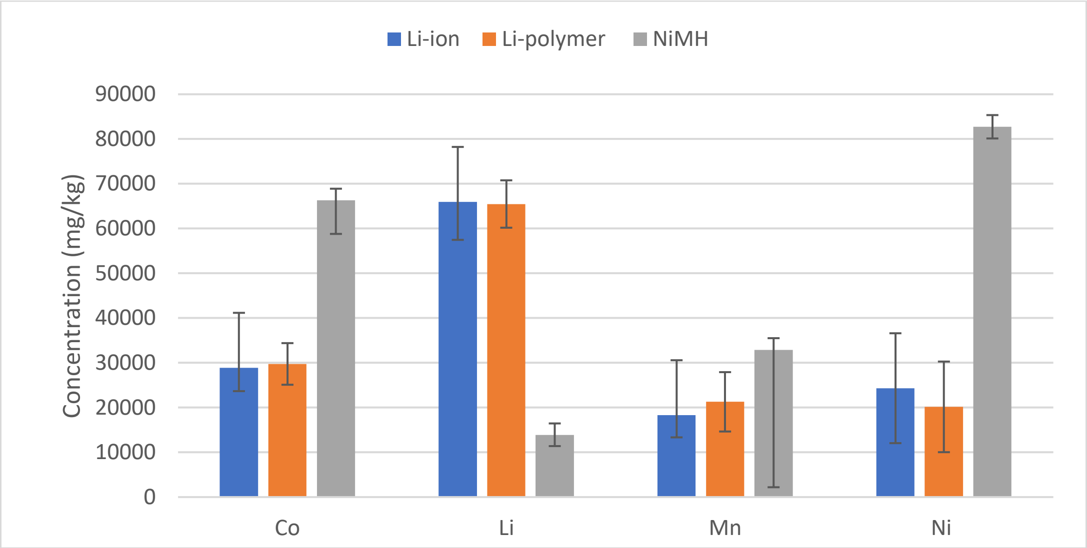

***Figure 1**: Comparison of metal contents of studied Li-ion, Li-polymer and NiMH batteries*

*3.2. **Comparison of Metal Contents of Studied Li-Ion, Li-Polymer and NiMH Batteries***

From the study results, Li contents of the li-ion and li-polymer batteries are higher as expected. The distribution of the Ni concentration is low. Co concentration is higher than Mn. There are sharp fluctuations in the distribution possibly because the batteries were of different sizes and applications. Lithium-ion batteries contain large quantities of Li and Co. On the other hand, the concentrations of Co and Ni are very high in NiMH batteries with slight differences probably resulting from differences in factory specifications. The concentrations are in this descending order: Ni, Co, Mn and Li. Higher Li was observed in Li-ion and Li-polymer batteries. Presented in Figure 1 is the summaries of the metal levels Li-ion and Nickel Metal Hydride batteries respectively.

3.3 ***Comparison of Results with Literature***

The results of the study show some closeness with recent researches. For NiMH, the Ni content is highest as expected with the value of 82735 mg/kg which is close to 75272 mg/kg as determined by Nnorom *et al*., 2009. Co concentration derived as 66287 mg/kg is equally high as obtained by Liu *et al*., 2019 (55900 mg/kg) ; same applies to Mn (32899 mg/kg) , which is similar to 30200 mg/kg obtained by Liu *et al*., 2019. For li-ion and li-polymer batteries which fall into the category of lithium batteries (LIBs), Li has the highest concentration (65961 and 65477 mg/kg). This has close values with results from Zhou *et al*; 2021 (50000-70000 mg/kg) , 51600 mg/kg from Jegan-Roy *et al*., 2021 and 70400 mg/kg from Ghassa *et al*., 2021. Also, results of Mn concentration (18310 and 21287 mg/kg) are closely related to the findings of Liu *et al*., 2019 (18700 mg/kg) as well as Ni concentration (24329 and 20159 mg/kg) which Liu *et al*., 2019 also determined as 29900 mg/kg. However, there is considerable reduction in the use of Co in the manufacture of electrode materials of PEDs as clearly reflected in the research results. In previous researches, Co concentration in LIBs ranged from 50000-311800 mg/kg but this research result shows (28899 and 29753 mg/kg). This could be as a result of a technological innovations towards the reduction in the cobalt content or complete withdrawal of cobalt from lithium battery production because of its high cost and toxic or harmful nature.

3.4. *Comparison of Metal Contents of Batteries with Regulatory Limits*

The results of this study were compared with limits used to classify waste materials as toxic such as the TTLC (Toxicity Threshold Limit Concentration), USEPA (United States Environmental Protection Agency) and EU (European Union) Allowable Limits. Presented in Table 1 are the mean values of metals alongside TTLC, EPA and EU allowable limits.

Table 1*: *Comparison of Metal Concentrations of Batteries with Allowable Limits.

Battery Chemistry	Co content (mg/kg)	Ni content (mg/kg)	Li content (mg/kg)	Mn content (mg/kg)
Li-ion	28899	24329	65961	18310
Li-polymer	29753	20159	65477	21287
NiMH	66287	82735	13851	32899
TTLC	8000	2000	-	-
EPA	250	560	-	750
EU	-	75	-	75

3.5 *Environmental Implication and Potential Health Hazard*

Improper disposal of waste rechargeable batteries can lead to the release of toxic chemicals and heavy metals into the air, soil and groundwater, posing great risk to plants, animals and humans when they spread through large areas, potentially entering the food chain leading diseases such as cancers, diseases of the central nervous system, kidney disorders, respiratory diseases, visual impairments, nausea, retarded cell growth, impairment of the reproductive system, cardiac arrest, etc. (Bolan *et al*., 2021; Melchor-Martinez *et al*., 2021). Recycling, which helps to reduce the environmental pollution caused by the improper handling of these waste batteries has some demerits such as the emission of harmful gases from pyro metallurgy and the production of harmful waste during hydrometallurgy (Bae and Kim, 2021). Rechargeable batteries can catch fire or explode if punctured or exposed to high temperatures. To mitigate these environmental implications and hazards, it’s essential to promote responsible consumption, proper disposal and recycling practices for rechargeable batteries such as battery collection programs, increasing public awareness about the environmental impacts of rechargeable batteries and the importance of recycling (Nnorom and Osibanjo, 2009).

4.0 ESTIMATION OF RECOVERABLE METALS FROM WASTE BATTERIES

Data was mined from UN Comtrade Database for the importation of batteries into Nigeria. This provided data on the quantities of rechargeable batteries imported into Nigeria from various countries (Table 2). It was assumed that at some points these batteries became waste and were disposed. Since the waste batteries contain valuable critical (scarce) raw materials, the study estimated the recoverable materials (metals) from the waste batteries. For a given year, the recoverable values were estimated using the relationship:

$$R_m = Q_b \times Mc \quad \ldots\ldots\ldots\ldots\ldots\ 1$$

Where R_m is the recoverable metal; Q_b is the quantity of battery imported; and Mc is the mean metal concentration (a given metal).

4.1 *Estimation of Recoverable Metals*

Presented in Table 2 are the recoverable metals (in metric tons) from the lithium batteries imported into Nigeria from 1999-2022.

Table 2: Recoverable Co, Li, Mn and Ni from batteries imported from 1999-2022

Year	Quantity of battery imported (tonnes)	Recoverable metals (t)			
		Co	Li	Mn	Ni
1999	179,308	5.2	11.8	3.3	4.4
2000	36,076	1.0	2.4	0.7	0.9
2001	42,259	1.2	2.8	0.8	1.0
2002	172,451	5.0	11.4	3.2	4.2
2006	69,760	2.0	4.6	1.3	1.7
2010	294,831	8.5	19.5	5.4	7.2
2015	1,835,634	53.0	121.2	33.6	44.6
Sum	2,630,319	75.9	173.7	48.3	64

Average concentration of the metals are: Co, 28.9 g/t; Li, 66 g/t; Mn, 18.3 g/t; and Ni, 24.3 g/t

4.0 CONCLUSION AND RECOMMENDATIONS

4.1 *Conclusion*

This study provides some insights into the metal levels of spent rechargeable batteries of portable electronics. The concentrations of Co, Li, Mn and Ni in Li-ion and NiMH batteries are so high and far above the TTLC, EPA and EU allowable limits for classifying these metals as toxic, some of which are 20, 40 or 100 percent beyond limits. As a result, spent batteries should be handled as toxic or hazardous wastes. Improperly handling of WRBs in Nigeria has the tendency of exposing residents and the entire ecosystem to health hazards. Recycling will make for resource conservation and generation of foreign exchange at the mineral market, thereby contributing to circular economy and economic growth. Extended Producer Responsibility (EPR) laws that hold electronics manufacturers responsible for the entire life cycle of their products including collection, recycling and disposal of electronic waste should be implemented. Advance Recycling Fee (ARF) can be introduced, in which case users pay for the end-of-life management of these batteries while purchasing the portable electronic devices. Products should be designed for durability, reparability and recyclability as well as promoting reuse to extend their lifespan. This helps to promote the principles of circular economy. Training programs and capacity-building procedures, recycling techniques and environmental regulations should be invested in.

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REVIEW

SUSTAINABLE FOOD SAFETY AND SECURITY: THE ROLE OF CHEMISTRY

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ABSTRACT

The availability, accessibility, use, and stability of wholesome food that is contaminant-free and satisfies everyone's dietary needs and food choices for an active and healthy life are all considered aspects of food safety and security. Food sustainability is the production of food in a way that improves human well-being, preserves the environment and uses natural resources as efficiently as possible. By 2050, it is predicted that there will be 10 billion people on the planet, and as people grow, food supplies will shrink. Therefore, it's imperative to find creative solutions for feeding the world's population enough food. This report aims to review the literature on the various threats to food security and safety, including climate change, reliance on fossil fuels, food losses, waste, biofuels, food additives, and allergies. It also looks at the factors that promote these threats, the general role that chemistry plays in these threats, and potential countermeasures to ensure sustainable food security and safety

Key words: Food sustainability, Hunger, Consumers, Contaminants

INTRODUCTION

Globally, food safety is a critical aspect of daily lives, affecting everyone from consumers to producers (De Boeck *et al*., 2019). It has emerged as one of the most challenging societal issues to solve in the majority of low and middle-income countries, including Nigeria (Onyeaka *et al*., 2021). Every year, millions of individuals are affected by diseases caused by eating contaminated food, particularly in underdeveloped nations (WHO, 2021). These illnesses impact children and other vulnerable populations disproportionately, including pregnant women and the elderly (GAIN, 2020). According to WHO, 600 million people, or about one in every ten, become unwell after consuming contaminated food, resulting in 420,000 fatalities each year (Havelaar *et al*., 2015). Consumption of unhealthy food is a major concern in Africa (WHO, 2021).

World Health Organization reported that 1 in 10 persons contract a foodborne illness each year, with Southeast Asia and sub-Saharan Africa having the greatest rates of food-borne illness, resulting to 91 million illnesses and 137,000 deaths annually (WHO, 2015). Food-borne diseases (FBDs) are linked to outbreaks, pose a threat to the security of global public health, and are increasingly becoming a global public health problem (Teferi *et al*., 2021). The World Health Organization (WHO) states that inadequate information, a lack of infrastructure, and improper food handling practices make foodborne illnesses (FBDs) extremely dangerous in impoverished countries. This is the outcome of inadequate food safety legislation, ineffective regulatory frameworks, a lack of funding, and improper application of food handling and sanitation procedures (Borchers *et al*., 2010).

Food security challenges have been a major global issue for many years. This is due to the fact that food security is a broad concept that spans various environmental, social, and economic spheres. Over 800 million people suffer from severe hunger worldwide, despite the fact that food production has doubled in the last three decades (Hashmi *et al*., 2018). As a result, the Sustainable Development Goals (SDGs) include SDG2 "Zero Hunger," which the United Nation has incorporated in the framework of the 2030 Agenda for Sustainable Development with the aim of eradicating global hunger and fostering universal access to food (GAU, 2015).

However, a number of factors, including the loss of agricultural land have made the global increase in food prices even more challenging in the fight against food insecurity (Yousif and Kahtani, 2014). In addition, population growth in both wealthy and developing nations has increased food consumption, which raises costs directly (Borsellino *et al*., 2020).

FOOD SAFETY AND SECURITY

The Food and Agricultural Organization of the United Nations (FAO) defines food safety as a science-based discipline, process, or activity that prevents food from containing materials that could be hazardous to a person's health. The aim of food safety is to have food that is safe to consume. Foodborne disease is a major global health concern (Havelaar *et al*., 2015). Hence, workers who come into touch with food during the stages of manufacture, processing, transport, and storage must closely adhere to hygienic norms in order to assure food safety and prevent foodborne illness (Gallo *et al*., 2020). Even with legal regulations and standards for recommended best practices, foodborne illness cases in food service outlets remain a problem. Food handler compliance with food safety regulations is intricate and incorporates multiple factors (Young *et al*. 2018), it is therefore necessary to understand the various behavioral and cognitive aspects that may affect food handler’s adherence to food safety standards and how they interact in order to design targeted methods for improving food safety in food service establishments (Veronika *et al*., 2024).

Foreign objects are the microphysical risks found in food, examples includes chips or pieces of bone, metal flakes, shotgun pellets, injection needles, pieces of product packaging, stones, glass, wood, insects or other filth, personal items, or any other foreign element that isn't often found in food products (Hyman *et al*.,1993). According to a review of medical studies, glass was the most common foreign object in food-related injury, accounting for 437 cases during a 21-years period or about 21 cases annually (Gorham and Zurek, 2006). However, each year in the US, 31 major food-contaminating pathogens result in 9.4 million illnesses and 1,350 fatalities. Given the percentage of illnesses brought on by microorganisms, microbiological quality is the most important aspect of food safety. Thus, preventing food contamination by pathogens is the primary objective of food safety (Scallan *et al*., 2011).

In order to determine the worldwide incidence of foodborne infections, the World Health Organization introduced a mechanism in 2007 (Kuchenmuller *et al*., 2009). An increasing number of foodborne illness outbreaks are linked to contaminated fruits and vegetables. The percentage of foodborne illnesses linked to fresh fruit and vegetables rose from 2% in 1990 to 16% in 2007. (Hanning *et al*., 2009).

Food security exists when all people, at all times, have physical, social, and economic access to sufficient, safe, and nutritious food which meets their dietary needs and food preferences for an active and healthy life, according to the Food and Agriculture Organization (FAO) of the United Nations. In 2010, the FAO projected that 925 million people were undernourished worldwide, this number was lower than during the 2008–2009 food and economic crisis, but it was still far too high. Climate change, reliance on fossil fuels, biodiversity loss, and the exploitation of food crops for biofuels are just a few of the many issues that impact food security.

The following are necessary for sustainable food security: (a) food availability or sufficient food production(b) food access and affordability (c) adequate nutrition, including energy, proteins, and micronutrients as well as safety and (d) stability and predictability of these conditions (Helland and Sorbo, 2014). To truly achieve the goal of ending hunger, food security and safety must complement one another. Unsafe food does not solve issues with food security, food shortages can however, occasionally be exacerbated by efforts to assure safety and quality, which results in a reduction in the quantity of food available (Vaygsholm *et al*., 2020).

Food sustainability refers to the process of growing food in a way that saves the environment, maximizes the use of available resources, guarantees farmers livelihoods, and improves the lives of all those involved in the food production process both humans and animals. A movement aimed at addressing the fact that many more resources enter our global food system than exit is propelled by this concept.

THREAT TO FOOD SAFETY, SECURITY AND SUSTAINABILITY

Sustainability of food and climate change

Crop yields can be lowered and agricultural productivity disrupted by unpredictable weather patterns, droughts, floods, and other climate related issues (Stuart Bowden, 2023). Climate change includes differences in atmospheric carbon dioxide, global temperatures, and precipitation (Delcour *et al*., 2015). These factors all have an impact on agricultural yields, soil quality, nitrogen deposition, plant variety, and crop diseases. Greenhouse gas (GHG) emissions are the main driver of climate change. Temperature, relative humidity, precipitation, and Ultra Violet radiation are among the climatic parameters that are impacted, leading to climate variability (Herrera *et al*., 2016).

Global warming is the primary outcome of the increased release of CO_2 into the earth's atmosphere, and it plays a significant role in climate change (Ramona *et al*., 2012). Warmer temperatures, changes in the water cycle, and increasingly severe and frequent extreme weather events, such as heat waves, droughts, and floods are some of the primary effects of climate change on the environment. Other effects of warming include the melting of ice caps, rising sea levels, increased erosion, and changes in deep ocean circulation (Hardy, 2003). Taken collectively, these will affect food security in the environment directly and food safety and human health indirectly.

Natural and chemical occurring toxins

Toxins are dangerous compounds that can endanger living organisms. They can be categorized according to their source, chemical makeup, and mode of action (Gupta, 2018). Toxins can be broadly classified into two groups; chemical and natural toxins. Natural toxins are substances that are created spontaneously by living things from various kingdoms of life and have a variety of biological properties and activities that, if consumed, may be harmful to human and animal health. These substances include microbial, animal, and plant toxins (Bucheli, 2014).

Contrarily, manmade materials known as chemical toxins have the potential to be harmful to living things. These compounds may consist of pesticides, herbicides, and other industrial pollutants, as well as heavy metals including lead, mercury, and cadmium (Gupta, 2018). Toxins can result in a number of ailments, such as mortality, cell death, and damage to organs (Ehtiati*et al*., 2023).

Reliance on fossil fuels

The degree of reliance on fossil fuels varies greatly between industrialized and developing nations. Even still, industrialized and developing nations use roughly the same amount of primary fossil energy in farming production. The climate change brought on by the use of fossil fuels may force changes to agro-ecological zones and have an impact on whether crops grow well in particular areas (Nakalembe *et al*., 2017). Traditional farming methods and the stability and security of food are threatened by these changes. Food security will be impacted by the growing scarcity of fossil fuels, particularly in nations that import a large amount of food. Mechanization in the agriculture sector has resulted in a significant rise in energy consumption and greenhouse gas emissions (Lin and Xu, 2018). About 44% of all agricultural energy inputs are thought to come from machinery (Olkkonen*et al*., 2023). Deforestation, greenhouse gas emissions that cause climate change, air and water pollution are all consequences of using fossil fuels. Because of these factors which includes temperature variations, altered precipitation patterns, and an increase in the frequency of extreme weather events, agriculture productivity has continued to be threatened (Stuart Bowden, 2023). Various data suggest that over 80% of the global energy production is derived from natural gas, coal, crude oil, and other fossil fuel derivatives (Wang *et al*., 2022). Nearly every economic sector, including transportation and agriculture, depends heavily on the use of fuels derived from nonrenewable sources (Wang *et al*., 2022).

These fuels have been subjected to a drastic depletion because of the continuous increasing energy demand of society, in addition to generating greenhouse gas emissions that influence climate change, deteriorate ecosystems, and cause potential risks to human health (Wu *et al*., 2023).

Food waste and losses

Food availability is decreased overall because a substantial amount of food is lost or wasted at different points in the supply chain (Stuart Bowden, 2023). Food waste is the discarding of safe and healthy food, whereas food loss is the loss of supply throughout the food chain between the producer and the market (FAO, 2011). Approximately 28% of the world's agricultural land and 8% of greenhouse gas emissions are attributed to food loss and waste (Vagsholm *et al*., 2020). Food loss and waste also indicate the resources such as land, water, energy and labour that were not used to produce the food. Important connections exist between food waste, food insecurity, and sustainability.

Along the production cycle, more than one-third of the food produced is lost or wasted (Lipinski *et al*., 2013). Food losses can also occur during and after harvest as a result of issues with handling, packing, processing, shipping, and retail. Pre-harvest errors may be the cause of food losses. For instance, over half of the vegetable crops in a US research on pre-harvest losses were not harvested (Johnson *et al*., 2018). Global food loss and waste amounts to 1.3 billion tonnes annually, according to the Food and Agriculture Organization of the United Nations (FAO, 2011). Consumers interpret best before dates as food being toxic thereafter increasing food waste and threatening food security. Other instances of food waste resulting from safety concerns are large-scale, non-targeted food recalls (Vaygsholm *et al*., 2020).

Biofuels

All forms of energy produced from renewable biological sources, such as organic, agricultural, industrial, urban, forestry, human and animal wastes, are referred to as biofuels (Powar *et al*., 2022). In certain situations, the production of food and biofuels may compete in a number of ways. Direct rivalry for resources such as land and water is one approach. In addition, using crops for biofuels might result in a loss in food availability and a rise in food prices, for instance, if they are planted on land that could be used to grow food crops (Rabbani *et al*., 2024).

The amount of land that may be utilized to produce biomass is limited and varies geographically. A greater demand for feedstock means more rivalry between biofuel and other land uses, which raises marginal costs, reduces the variety and nutritional value of the foods that are available, and may jeopardize food security. Large production facilities also come with high upfront costs, as do the expenses associated with transporting biomass and biodiesel (Nordin *et al*., 2021).

Food additives and allergies

Chemicals known as food additives are added to food to preserve it's freshness or to improve it's flavor, color, texture, and preservatives (Winter, 1994). Examples of Food additives includes food coloring, flavor enhancers, preservatives, and artificial sweeteners which can result in allergic reactions (Inetianbor *et al*., 2015). Certain persons are sensitive to specific food additives and may experience reactions such digestive diseases, nervous disorders, respiratory issues, or skin problems. Food safety is at risk due to the detrimental impacts of food addictions and the allergies that arise from them (Pandey and Upadhyay, 2012).

The role of chemistry in preserving food safety and security

The food industry places a great deal of attention on chemistry. Food chemistry is the study of chemical processes and interactions between all biological and non-biological food components (Krishan *et al*., 2016). To ensure that everyone has access to food sources, it is imperative that the unsustainable nature of the current eating practices be addressed and that more sustainable patterns be implemented.

At any stage of the production process, food can get contaminated, in order to lower the risks to food safety, control programmes like Hazard Analysis and Critical Control Points (HACCP) have been developed and put into practice in the industry. HAACP focuses primarily on pathogen reduction and prevention because microorganisms cause more illnesses than foreign items or allergens (Gorham *et al*., 2006). Therefore, more control programs should be established to monitor and control contaminants in food.

The development of efficient solutions for lowering emissions and raising resource efficiency requires an understanding of the effects that agricultural operations have on the environment and the availability of natural resources. Due to increased soil erosion, decreased soil quality, decreased agricultural productivity, and decreased food security, climate change poses a challenge to the agricultural industry and populations that depend on natural resources (Gezie, 2019). It is recommended to promote the use of particle filters in heavy-duty vehicles (HDVs), non-road mobile machinery (NRMM), ships, locomotives, and Peugeot light-duty vehicles (LDVs) (Mooney, 2007). Soot particles were classified as a class one carcinogen by the World Health Organization (WHO, 2021). The use of more than 300 million filters has significantly decreased health hazards and global warming by reducing soot particle emissions by 0.5 Mt annually (Vohra *et al*., 2021).

Because of their great efficiency, low noise, low emissions, and flexibility, electric vehicles including battery/plug-in, fuel cell, and hybrid models offer a viable substitute for traditional diesel or gasoline-powered automobiles (Das *et al*., 2020). Hydrogen fuel cells (HFCs) present an alternative energy source for various transportation applications, including heavy-duty vehicles. In Using hydrogen and oxygen, HFCs employ the proton's passage over an electrolyte membrane to transform chemical energy into electrical energy (Alavi *et al*., 2017).

The high cost of producing hydrogen, inadequate infrastructure for refueling, inadequate control strategies for efficient vehicle operation, high pressure hydrogen storage onboard, high fuel cell system cost, fuel cell deterioration, and low fuel cell stack durability in comparison to the necessary lifetime for competing with fossil fuel-powered vehicles are some of the challenges associated with HFC-powered vehicles (Mori and Hirose, 2009).More study and research should be done on the development of low-cost emerging materials for hydrogen storage, low-cost hydrogen production technologies, and fuel cell stacks to lower costs and increase durability (Ramprakash *et al*., 2022) (El-Emam and Ozcan, 2019).

Approximately 1.3 billion tons of food are lost or wasted every year in the production and supply chain that was originally meant for human consumption. The by-products of edible plants have steadily risen to the top of the food production resource hierarchy in recent years due to growing concerns about environmental and public health (Rashwan *et al*., 2023). The extraction of oil and bioactive compounds, the creation of vinegar and wine, the creation of edible coatings, and the production of biofertilizer, biogas slurry, biochar, and bottom ash are a few culinary applications for food and agricultural by-products (Peng *et al*, 2023). Animal supplements and silage can be made from food and agricultural waste. Recycling food waste and agricultural by-products can be used to make chemicals, medicines, and cosmetics (Schieber *et al*., 2001). By using these by-products in their original state or after appropriate processing, numerous important new products can be obtained with the help of pertinent industrial extraction technologies. Mechanical pressing, supercritical fluid extraction, ultrasonic-assisted extraction, microwave-assisted extraction, ionic liquid extraction, and microbial fermentation extraction are the primary extraction methods used in these applications.

Depending on the type and source of the raw materials used to produce biofuels, they can be categorized as first to fourth generation fuels (Priya *et al*., 2022). First generation biofuels are obtained from edible raw materials such as high lipid-containing seeds e.g soybean, neem, palm, sugar cane, sugar beet, potato, sorghum, wheat and corn. One of the main drawbacks of this generation of biofuels is the substantial financial, energy, and time investment required to obtain the raw materials (food crops). This, combined with their detrimental effect on the food sector, has led to conflict and debate among the global populace because of the possibility that they will become scarce as a result of price fluctuations and instability (Liu *et al*., 2021) (Astolf *et al*., 2020).

In light of this, it is recommended to use third generation biofuels, which are based on the use of aquatic crops as feedstock, such as microalgae (Choi *et al*., 2019), and fourth generation biofuels, which are derived from electro-biofuels, photobiological solar fuels, and genetically modified microorganisms, such as yeast, cyanobacteria, and microalgae (Malode *et al*., 2022).The high lipid and nutritional content of algae is one of their primary characteristics that sets them apart from other energy sources and makes them a desirable substitute for the manufacture of biofuel (Srivastava, 2019). This energy source also performs well in absorbing greenhouse gasses (CO_2), easily adaptable, grows quickly in a variety of water types (freshwater, seawater, and wastewater), and has a high photosynthetic efficiency (Choi *et al*., 2019).

In addition to improving wastewater treatment and photosynthesis, these fourth generation modified microorganisms also show that they can absorb higher CO_2 concentrations than other raw materials (Leong *et al*., 2019). Consequently, this encourages environmental preservation and makes biofuel manufacturing easier. These modified photosynthetic feedstocks are readily available, extensively distributed, affordable, and renewable (Abdullah *et al*.,2019).

To ensure the strictest regulation and control over the use of food additives that indicate their level of tolerance and any detrimental physiological effects on humans, food control laboratories and trustworthy analytical techniques should be utilized. This might be readily fixed by cutting back on the widespread usage of unnecessary food additives. This would simply limit the quantity of unhealthful meals currently available for purchase, encouraging a greater consumption of foods that are higher in nutrients (Inetianbor, 2015).

CONCLUSION

It is essential for chemist to implement practices and policies that promote sustainability and mitigate the effects of the factors influencing the food system in order to preserve the long-term viability of global food safety and security.

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Full Length Research Paper

COMPARATIVE ASSAY OF THE BIOCHEMICAL CONSTITUENTS AND SEM-EDX CHARACTERISATION OF NANOPARTICLES SYNTHESIZED FROM *Mucuna sloanei* AND *Afzelia Africana* SEEDS

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ABSTRACT

This research studied the biochemical constituents of two selected soup thickeners; *Mucuna sloanei* (ukpo) and *Afzelia africana* (akparata) by analyzing their proximate, phytochemical, vitamin and mineral compositions, as well as characterized the nanoparticles synthesized from the soup thickeners according to the requirements for green synthesis of nanomaterials using Scanning Electron Microscopy – Energy Dispersive X-ray (SEM-EDX). The samples were further subjected to GC-MS analysis. Results of proximate composition revealed that *Mucuna sloanei* had a higher carbohydrate content of 62.28±0.62% while *Afzelia africana* had a higher crude fibre content of 10.80±0.1%. Phytochemical screening results showed a higher concentration of phenol in *Afzelia africana* (212.21±3.3 mg/100g) while reducing sugar concentration was higher in *Mucuna sloanei* (16.01±2.82 mg/100g). Vitamin analysis showed that both samples contained ascorbic acid, niacin, riboflavin and thiamine. While *Afzelia africana* had relatively high niacin concentration of 136.02±4.92 mg/100g, *Mucuna sloanei* had a concentration of 84.17±3.11 mg/100g. Mineral analysis results showed that carbon and nitrogen were the most abundant elements in the samples. Both samples contained essential elements like magnesium and potassium. GCMS results showed the presence of seven bioactive components in the chromatogram of *Afzelia africana* with linoelaidic acid as the most abundant compound, identified at 33.14 minutes retention time. Whereas, the chromatogram of *Mucuna sloanei* showed three bioactive compounds with 9, 12-octadecadienoic acid (Z, Z)- as the most prevalent compound. . SEM analysis result showed the microstructures and sizes of the nanoparticles synthesized from the soup thickeners, and their shapes were spherical/ spherically distorted. These inherent properties in the soup thickeners extend/herald their uses in nutrition, pharmaceuticals, industries, and nanosynthesis as a cheaper alternative to the use of glucose as a reducing agent.

Keywords: Nanoparticles, phytochemicals, *Afzelia africana, Mucuna sloanei,* Soup thickeners, GCMS, SEM-EDX.

INTRODUCTION

Mucuna sloanei and *Afzelia africana* are seeds used as traditional soup thickeners, native to Africa and, for the most part, common among the Igbo people in South-Eastern Nigeria. Albeit their popularity in the South-Eastern parts of Nigeria, they are sparsely known or used in other parts of the country and the globe at large despite the wealth of nutrients they contain. Consequently, these readily available soup thickeners have been insufficiently utilized.

Soups constitute a large part of diet across many ethnic groups. Soups are a flavourful and tasteful liquid broth made by combining ingredients of vegetables, meat or milk, characterized by boiling, usually served hot or warm but can be served cold. Thick soups are usually emulsified with soup thickeners to get a desired consistency (Goltz, 2008).

Thickeners or thickening agents are a heterogeneous group of long chain polymers called hydrocolloids that give a thickening or gelling effect and when dispersed in a solution, increases its viscosity without significantly affecting its properties such as taste (Gavin, 2020). Soup thickeners are therefore, edible hydrocolloids used to thicken soups.

Biochemical composition in its simplest term is the particular amount and combination of different biological components in an organism or substance. It is capable of affecting the functionality, biological activity and possible applications of an organism.

SEM-EDX (scanning electron microscopy-energy dispersive X-ray) analysis is a combination of a microscopic technique (SEM) and EDX. While SEM provides detailed images of the surface morphology and analyses of micro and nanoparticle characterization, EDX is focused on analyzing the elemental composition of a sample (Nidhi *et al.,* 2019).

Nanotechnology is concerned with materials and devices and with processes taking place in the nanoscale (Jeremy, 2016). One nanometer (nm) is one billionth, or 10^{-9}, of a meter (Drexler, 1986).

Afzelia africana is the botanical name for mahogany seed. It belongs to the kingdom plantae. It is an underutilized leguminous plant in the family fabaceae. It is a famous soup thickener used in the South Eastern part of Nigeria and called akparata by the Igbos. *Afzelia africana* is an excellent source of protein as well as soluble dietary fiber, it has relatively high quantities of iron, zinc, phosphorus (Ene- Obong and Carnovale, 1992).

Mucuna sloanei is commonly known as hamburger beans and popular in Nigeria. It is a climbing plant, perennial in nature, with tripartite leaves and groups of large, greenish yellow flowers accompanied by large pods with big, very hard seeds (Rare Palm Seeds, 2023). *Mucuna sloanei is called ukpo by the Igbo people of Nigeria, yerepe by Yorubas, karasau by the Hausas and known by some others as velvet beans.* This seed belongs to the family of Fabaceae (legume plants), and is mainly cultivated in tropical regions and *form major sources of their soup thickener. Mucuna sloanei* seed is mainly used as a soup thickener; however, its benefits are not just limited to its thickening abilities. *Mucuna sloanei* has some impressive health benefits, making it one of the most sought-after thickeners.

Plate 1: *Fresh and roasted Afzelia africana (akparata) seeds*

Plate 2: *Mucuna sloanei (ukpo) seeds*

Materials and Methods

Sample Collection

Seeds of *Mucuna sloanei* and *Afzelia africana* were purchased from Onu-Imo, a market in the boundary axis of Imo and Abia States in the South Eastern part of Nigeria. The samples were identified by a Professor of Organic Chemistry in the Department of Pure and Industrial Chemistry, Abia State University, Uturu, Nigeria.

Sample Preparation and Processing

The seeds of *Mucuna sloanei* were sorted and cooked on medium heat for about 60 minutes. They were allowed to cool, dehulled and cut into small pieces. The cut pieces were spread on a tray and sundried for four days. The dried seeds were ground into flour and stored in an air-tight plastic container. *Afzelia africana* seeds were already roasted before purchase. The seeds were dehulled, washed and allowed to dry. This was followed by grinding and storage. Both processed samples were stored in air-tight plastic containers for further analysis.

Proximate Analysis

Proximate analysis was done using standard methods.

Phytochemical Screening

Qualitative and quantitative phytochemical tests were carried out using standard methods.

Determination of Vitamins

Vitamins were analysed using standard methods.

Synthesis of Iron Nanoparticles (FeNPs)

1 millimolar (mM) solution of $Fe_2SO_4 .7H_2O$ was prepared according to the requirement for generating FeNPs. (Briefly, since mass of 1 mole of $Fe_2SO_4 .7H_2O$ = 334 g, mass of 1 millimole (mM) of $Fe_2SO_4 .7H_2O$ = 334 g/1000; this gives 0.334 g. To prepare 1 L of 1mM $Fe_2SO_4 .7H_2O$, weigh out 0.334 g of $Fe_2SO_4 .7H_2O$ into a standard flask and add the required amount of water, that is, 1000 ml). Each prepared sample extract was added for the reduction and capping of Fe ions. 5 0ml of the prepared solution of $Fe_2SO_4 .7H_2O$ was added to 2 ml of each sample extract. The mixture was boiled for 30 minutes at 65 ◦C. This was followed by incubation for 24 hours at room temperature. There is a colour change from pale yellow to dark brown which confirmed the formation of FeNPs. The obtained solutions were periodically rinsed with distilled water after centrifugation at 3000 rpm for 10minutes (Deepa *et al.*, 2023).

Characterization of Iron Nanoparticles

The synthesized Iron nanoparticles were further characterized using Scanning Electron

Microscopy Energy Dispersive X-ray (SEM-EDX) analysis.

Results and Discussion

Proximate Analysis

Results of proximate analysis of *Mucuna sloanei* and *Afzelia africana* are as presented in table 1 below. The soup thickeners were primarily carbohydrates. They contained substantial amounts of protein, and contained all other primary metabolites in amounts suitable for human consumption.

Phytochemical Screening

The qualitative and quantitative phytochemical tests results of the samples are as presented in tables 2 and 3.

Table 1: Result of Proximate Analysis of the samples

Parameter (%)	*Mucuna sloanei*	*Afzelia africana*
Crude Protein	$12.49^a \pm 0.30$	$11.28^b \pm 0.40$
Crude Fibre	$4.28^b \pm 0.20$	$10.80^a \pm 0.10$
Moisture Content	$11.67^a \pm 0.10$	$3.80^b \pm 0.05$
Fat Content	$6.10^b \pm 2.02$	$12.32^a \pm 2.61$
Ash	$3.18^b \pm 0.50$	$3.51^a \pm 0.40$
Carbohydrate	$62.28^a \pm 0.62$	$58.29^b \pm 0.70$

Values show means of triplicate analysis ± standard deviation. Figures with different superscript across the rows are significantly different at ($p \leq 0.05$).

Table 2: Qualitative Phytochemical Screening Results

Parameters	*Mucuna sloanei*	*Afzelia africana*
Flavonoids	−	+++
Alkaloids	+++	−
Saponins	−	−
Tannins	+++	+
Protein	++	+++
Terpenoids	+	−
Phenol	+++	+++
Steroids	+++	++
Cardiac glycoside	−	+++
Reducing sugar	+	+
Anthraquinones	−	+

KEY: +++ Significantly present, ++ moderately present, + weakly present, − absent

Table 3: Quantitative Phytochemical Screening Results in mg/100g

Parameters	*Mucuna sloanei*	*Afzelia africana*
Flavonoids	$0.83^{b}\pm0.01$	$144.38^{a}\pm7.50$
Alkaloids	$160.44^{a}\pm8.40$	$0.62^{b}\pm0.05$
Saponins	$0.65^{b}\pm0.01$	$0. 80^{a}\pm0.01$
Tannins	$82.02^{a}\pm2.67$	$54.32^{b}\pm2.56$
Protein	$65.99^{b}\pm3.04$	$78.92^{a}\pm3.11$
Terpenoids	$108.01^{a}\pm6.04$	$68.76^{b}\pm8.08$
Phenol	$205.09^{b}\pm4.89$	$212.21^{a}\pm3.30$
Steroids	$72.38^{a}\pm4.01$	$52.03^{b}\pm1.95$
Cardiac glycoside	$0.34^{b}\pm0.10$	$10.01^{a}\pm0.22$
Reducing sugar	$16.01^{a}\pm2.82$	$10.22^{b}\pm0.92$
Anthraquinones	$0.84^{b}\pm0.10$	$3.03^{a}\pm0.36$

Values show means of triplicate analysis ± standard deviation. Figures with different superscript across the rows are significantly different at ($p \leq 0.05$).

For the phytochemical tests, the secondary metabolites were present to different degrees and in varying concentrations as presented in the preceding tables. These phytochemicals exhibit anticancer, antimicrobial, antioxidative, anthelmintic and a host of other properties making them useful in a number of industries. (Jaeger and Cuny, 2016; Sharma *et al.,* 2016).

Vitamin Analysis

Results of vitamin analysis of both samples are as shown in table 4 below.

Results on Mineral Compositions (Energy dispersive X-ray analysis)

The results of Energy dispersive x-ray (EDX) analysis for mineral (elemental) compositions of the samples are presented in table 5. EDX analysis proved the presence of all the elements presented in table 5 in the iron-synthesized nanomaterials. Carbon and nitrogen were the most abundant elements in both samples. Calcium and titanium were absent in the two samples (Dangi *et al*., 2020).

GCMS Analysis Results

The results of GCMS analysis of the samples are as presented in Tables 6 and 7 below.

Table 4: Vitamin Contents of Soup Thickeners in mg/100g

Parameter	*Mucuna sloanei*	*Afzelia africana*
Ascorbic acid (Vitamin C)	$84.17^{b}\pm3.11$	$136.02^{a}\pm4.92$
Niacin (Vitamin B3)	$3.76^{b}\pm0.62$	$4.99^{a}\pm0.64$
Riboflavin (Vitamin B2)	$29.80^{a}\pm1.44$	$26.85^{b}\pm2.00$
Thiamine (Vitamin B1)	$10.09^{b}\pm2.23$	$50.82^{a}\pm3.64$

Values show means of triplicate analysis ± standard deviation. Figures with different superscript across the rows are significantly different at ($p \leq 0.05$).

Table 5: EDX elemental composition of the iron-synthesized nanoparticles

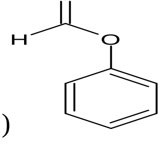
Element	*Mucuna sloanei*		*Afzelia africana*	
	Atomic Conc.	Weight Conc.	Atomic Conc.	Weight Conc.
C	72.00	67.10	81.42	76.66
N	26.24	28.51	16.47	18.08
Si	0.16	0.35	0.40	0.88
Fe	0.13	0.58	0.20	0.88
K	0.34	1.03	0.27	0.82
Al	0.12	0.24	0.35	0.74
P	0.25	0.60	0.23	0.55
Na	0.29	0.52	0.25	0.46
S	0.20	0.50	0.14	0.36
Mg	0.19	0.36	0.19	0.36
Cl	0.08	0.21	0.07	0.20
Ca	ND	ND	ND	ND
Ti	ND	ND	ND	ND

ND = Not Detected

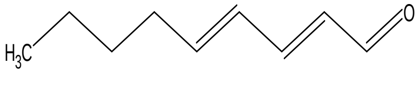
Table 6: GC-MS Results of *Afzelia africana*

RT (min)	Compound	Molecular Formula	MW gmol^{-1}	Peak Area %
12.80	Formic acid phenyl ester	$C_7H_6O_2$	122	1.71
13.24	2,4-Nonadienal, (E,E)-	$C_9H_{14}O$	138	2.88
29.76	n-hexadecanoic acid	$C_{16}H_{32}O_2$	256	18.82
31.71	Octadecanal	$C_{18}H_{36}O$	268	1.85
32.19	Octadecane, 1-(ethenyloxy)-	$C_{20}H_{40}O$	296	4.28
33.14	Linoelaidic acid	$C_{18}H_{32}O_2$	280	60.57
34.25	Gamolenic acid	$C_{18}H_{30}O_2$	278	9.89

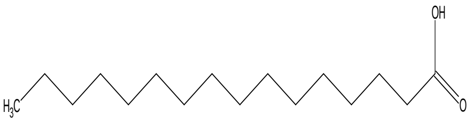
(1)



(2)

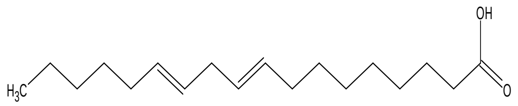


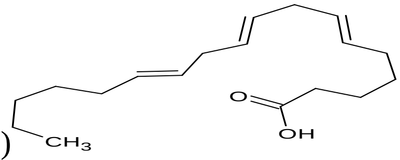
(3)



(4)

(5)

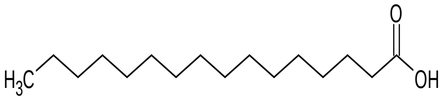
(6) 

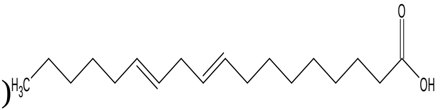
(7) 

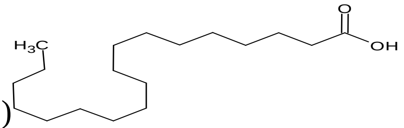
Structure 1: Formic acid phenyl ester **Structure 2:** 2,4-nonadienal, (E,E)- **Structure 3:** n-hexadecanoic acid **Structure 4:** Octadecanal **Structure 5:** Octadecane, 1-(ethenyloxy)- **Structure 6:** Linoelaidic acid **Structure 7:** Gamolenic acid

Table 7: GC-MS Results of *Mucuna sloanei*

RT (min)	Compound	Molecular Formula	MW gmol^{-1}	Peak Area %
30.08	n-hexadecanoic acid	$C_{16}H_{32}O_2$	256	12.28
33.54	9,12-octadecadienoic acid (Z,Z)-	$C_{18}H_{32}O_2$	280	46.85
34.06	Octadecanoic acid	$C_{18}H_{36}O_2$	284	40.87

(8) 

(9) 

(10) 

Structure 8: n-hexadecanoic acid **Structure 9:** 9,12-octadecadienoic acid (Z,Z)- **Structure 10:** Octadecanoic acid

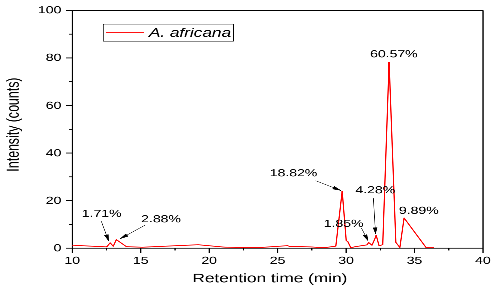


Figure 1: GC-MS Chromatogram of *Afzelia africana* extract

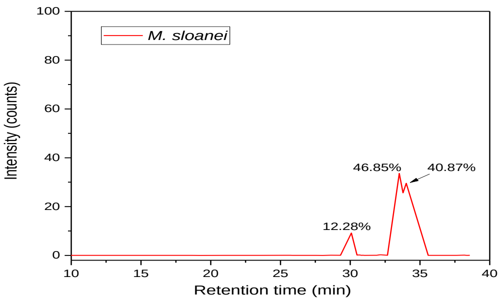


Figure 2: GC-MS Chromatogram of *M. sloanei* extract

Results on Characterization of Nanoparticles of the Samples

The results of Scanning Electron Microscopy of the iron-synthesized nanoparticles from the extracts of both samples with their respective histograms are as shown in figure 3 and table 8. The soup thickeners were characterized by scanning electron microscopy (SEM) with the micrographs presented in figure 3. Interestingly, the micrographs in both cases illustrated the surface morphology of the materials, the values of average particle size and average area of the samples. The fabricated nanoparticles have a spherical structure and/or distorted spherical structures. It is important to establish that the average particle sizes for the materials observed herein confirm their nanomaterials status. This observation agrees with those of other researchers for similar kinds of materials (Ravindra *et al*., 2012; Lee *et al*., 2019).

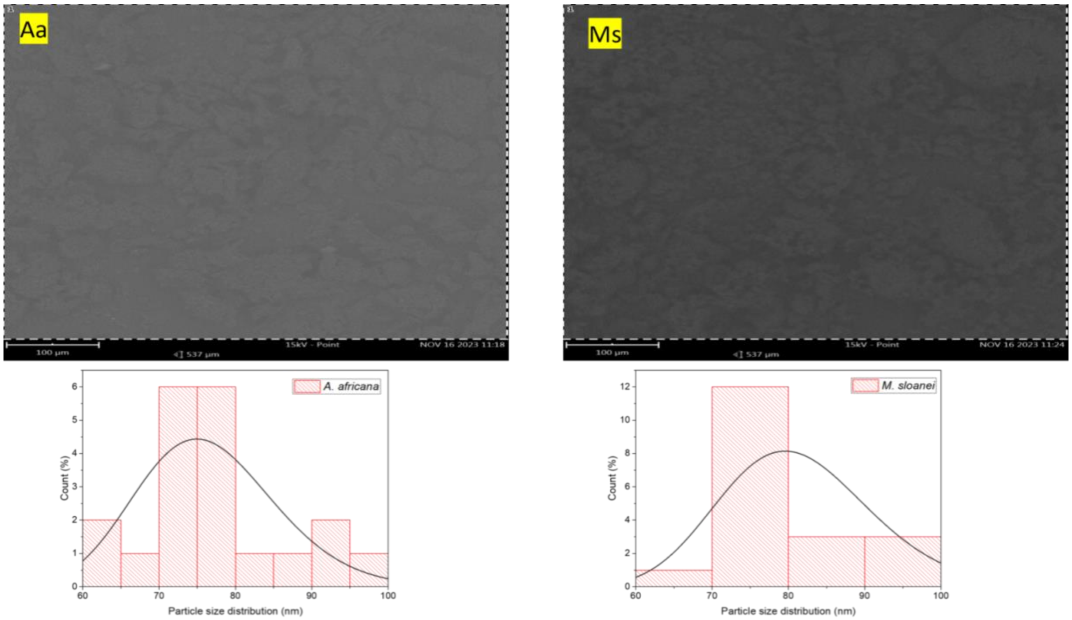


Figure 3: Scanning Electron Microscopy images of iron-synthesized nanoparticles using *Afzelia africana* (akparata) and *Mucuna sloanei* (ukpo) extracts with their respective histograms showing particle size distribution.

Table 8: Particle size and area of the phyto-synthesized nanoparticles of the samples

Sample	Average particle size (nm)	Average area (nm^2)
Mucuna sloanei	81.36	40.93
Afzelia africana	76.53	39.69

CONCLUSION

Despite the ready availability of these soup thickeners, they have been largely underutilized. This research made apparent the promise these thickeners hold as evidenced in the different parameters investigated. They contain a vast number of vital nutrients necessary in diet for proper bodily functions, and their inherent biochemicals confer on them antimicrobial, antioxidant, anticancer as well as therapeutic properties. This makes them a great choice in drug binding to improve the protein and value content of drug delivery systems. Their nanoparticle properties also make them a great alternative to the use of glucose as reducing agent in nanosynthesis. As far as we know, this investigation is the first to examine the nanoparticle properties of *Mucuna sloanei* and *Afzelia africana*. From this viewpoint, we will harness their use in green synthesis of nanomaterials and in drug delivery systems.

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CHEMICAL SOCIETY OF NIGERIA (CSN) ABIA CHAPTER
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Conference Proceedings

Full Length Research Paper

IDENTIFICATION AND CHARACTERIZATION OF POTENTIAL PATHOGENIC BACTERIAL PRESENT IN FRESH MEAT OBTAINED FROM UMUNGASI MARKET.

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ABSTRACT

Food borne diseases are a major problem affecting people in poor societies and a variety of these disease come as a result of microbial contamination during handling of the food especially fresh meat which are slaughtered in an unhygienic abattoir. Microbiological quality of meat is of great public health consideration since consumption of contaminated meat has been reported as one of the major causes of food-related diseases. This study was aimed to investigate the load of bacterial contaminant in fresh meat with different types of bacteria. Ten samples of fresh meats from 10 different butcher shops in a local market were collected. All samples were cultured on different selective media using pour plate technique to isolate any possible pathogenic bacteria present in the meat .The bacteria isolates were identified and characterized using various standard biochemical tests. The identified organisms include *Bacillus species, Lactobacillus species, Staphylococcus aureus, Samonella species, Escherichia coli and Micrococcus species* respectively. The total bacteria count ranges from to 1.2 x 10^4 to 3.5 x 10^4 while the total coliform count ranges from 1.0 x 10^4 to 2.0 x 10^4. High mesophilic aerobic bacterial counts and the presence of potentially pathogenic bacteria such as *Salmonella, Escherichia coli* pose a serious potential health hazard. Authorities and interested party should, therefore, enhance efforts to ensure that quality control and hygiene measures are put in place during meat handing.

Keywords: Bacteria, Fresh meat, Pathogenic Bacteria, Microbial contamination.

1.0 INTRODUCTION

A large variety of micro-organisms or their toxins with different mechanisms are involved in causing foodborne illness (WHO, 2007). It is estimated that 30% of people in industrialized countries suffer from diseases caused by food at least once a year (Abdollahzadeh *et al.*, 2012). Despite refrigeration chains, chemical preservatives and the application of recent techniques, it has been estimated that 25% of all food produced globally is wasted post-harvest or post slaughter due to microbial spoilage, so that this is actually the most common cause of alterations in food quality (Gram *et al.*, 2002; Cenci-Goga *et al.*, 2014).The safety of meat and meat products, which is delineated by a series of challenges associated with either microbial pathogens or other (biological or not) issues, has been one of the major societal concerns. Various events have been identified as potential explanations for the rising meat safety concerns of recent years including: changes in animal production, product processing, and distribution; increased international trade; increased worldwide meat consumption; changing consumer needs and consumption patterns (e.g., preference for minimally processed foods); higher numbers of consumers at risk for infection; and increased interest, awareness, and scrutiny by consumers (Sofos, 2008).Although various non-biological concerns have been, and are expected to continue to be, related to meat safety, such as food additives, chemical residues, and genetically modified organisms, microbial pathogens are traditionally associated with the most serious meat safety issues in terms of both foodborne illness and product recalls (Sofos, 2008). Indeed, well-identified causes of concern with regard to the safety of fresh meat and poultry are enteropathogenic bacteria, such as enterohemorrhagic *Escherichia coli* (EHEC) and *Salmonella enterica*, whose primary reservoirs are foodproducing animals (Rhoades *et al*., 2009). On the other hand, the pathogenic bacterium *Listeria monocytogenes* has been regarded as the pathogen of concern in ready-to-eat (RTE) meat and poultry products exposed to postprocessing contamination and supporting the organism's growth during storage (USFDA/USDA-FSIS, 2003). Meat represents one of the most perishable (Doulgeraki *et al*., 2012): first, for the presence of chemical and enzymatic activities, and second, because it constitutes a perfect pabulum for the growth of a wide variety of microorganisms, especially as a result of its nutrient composition, high water content and moderate pH (Dave and Ghaly, 2011). Microbial growth, oxidation and enzymatic autolysis are the three basic mechanisms responsible for the spoilage of meat. In addition to lipid oxidation and enzyme reactions, meat spoilage is almost always caused by microbial growth. Therefore, this study was conducted to evaluate the bacteriological quality and safety of fresh meat sold in some local markets within Aba North Metropolis.

2.0 MATERIALS AND METHODS.

2.1 Sample collection

Ten samples of fresh meats from 10 different butcher shops in a local market within Aba North LGA in Abia state were purchased and transported to the laboratory in a clean dry and sterile bag packed in insulated containers with ice packs. Analysis was carried out within 6hours after sampling.

2.2 Sample/ Microbiological analyses

The samples were aseptically cut into thin smaller pieces using sterile knife. The analytical portions were placed in separate sterile plastic bags and homogenised in 200 mL of distilled water, this was used as stock. Serial dilutions were achieved up to five fold (10^5) using normal saline as the diluent . The serially diluted samples (0.1 mL) were inoculated using pour plate technique on Nutrient, Mac-Conkey, Salmonella Shigella(SSA) Chromocult, Mannitol salt, and Mannitol Yolk Polymyxin Agar(MYP) for the enumeration of total bacteria count, total coliform count, *Salmonella sp, Escherichia coli, Staphylococcus sp* and *Bacillus* sp. The plates were incubated at 37°C for 24 hours. Isolates were identified and characterized by cultural, morphological characteristics and Gram staining technique, as well as biochemical tests using the methods described by Cheesbrough (2010).

2.3 Biochemical tests employed in the Identification.

Catalase test: Two drops of 3% hydrogen peroxide was placed on a clean grease free slide and the test organism was placed on the slide using a sterile wire loop. The reaction was observed for effervescence (Cheesbrough 2010).

Oxidase test: A piece of filter paper was placed in a clean Petri dish, 2drops of freshly prepared oxidase reagent (tetramethyl p-phenylenes diamine dihydrochloride) was placed at the centre of the filter paper using a glass rod, the test organisms was collected and smear on the filter paper. The paper was examined for purple-Blue colour within 10 seconds (Cheesbrough 2010).

Indole test: The bacterial isolate was inoculated into a bijou bottle containing 3ml of sterile typtone broth and was incubated for 48hrs at 37^0C. 0.5ml of Kovac,s indole reagent was added. The solution was observed within 10minutes for colour change. Appearance of red colour indicates a positive reaction (that is presence of indole) while a green colour indicates a negative result (Cheesbrough 2010).

Citrate utilization test: This test was used to identify which of the isolates can utilize citrate as the sole source of carbon for metabolism. The test is usually used as an aid in the differentiation of organisms in the entrobacteriacceae and most other genera. The medium used for this test was the Simon's citrate agar. Slant tubes of Simon's citrate agar were inoculated with young culture of the isolate the inoculation was done by streaking and stabbing the medium on the tubes using sterile inoculating wire loop containing the culture. The tubes were then incubated at $37^0{}_C$ for about 24-48hours. A change in colour from green to bright blue after about 24-48 hours of incubation indicates positive result (Cheesbrough 2010).

Methyl red: The methyl red test was employed to detect the production of sufficient and during the fermentation of glucose and the maintenance of condition; the pH of a 24hours old culture was sustained below a value of about 4.5 as shown by a change in colour of the incubation. The voges-proskauer test was ran to test the ability of the organisms to produce acetylementhylecarbinol. The tests were ran using the commercially prepared MR (methylred) medium. Large inoculum of the test organism was picked and inoculated into the prepared and sterilized test tubes. Three (3) drops of methyl red indicator was added into the culture to the test-tube and the test tube was shaken. A red colour indicates a positive reaction while a yellow colour indicates a negative result (Cheesbrough 2010).

Sugar Fermentation test: The fermentation medium was inoculated with two loops full of the isolate suspension. The tubes containing inverted Durham tubes were then incubated at 37^0C and observed 24hourly for two drops. Growth acid and or gas production were observed and recorded. The sugar tested was mannitol (Cheesbrough 2010).

2.4 Gram reaction /Microscopy

The cultural characteristics suchas size, pigment, margin, elevation, form and surface of the isolates on the agar plate were observed. The smears of the isolates were prepared on clean grease-free slides and heat-fixed. Two drops of Crystal violet was added for 60 seconds, followed by Gram's iodine for 60 seconds. The slides were rinsed with water and decolorized using alcohol for 15 seconds and rinsed with water. The decolorized slide was counter stained with Safranine for 60 seconds. It was rinsed off using water. The slides were air-dried and viewed under the microscope using oil immersion lens.

- **RESULTS.**

The results of the experiments are shown below.

Table 1. Morphological characteristics of the bacterial isolate

Shape	Colour	Opacity	Edge	Elevation
Circular	creamy	Opaque	entire	Convex
Irregular	Creamy	Opaque	Rhizoid	Flat
Irregular	Greenish blue	Opaque	Rhizoid	Flat
Circular	creamy	Opaque	entire	Convex

Table 2: Mean colony count for total bacterial count (TBC), total coliform count (TCC) and total fungal count (TFC) of minced meat.

Samples	TBC	TCC
A	2.0×10^4	1.1×10^4
B	1.2×10^4	2.0×10^4
C	2.4×10^4	1.0×10^4
D	1.4×10^4	0.2×10^4
E	3.5×10^4	0.3×10^4

Table 3: Gram reaction and biochemical characteristics of bacterial isolates from meat.

Morphology	Gran	Catalase	Coaqulase	Oxidase	Citrate	Indole	M/R	V/P	Glucose	Lactose	Most Probable Isolates
Bacilli	-	-	-	-	-	+	-	-	-/-	A/-	*Shigella* sp
Cocci	-	+	-	-	+	-	-	+	A/G	A/-	*Proteus* sp
Bacilli	-	-	-	-	-	+	+	-	A/G	A/-	*Enterobacter* sp
Baccilli	-	+	-	+	-	-	+		A/G	A/G	*Pseudomonas* sp

Table:4: Occurrence of each isolates in the sample

Samples	*Shigella*	*Proteus*	*Enterobacter*	*Pseudomonas*	Percentage (%) Occurrence
A	+	+	-	-	50
B	-	+	+	-	50
C	+	-	+	-	50
D	+	-	+	+	75
E	+	+	-	+	75
Total	60	40	40	40	

DISCUSSION

The study revealed that some of the meat were contaminated having significant growth at varying counts (Table.2) and a total of four (4) bacteria were associated from the food products(Table 3). These finding supports that reported by Odu and Akano. (2012); Nwachukwu and Nwaigwe (2013) who reported similar findings. The study also collaborates with the findings of Ghosh *et al*. (2005) and Laumar *et al*. (2006) who reported equally a high prevalence of *Enterobacter* and *Staphylococcus* sp in vended meat (Table 5). The sources of bacterial contamination of these product may differ. It is however most likely that the presence of coliforms bacteria (*Enterobacter* sp) indicates possible feacal contamination of the meat, water and other utensils used in the processing. According to Akbar and Anal (2013), *Salmonella* and *Staphylococcus* sp. are the most common food borne pathogens and responsible for food poisoning and food associated infections

CONCLUSION

The findings of this study of fresh meat sampled revealed that some of the samples have high microbial load in the samples and showed that the total aerobic colony counts were above the acceptable limit. The result obtained indicated that the meat were contaminated with different bacterial pathogens such as *Staphylococcus, Bacillus, Enterobacter,* and *Pseudomonas*. The presence of these food pathogens in the foods could pose a serious public health hazard to unsuspecting consumers as all these bacterial pathogens have been implicated in food borne illnesses and diarrheal diseases.

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CHEMICAL SOCIETY OF NIGERIA (CSN) ABIA CHAPTER

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Conference Proceedings

Full Length Research Paper

PHYSICOCHEMICAL STUDIES OF BOTTLED WATER BRANDS SOLD IN ABAKALIKI AND EVALUATION OF THE MICROPLASTIC CONTENTS USING A SPECTROSCOPIC TECHNIQUE

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ABSTRACT

Water is life to both plants and animals. It is detrimental and life threatening when polluted water is ingested. Physicochemical and spectroscopic methods were used to determine the quantities of microplastics in water. The results of the physical parameters of the samples of the bottled water conducted showed that they were tasteless, colourless and odourless. This showed that the bottled water samples had good aesthetic value in terms of their physical properties when compared to the World Health Organization standard limit for drinking water. The temperatures of the bottled water samples were within the range of 20.0 ℃ to 30.0 ℃, while pH ranged from 6.5 to 7.5, which are within the acceptable limit of WHO. Acidity, alkalinity, TDS, TSS, SO_4^{2-} and Cl^- were observed to range from 74 to 122 for acidity while that of alkalinity ranged from 30 to 150. The result of the TDS, TSS, SO_4^{2-}, and Cl^- had a range of 5.01 to 5.014; 21.07 to 23.21; 0.78 to 0.84; 24.8 to 30.5 respectively. From the results of the FTIR analysis carried out on the bottled water samples, the absorption peak of sample A1 were 1397, 1636, 1830, 2303, 3261, and 3749 cm^{-1}; A2: 1640, 2117, 3268; A3: 1640, 2120, 3268; A4: 1640, 2124, 3268; A5: 1640, 2105 and 3273 cm^{-1}. There were three absorption peaks each of samples A1 to A5 except sample A1 which had six absorption peaks. The functional groups that correspond to the absorption peak of samples A1 to A5 were C=C, C=O, O-H, and an additional C-O for sample A1. Interestingly, all the studied samples were absorbed at 1640 cm^{-1} while other absorption peaks varied. The polymer types detected were PET and PE.

Key Words: Physicochemical, micro-plastic, bottle-water, spectroscopy

INTRODUCTION

Water is an essential resource for human health, and the quality of drinking water is of paramount importance. Water is a chemical substance composed of hydrogen (H) and oxygen (O) in the ratio of 2:1. It is formed by the chemical reaction of hydrogen and oxygen and exists as solid, liquid, and as well gas. Water is very essential to both plants and animals. It can dissolve other chemical substances. Water gets to the sea through continual movement of the water cycle such as evaporation, transpiration, condensation, precipitation, and runoff. Water plays a vital role in the economic growth of any country. Transportation of agricultural products from one country of the world to the other is majorly done using boats or ships through the seas, rivers, and as well oceans. Without the existence of water, fishing and other agricultural activities would not be possible. Water is used in industrial processes due to its excellent solvents for a variety of substances both minerals and organic. Water is used for entertainment and sports such as swimming, boat racing, diving, etc. All these uses of water will hampered if the water is polluted and in recent years, concerns have arisen regarding the presence of emerging contaminants like microplastics (MPs) in water which presents a potential health risk to humans and the environment. According to a complete assessment of clinical proof posted through the European Union's Scientific Advice Mechanism in 2019, microplastics are found in every environmental matrix Baldwin *et al.*, (2016) While there may be no proof of a huge ecological change from microplastics yet, dangers associated with them may probably become enormous within a century if they are discharged at the current levels in the environment Helcoski *et al.*, (2020). Microplastics are not conspicuous, being less than 5 mm in size and are typically invisible to the bare eye. Particles of this size are available to a much broader variety of species, enter the food chain at the bottom, become embedded in animal tissue, and are then undetectable through unaided visible inspection (Eerkes *et al.*, 2015). The large quantities of plastic presently in the environment portend extended periods of degradation, release of poisonous compounds and toxicity to biota (Rillig *et al.*, 2021). Microplastics have been detected not just in marine but also in freshwater systems which include marshes, streams, ponds, lakes, and rivers in (Europe, North America, South America, Asia, and Australia) (Eerkes *et al.*, 2015; Baldwin *et al.*, 2016; Helcoski *et al.*, 2020). This study focuses on the physicochemical and spectroscopic evaluation of microplastics in bottle water samples sold in Abakaliki, Nigeria

MATERIALS AND METHODS

Study Area and Sampling Location

The study was carried out in the Abakaliki metropolis. Abakaliki is the capital of Ebonyi State. It is located in the southeastern part of Nigeria at longitude 8^o 061 49.25E and latitude 6^o 191 29.46N. It is about 64 km from Enugu.

Sample Collection

Five (5) different bottled water samples were purchased in triplicate and labeled A1, A2, A3, A4, and A5. They were stored in an ice chest before transportation to the laboratory for analysis.

Sample Processing

The water samples were filtered using Whatman 1823-047 grade GF/D glass fibre filter paper with a pore size of 2.7 µmin to separate the MNPs from the bulk water (Olarinmoye *et al.*, 2020). The MNPs obtained from filtration were thoroughly washed with distilled water and oven-dried at 65 °C. The mass of the MNPs was then determined by weighing the dried solid MNPs using an analytical balance to the nearest 0.1 mg (Masura *et al.*, 2015).

Physicochemical Parameters

Temperature, pH, and total dissolved solids (TDS) were determined at the point of sample collection with a pre-calibrated Hanna HI98194 pH/EC/DO multi-parameter Test Meter.

Sulphate

Sulphate was determined by measuring 25 mL of distilled water as blank and 25 mL of sample into a 250 mL conical flask followed by the addition of 1 mL conditioning reagent and thorough mixing. $BaCl_2$ crystals (0.5 g) were added and the mixture stirred for 1 min. A Bio-base double beam UV-VIS spectrophotometer was blanked with distilled-deionized water before the sample was read off at 450 nm at 60s intervals.

Chloride

Chloride was determined by measuring 50 ml of the sample into a 250 ml conical flask and adding 1 mL of K_2CrO_4 indicator, shaking the flask before titrating with 0.0141M $AgNO_3$ to a pinkish-yellow end-point. A reagent blank value was established by titrating distilled water as above. Chloride was calculated as follows:

$$\text{mgCl}^{-}/\text{L} = \frac{(\text{A}-\text{B}) \text{ x M x } 35450}{\text{mL of Sample}}$$

(A = volume of 0.0141 M $AgNO_3$ used for titration, B = Volume of $AgNO_3$ used for Blank titration, M = molarity of $AgNO_3$)

Colour

The colours of the samples were determined with the platinum-cobalt method, by measuring 10 mL of a well-mixed and filtered sample (with 0.45 µm membrane filter) into a sample cuvette. The true colour was read off in platinum cobalt units (PCU) from the photometer following blanking with deionized water and determination of apparent colour by inserting a cuvette filled with 10 mL of unfiltered sample.

Odour

After sample collection, clean bottle was half filled with the water sample. A stopper was inserted on it and it was shaken vigorously for 2 to 3 seconds then quickly observing by placing nostrils close to bottle neck and perceiving the released smell (sample was at room temperature)

Alkalinity

Anhydrous Na_2CO_3 (3g) was heated for 16 min at moderate heat with continuous stirring in a clean crucible, cooled in a desiccator and weighed. The cycle was repeated until constant weight was attained. 1.325g of Na_2CO_3 was dissolved in a small quantity of hot distilled water in a beaker and transferred into a 250 ml volumetric flask. The beaker was washed into the flask and the flask was made up to mark with distilled water giving 0.05 mol dm^{-3} Na_2CO_3. 2 ml of concentrated HCl (37 %; Specific gravity, 1.19) was dissolved in 250 ml of distilled water and was standardized with the Na_2CO_3 solution (methyl orange as indicator). 100 ml of water sample was measured into a conical flask and 3 drops of methyl orange were added. It was titrated with 0.01mol dm^{-3}HCl until a faint orange colour appeared (methyl orange end-point).

$$\text{Total alkalinity (mg/lit } CaCO_3) = \frac{\text{Total titre (ml) x500}}{\text{ml of sample}}$$

MNPS Characterization

Visual Sorting –This identifies MNP numbers, sizes, shapes and colours. MNPs were identified using a Nikon SMZ 745T stereomicroscope at 20–40× magnification (Crossman *et al*., 2020).

FTIR Analysis

Larger microplastics N300 µm, excluding fibres, were analyzed on an Agilent Cary 630 single bounce attenuated total reflectance-FTIR (ATR-FTIR). All smaller particles and fibers were analyzed on a PerkinElmer Spotlight 400 micro-FTIR (µFT-IR). Spectra were compared to several libraries including the Agilent Polymer and Elastomer, Oring and Seal ATR, PerkinElmer ATR Polymer, and BASEMAN libraries (Primpke*et al*., 2018). The a, b and c axes of each identified particle were recorded and used to establish particle volume, to facilitate a mass-based conversion between particle counts and particle masses. ATR-FTIR and µFTIR were used to identify particle sizes, numbers, and particle polymer composition.

RESULTS AND DISCUSSION

Table 1 shows the sample IDs, company name and the corresponding National Agency for Food Drugs Administration and Control (NAFDAC) registration numbers and as well the size and quantity of the microplastics obtained through visual sorting. The shape of the polymer obtained was pellet in sample A1 and granules in samples A2, A3, A4 and A5 while the colour were all white.

Table 1: Sample ID's, Brand Name and Their Respective NAFDAC Numbers

Sample ID's	Brand name	NAFDAC No.	Size of MNPs (μm)	Quantity of MNPs
A1	Smart	D1-2155L	18	16
A2	EndyBest	C1-2247L	34	5
A3	Ucheoma	A1-101727L	44	6
A4	Om-classic	A1-101888L	31	8
A5	Chex	A1-101603L	17	8

All the samples had NAFDAC numbers manufacturing date, expiring date, but had no batch number.

Table 2 shows the physicochemical parameters of the bottle water samples. The results indicated that the samples were tasteless, colourless, and odourless. This showed that the bottled water samples had good aesthetic value in terms of their physical properties when compared to the World Health Organization (WHO) standard limit for drinking water. The temperatures of the bottled water samples were within the range of 20.0 – 30.0 ℃ while pH ranged from 6.5 to 7.5. A change in the pH can change the forms of some chemicals in the water but the pH of all the samples were within the recommended range of 6.5 to 8.5 (WHO, 2011).

Total Suspended Solids (TSS) ranged from 0.78 to 0.84 mg/L. The TDS content of all samples were below the maximum limit set by WHO and are similar to the results obtained by Aktar *et al*. (2017). Low TDS values of drinking water have no harmful effects on consumers (Okorondu and Anyadoh-Nwadike, 2015). Total dissolved solid is a measure of the level of dissolved solid in water and it influences the taste of drinking water when it is above the WHO limit of 500 mg/L. These results showed that all the water samples were safe for consumption. This is also in line with the result obtained by (Ajewole, 2005), who reported the pH range of the water sample as 6.0 to 7.13. Chloride ions concentration was determined to vary from 25.4 to 30.5 mg/L. The result is appreciably lower than the WHO guideline value of 250 mg/L. This chloride limit was set, primarily based on taste considerations. However, no adverse health effects on humans have been reported from the intake of water containing even higher concentrations of chloride (Ndinwa *et al*., 2012). However, a higher concentration of chloride ions in drinking water can add taste to the water. Chloride occurs naturally in groundwater, streams, and lakes, but the presence of relatively high chloride concentration in fresh water (250 mg/L or more) may indicate wastewater pollution (Chatterjee, 2001). Chlorides are not usually harmful to people; however, the sodium part of table salt has been connected to kidney and heart diseases (Nwachukwu and Ume, 2013). The alkalinity of water is its acid-neutralizing capacity comprised of the total of all titratable bases (Ajewole, 2005). The values of alkalinity vary from 30 to 150 mg/L for all brands of bottle water which is below the WHO maximum limit of 200 mg/L. Sulphate ions (SO_4^{2-}) occur in natural water and wastewater. The maximum level of sulphate suggested by the World Health Organization (WHO) in the Guidelines for Drinking-water Quality is 250 mg/L. The sulphate concentrations of the studied samples ranged from 20.14 to 23.21 mg/L. If high concentrations of SO_4^{2-} are present in drinking water, there may be objectionable tastes or unwanted laxative effects (Ibe and Okplenye, 2005), but there is no significant danger to public health.

Table 2: Physicochemical parameters of the bottled water samples (mg/L)

Sample ID's	pH	Temperature °C	Colour	Odour	Acidity	Alkalinity	TDS	TSS	SO_4	Chloride
A1	6.7	26.0	Colourless	Odourless	94	100	5.01	0.8	23.21	25.4
A2	7.5	20.0	Colourless	Odourless	122	30	5.003	0.79	22.71	28.1
A3	6.5	29.0	Colourless	Odourless	112	80	5.013	0.84	21.56	24.8
A4	7.0	30.0	Colourless	Odourless	74	150	5.011	0.78	21.07	30.5
A5	6.5	22.0	Colourless	Odourless	76	120	5.014	0.78	20.14	26.2
(WHO,2011)	6.5-8.5	Ambient	No visible colour	Odourless	8.2	200	500	25	250	250

FTIR Results

The Fourier Transform Infrared (FTIR) spectroscopy was conducted to ascertain the functional groups present in the sample under investigation. The FTIR works on the principle that the molecule vibrates at specified frequencies and ranges from 200 cm^{-1} to 4000 cm^{-1} which falls within the IR portion of the electromagnetic spectrum. When an IR is incident on a sample, it absorbs radiation at a frequency similar to its molecular vibration frequency and transmits other frequencies. The infrared spectrometer detects the frequencies of absorbed vibrations, and a plot of absorbed energy against the infrared spectrum is obtained. The table below shows the results obtained from the infrared spectrum of the studied samples.

Table 3: FTIR results for sample A1 to A5

S/N	Sample ID's	Absorption peak (cm^{-1})	Functional groups	Polymer Type
1	A1	1397, 1636, 1830, 2303, 3261, 3749	C-O, C=C, $C \equiv C$, O-H	PE, PET, PVC
2	A2	1640, 2117, 3268	C=C, C=O, O-H	PE, PET
3	A3	1640, 2120, 3268	C=C, C=O , O-H	PE, PET
4	A4	1640, 2124, 3268	C=C, C=O, O-H	PE, PET
5	A5	1640, 2105, 3272	C=C, C=O, O-H	PE, PET

Figures 1 to 5 below were the FTIR spectrum results obtained from the bottled water samples labeled A1to A5.

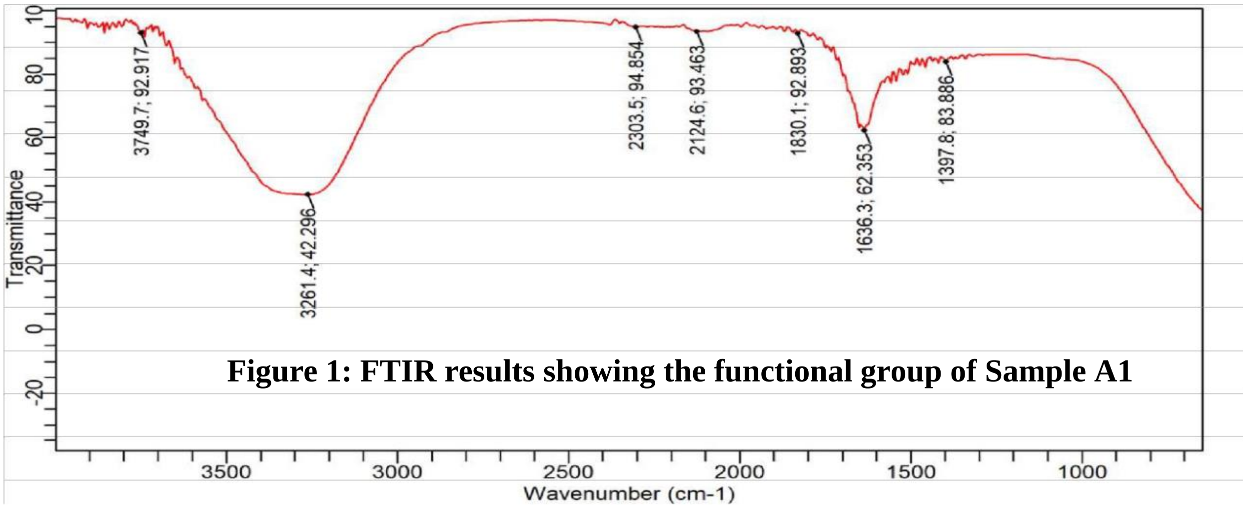

Figure 1: FTIR results showing the functional group of Sample A1

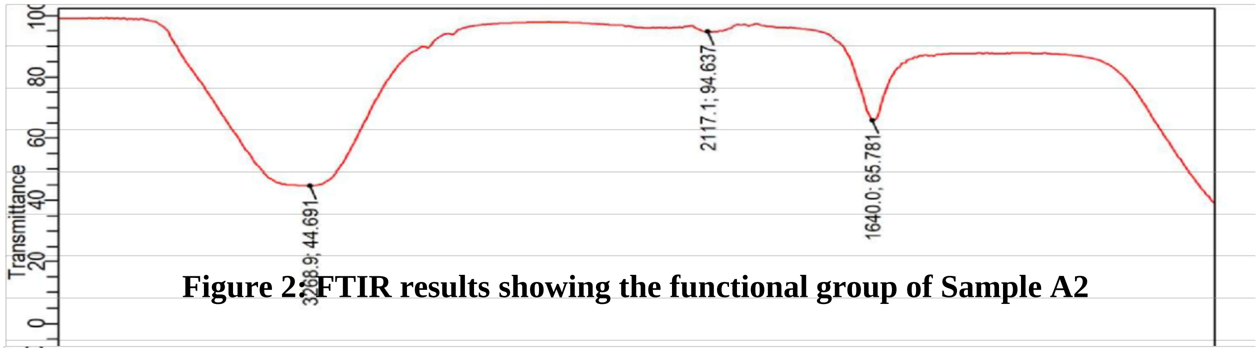

Figure 2: FTIR results showing the functional group of Sample A2

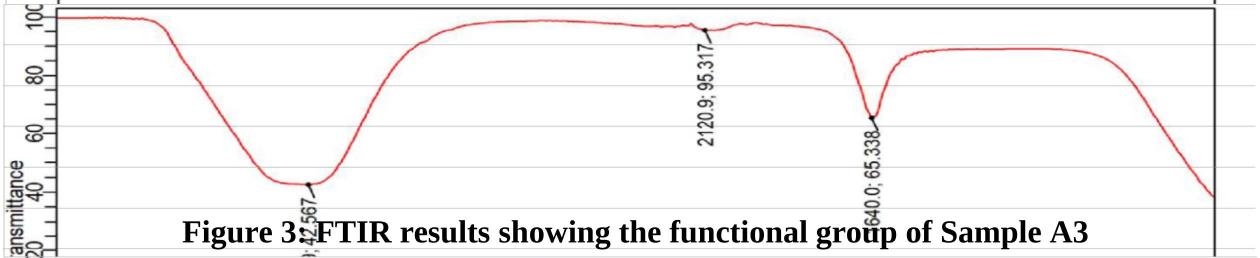

Figure 3: FTIR results showing the functional group of Sample A3

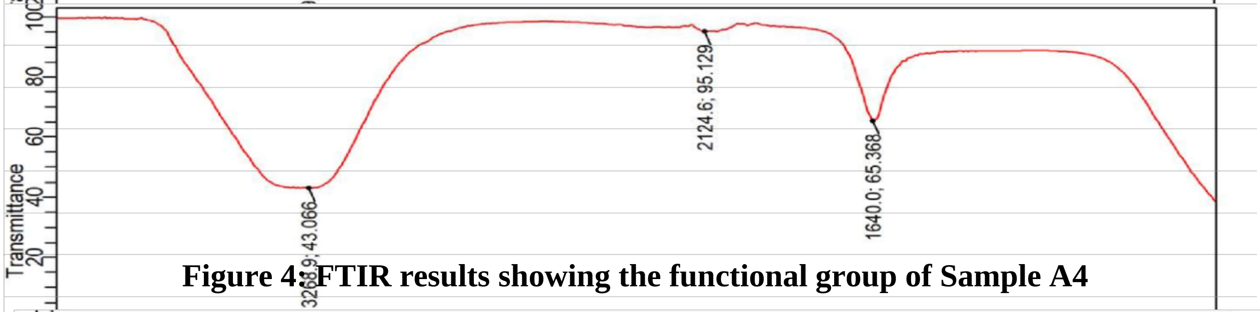

Figure 4: FTIR results showing the functional group of Sample A4

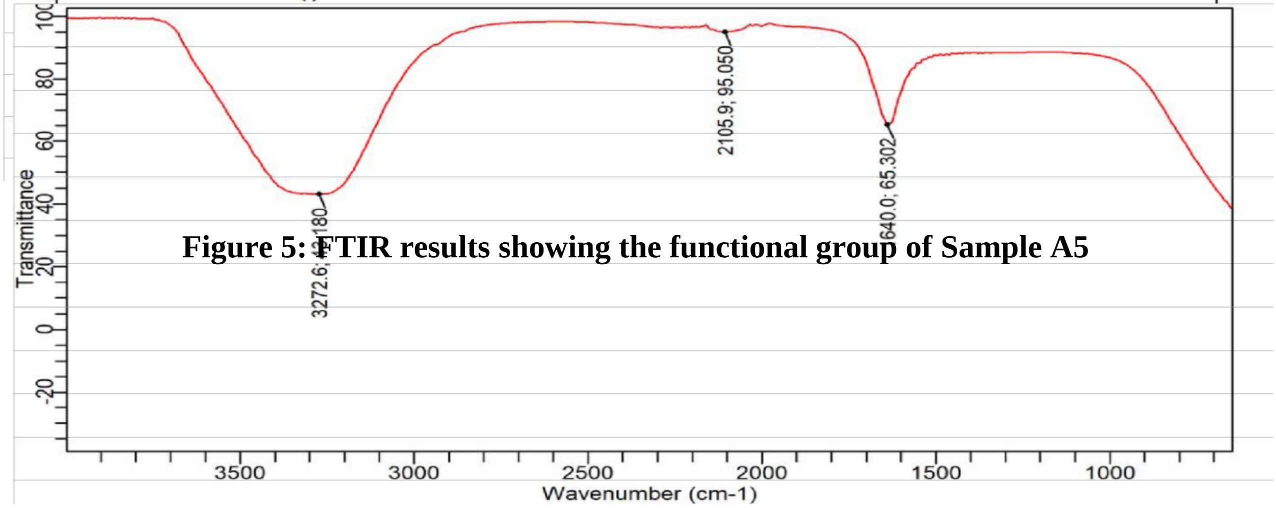

Figure 5: FTIR results showing the functional group of Sample A5

From the results of the analysis carried out on the bottled water samples, the absorption peak of sample A1 were 1397, 1636, 1830, 2303, 3261, and 3749 cm^{-1}; A2: 1640, 2117, 3268; A3: 1640, 2120, 3268; A4: 1640, 2124, 3268; A5: 1640, 2105 and 3273 cm^{-1}. There were three absorption peaks each of samples A1 to A5 except sample A1 which had six absorption peaks. The functional groups that correspond to the absorption peak of samples A1 to A5 were C=C, C=O, O-H, and an additional C-O for sample A1. Interestingly, all the studied samples absorbed at 1640 cm^{-1} while other absorption peaks varied. The IR result obtained by Belal *et al* (2023) in plastic bottled water showed strong peaks at 2916 cm^{-1}, 2846 cm^{-1}, and 2914 cm^{-1} showing C-H stretch, CH_2 bend at the peak of 1466 cm^{-1}, 1462 cm^{-1} and 1747 cm^{-1} indicating C=O, while 1241 cm^{-1}, 1035 cm^{-1} indicate C-O bond stretching. The results were applicable to what was obtained in sample A1 of this study. Jung *et al* (2021) in their study obtained 2920 cm^{-1}, and 2850 cm^{-1} to show C-H bond stretching vibration. The presence of a peak at 1394 cm^{-1} in sample A1 corresponding to C-O stretching vibration indicates the presence of ester groups Cingolain *et al* (2022). This suggests that the plastic identified in the sample may be composed of polyester materials which are commonly used in the production of various plastic products including packaging materials. Furthermore, the detection of peaks at 2117cm^{-1}, 2118 cm^{-1}, 2102 cm^{-1}, 2109 cm^{-1}, 2113 cm^{-1}, and 2124 cm^{-1} in the various water samples is an indication of the presence of C=O bond stretching vibration pointing toward the presence of carbonyl groups in the polymer Huang *et al* (2022) and the presence of 1640 cm^{-1}, 1636 cm^{-1}, and 1830 cm^{-1} in sample A1 represent C=C bond of an aromatic. These C-O and C=C arid associated with plastic like polyethylene terephthalate (PET), widely used materials in the manufacturing of beverage bottles and food containers Murray and Omeci (2020). More so, the identification of peaks at 3261 cm^{-1}, 3268 cm^{-1}, 3272 cm^{-1}, and 3749 cm^{-1} correspond to O-H stretching vibration, suggesting the presence of a hydroxyl group in the sample. This O-H can be attributed to the additive or surface modification applied to the plastic materials. In the determination of micro-plastic in water samples in various other studies, the most frequently identified plastics were PE, PET, PP, PS, and PVC (Oßmann *et al*., 2018, Schymanski *et al*., 2018, Danopoulos *et al*., 2020, Kankanige Babel, 2020). This is similar to the PE, PET, and PVC obtained in this study.

CONCLUSION

The physicochemical and spectroscopic evaluation of microplastic in bottled water sold in the Abakaliki metropolis was investigated. The result obtained showed the presence of polymers. The physical properties of the bottled water samples analyzed also indicated that the bottled water sold in Abakaliki has good aesthetic values as it complies with World Health Organization standards for drinking water. As water is life to both plants and animals it is detrimental and life threatening when polluted form of water is ingested. Even though there is no backing evidence of the dangers of nanoplastic consumption to human health but can bio-accumulate in the body tissue and this may result in future life-threatening.

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CHEMICAL SOCIETY OF NIGERIA (CSN) ABIA CHAPTER
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Conference Proceedings

Full Length Research Paper

EFFECT OF PROCESSING METHOD ON CAROTENOID PROFILES OF OIL EXTRACTED FROM THREE VARIETIES OF NIGERIAN PALM FRUITS (*Elaeis guineensis*)

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ABSTRACT

This study assessed the effect of processing method on the carotenoid profile of oil from three varieties of the Nigerian oil palm fruits (*elaise guinensis*). Specific varieties of the elaise guinensis, which are the dura, pesifera and tenera were obtained from National Institute for oil palm research (NIFOR) in Edo state. Each sample was divided into two and processed in two different methods as commonly practiced in the East, the hot and cold processes. The oil extracted from each of the process was then analyzed for oil characteristics using standard analytical methods while the carotenoid profile was analyze using HPLC C_{21} column. The results generated were subjected to one-way analysis of variance (ANOVA). The results of carotenoid constituent indentified include: lutein, neurosporene (trans), neurosporene (cis), α-Zeacarotene(cis), α-Zeacarotene(trans), phytoene, phytofluene, β-zeacarotene, 13 and 13' cis α-carotene, 13 cis β-carotene, trans α-carotene, 9 cis α-carotene, trans β-carotene, αcarotene a(cis), α-carotene b(cis), α-carotene (trans), γ-carotene (trans), γ-carotene b(cis), lycopene (cis) and lycopene (trans). The results of physicochemical characteristics of the oil samples extracted range from 0.922±0.004 - 0.916±0.001 for specific gravity (SG), 8.10±0.17 - 4.88±0.04 mg KOH/g for acid value, 4.29±0.02 - 2.44±0.02 % for free fatty acid value (FFA), 6.00±0.21 to 204.67±0.98 mgKOH/g for saponification value and 9.53±0.23 - 5.25±0.33 mEq/kg; for peroxide value while the carotenoids values were between 53.735±0.10 and 123.389± 0.20 mg/100g. From the result we can observe that the main constituent of the palm oil carotenoid is the β -carotene which makes up to about 80% of the total carotene. Statistical analysis revealed that no significant difference exists between the mean of each of the processing method on the carotenoid profile of the oil sample analyzed.

Keywords: *Elaise guinensis, Carotenoid, Acid value, free fatty acids, β-carotene, Palm oil, Nigeria.*

INTRODUCTION

The oil palm tree is one of the important economic crops in the tropics. It is a monocotyledon belonging to Genus of *Elaeis.* The genus *Elaeis* consist of two species, namely *E. guineensis* and *E. oleifera*. *E. guineensis* originates from West Africa and the commercial planting material is mainly of this species, yielding three types of fruit, namely dura (thick shell), pisifera (without shell), and tenera (thin shell). *E. oleifera* is a stumpy plant of South American origin and its oil is characterised by a high oleic acid content and linoleic acid content and lower content of palmitic and other saturated acids. (Rees, 2015). The oil palm fruit bears two types of oils, one derived from fleshy but fibrous layer, the mesocarp and usually known as the "palm oil" and the other derived from the nut seed, the palm kernel and usually known as the "palm kernel oil". The composition of palm oil is rather unique when compared to that of the other major fats and oils (Bonnie, 2016). Palm oil is one of the most widely used edible oil in various food products, by households and by foodstuff factories. Its use is numerous in particular in manufacture of industrial products such as margarines, shortenings, cooking oils, confectionery fats and has usefulness for other food applications. Crude palm oil contains approximately 1% of minor components: carotenoids, vitamin E (tocopherols and tocotrienols), sterols, phospholipids, glycolipids, terpenic and aliphatic hydrocarbons, and other trace impurities (Goh *et al.,* 1985). The most important are carotenoids and vitamin E, both of which possess important physiological properties. Carotenoids are made-up of a pigment family containing over 700 different species, consisting of a C-40 polyene backbone with conjugated double bonds. Their structure could be modified at one or both ends, that is, cyclization or the introduction of oxygen to yield different species. The carotenoids give the palm oil its characteristic colour (Goh *et al.,* 1985), (Eric *et al*, 2010). These pigments have been used mainly in food, pharmaceutical, and cosmetic industries. Carotenoids also play an important potential role by acting as biological antioxidants, protecting cells and tissues from the damaging effects of free radicals. Carotenoids are the precursors of vitamin A, with α carotene having the highest provitamin A activity. Due to the beneficial properties of carotenoids and their high quantitative levels in palms fruits, their identification and quantification has been performed in the mesocarp of several species (buriti, pupunha and tucuma). However, the oils extracted from palm fruits have only been characterized spectrophotometrically for their total carotenoid content (Faessier, 2014). There is little literature on the effects of traditional processing method of palm oil on its carotenoid profile. Therefore, the present work aims to assess the effects of processing methods on physico chemical properties and caroteniods profiles of oils from three varieties of Elaeis guineensis.

MATERIALS AND METHODS

Sample collection and preparation

The palm fruits were collected from National Institute for Oil Palm Research (NIFOR) Edo State, Nigeria and duly identified by a taxonomist at the Botany department of Abia State University, Uturu. The three varieties were separated into two portions each, where each variety was extracted one part by hot process and the other part by cold process using the palm oil extraction method as practiced locally in the Eastern part of Nigeria. The oils were stored in an Amber bottle under room temperature till further analysis.

Plate 1. Samples used for analysis

Physico-chemical characterization

The percentage free fatty acid, iodine value accomplished by gravimetric and titrimetric methods, saponification value using reflux boiling and titration methods was performed as described by Pearson (Pearson, 1976). While viscosity, peroxide and acid values were determined by standard method as describe by AOCS (AOCS, 2005).

Carotenoid Profiles

5g of each oil sample and 5ml of 50% ethanolic KOH were heated at 50°c in a water bath under a stream of nitrogen for 30mins. The saponified sample was then cooled to room temperature and extracted with 50ml portion of petroleum ether until the supernatant becomes colourless. The pooled petroleum ether extract was washed four times with 50ml portion of distilled water and dried over anhydrous sodium sulphate. Then the extract was dried in a rotary evaporator at 50°C. Then the dried extract was dissolved in a known volume of mobile phase containing an antioxidant before it will be injected into the RP-HPLC-UV visible. The carotene profiles analysis was performed using a Reverse Phase HPLC with Waters 990 series UV-Visible detector at spectral range of 222 -800nm. With C18 column (4.6mmi.dx 25cm; stainless steel 5μm spherical particles) and the solvent system was acetonitrile: dichloromethane (89:11 v/v) at flow rate of 1.0ml min-^{1} as described by (Yap *et al.,* 1999)

Statistical Analysis of Data

All experiments were carried out in triplicate. Data were expressed as mean ±SD (Standard deviation). The data were analyzed for significant differences among means using one way analysis of variance (ANOVA). Duncan's multiplerange test was used as a post hoc comparison of statistical significance (p values<0.05). All statistical analyses were performed using SPSS version 20, 2018.

RESULTS AND DISCUSSION

Table 1 and 2 reveals the physicochemical parameters and Carotenoid profiles of oil extracted from the three varieties of Elaeis guineensis respectively. The results indicated that Iodine values ranged between from 47.87±0.23 to 49.33±0.12 wiji, Acid value from 8.10±0.17 - 4.88±0.04 mgKOH/g, free fatty acid value from 2.35±0.01 to 3.97±0.06 %, saponification value from 6.00±0.21 to 204.67±0.98 mgKOH/g, peroxide value range between 5.25±0.33 to 9.53±0.23 mEq/kg; while the carotenoids values were between 53.735±0.10 and 123.389± 0.20 mg/100g. Statistical analysis revealed that slight significant difference exists between the mean of one sample and another for each of the parameters determined.

Table 1: Physicochemical properties of the extracted palm oil

Sampling codes	Iodine value (Wiji)	Peroxide value (Meq/kg)	Saponification value (mgKOH/g)	Acid value (mgKOH/g)	Free fatty acid value (%)
MS 1	48.53±0.31	49.02±0.20b	197.33±0.58	4.88±0.04	2.44±0.02
MS2	48.55±0.30	48.55±0.30b	196.99±0.51	5.14±0.05	2.49±0.03
MS3	49.02±0.20	48.52±0.31b	197.04±1.15	5.36±0.03	2.35±0.01
MS4	48.52±0.31	48.50±0.29b	198.02±1.03	6.60±0.02	3.01±0.01
MS5	48.50±0.29	48.53±0.31b	199.32±0.40	6.51±0.04	2.89±0.02
TCP	49.07±0.23	8.27±0.12a	203. 33±0.58	7.95±0.12	3.97±0.06

THP	49.07±0.29	7.87±0.21a	202.69±0.58	7.53±0.23	3.77±0.06
PCP	48.77±0.29	6.93±0.23a	201.33±0.58	6.93±0.23	3.47±0.12
PHP	47.87±0.23	7.87±0.12a	199.33±0.58	5.67±0.12	2.83±0.06
DCP	49.33±0.12	9.53±0.23a	204.67±0.98	8.57±0.06	4.29±0.02
DHP	49.07±0.2	7.53±0.06a	202.67±1.6	8.10±0.17	4.05±0.09

*Values are Means ± standard deviations of triplicate determinations. Values in the same row having the same superscript letters are not significantly different ($p < 0.05$). MS 1- Ahunta market, MS 2- Eke Okigwe market, MS 3- Orie Ugba market, MS 4- Ubani Market, MS 5- Ukwunwangwu market, DHP- Dura hot process, DCP- Dura cold process, PHP- pesifera hot process, PCP-pesifera cold process, THP- Tenera hot process, TCP- Tenera cold process.

Iodine value is an important property of oil, which measures the unsaturation of oil and is a useful criterion for purity. The iodine values observed across the samples were generally low. The relative low iodine value in oils may be indicative of the presence of few unsaturated bonds and hence low susceptibility to oxidative rancidity. The hot processed oils had higher iodine values which show greater liability of the oil to go rancid by oxidation which might be caused by the heat effect. The values were low compared to results of (Omokpariola *et al*., 2021) oil extracted from Akparata seed and prescribed 75- 94 Wij's value for vegetable oils (Codex, 2011), but within 53.1 ± 0.4 and 56 ± 0.3 g I2/100 g values reported by (Japir *et al*., 2017) on crude palm oil. Generally, oils and fats with low iodine values enjoy the advantages of being less susceptible to oxidative spoilage than those with higher values. The oil samples obtained from the hot and cold process of specific varieties had higher saponification values as compared with market samples. The highest value was observed in cold process Dura with a value of 204.69±0.98 followed by cold processed tenera with a value of 203.33±0.58, significant difference (P< 0.05) were observed between the processed seed oil samples. The higher the saponification value, the higher the unsaturated level of the oil, it can thus be deduced that hot process palm oil possess more unsaturated fatty acids than those of cold process and market samples. Saponification value (SV) is used to determine the saponification number of a fat or oil which is an index of the average molecular weight of the triacylglyceride in the sample (Yap *et al.*, 1991). Saponification Value is an important parameter for characterizing the industrial use of oil, specifically for soap production. The high saponification value is suggestive of industrial potentials of the oil especially in soap making, but it was observed that there are slight but significant variations in the oils obtained through the different treatment. Due to an inverse relationship between saponification number and molecular weight of fatty acids in oil, it can be inferred that the oils contain a great number of fatty acids of low molecular weight and could be employed in soap making. Oils with low Saponification value can be used for the production of soap, candle, and raw materials for lubricants (Agatemor, 2006). The peroxide value is used to monitor the development of rancidity through the evaluation of the quantity of peroxide. The hot and cold processed oil sample of the three varieties had low peroxide values compared to the market samples, the cold processed oil samples had 8.27±0.12, 6.93±0.23 and 7.53±0.06 mEq/kg in Tenera, Pisifera and Dura respectively. While the hot process had peroxide values of 7.87±0.12, 9.53±0.06 and 7.93±0.12 mEq/kg in Tenera, pisifera and Dura respectively. This finding implied that the hot processed oil had higher peroxide value than the cold processed oil though the values were not really significant. The primary products of lipid oxidation are hydro peroxides; therefore, the result of peroxide value gives a clear indication of oxidation (Onwuka, 2015). Oils with higher peroxide value have been reported to have greater chances of going rancid (Onwuka, 2015). Rancidity begins to be noticeable when the peroxide value is well above10 mEq/kg (Pearson, 1976). Acid value is a factor that significantly affects the use of oil for industrial applications or human nutritional end uses (Japir *et al.,* 2017). The acid values of all the processed samples were generally below the stipulated permitted maximum values of 10 mg KOH/g (Aremu and Amos, 2010). There was no significant differences (P< 0.05) observed. The quality of oil is determined by the acid value of the oil, the higher the acid value the lower the quality of the oil. The amount of free fatty acid in palm oil is an indicator of the quality of the palm oil, and high level of free fatty acid is a presage of lipid oxidation (Abdulkadir and Jimoh, 2013). The value of free fatty acid range from 2.44 to 4.29 %. The result was within 3-5% maximum permissible values for Free Fatty Acid contents in a good quality palm oil (NIFOR, 1978). Acid Value and Free Fatty Acid are analytically used to detect the level of unesterified fatty acid in a lipid sample to define its quality.

The characteristics of the carotenoids identified in the analyzed oil samples are revealed in Table 2. Carotenoids are a class of tetraterpenoids that play an important role in plants and animals (Saini and Keum, 2018). Ten (10) different carotenoids were detected in all the oil samples, which includes; beta-cryptoxanthin, lycopene, alpha-carotene, beta-carotene, lutein, zea-xanthin, antheraxanthine, anstaxanthin, violaxanthin and neoxanthin. Of all the carotenoids detected, beta-craotenoid has the highest concentration in the all the oil samples with a value of 84.200±0.10 mg/100g in Eke Okigwe sample, followed by a value of 84.182±0.10 mg/100g in Ahunta and Orie Ugba market. The least value for beta-carotenoid was detected in cold processed tenera where it has a value of 28.537mg/100g. This high value of the beta-carotenoid for the market samples can be attributed to the fact that the market samples are actually gotten from a mixture of several varieties including the wild grown varieties. Zeaxanthin has the second concentration after beta-carotenoid with the highest value of 9.400 mg/100g observed in Eke Okigwe market sample, followed by 9.301mg/100g observed in Ahunta and Orie Ugba market.

No regular pattern of either lowering or increasing in concentration of any of the carotenoids; these findings can be attributed to the fact that in the so-called hot processed, the samples are not heated to temperatures high enough to affect the carotenoid contents of the oil palm. As a result, the processing method does not affect the carotenoid profile of the oils. From Table 2 we can deduce that most dominant carotenoid present in the entire sample is β-carotenoid. This was in line with the result of (Sundram *et al.,* 2010) which says that 85% of the total crude palm oil is β - carotenoid. It can also be observed that the hot processed samples have higher values for all the carotenoids. While the market samples has the highest carotenoid values. This could be attributed to the fact that heat releases the carotenoids from the oil sample and makes it readily available for detection; this heat will eventually damage the carotenoid if the oil samples are further exposed to heat or sunlight (Omokpariola *et al.,* 2021). Carotenoids have various functions in human health, such as antioxidant effects, eye health, heart health, improved cognitive function, and prevent certain types of cancer. β carotene, the main dietary source of provitamin A, is necessary for maintaining optimal human health (Roomi et al., 2018; Zhou *et al.,* 2018).

Table 2: Carotenoids profile of Oil samples

5	DURA Mg/100g		PESIFERA Mg/100g		TENERA Mg/100g		Mg/100g Ahunta	Mg/100g Eke Okigwe	Mg/100g Orie Ugba	Mg/100g Ubani	Mg/100g Ukwunwangwu
	HOT	COLD	HOT	COLD	HOT	COLD					
β-cryptoxanthin	2.769 ±0.120	1.973b ±0.120	3.22±0.120	2.220 ±0.120b	3.959 ±0.120a	3.03±0.120b	4.203 ± 0.122C	4.20±0.1220c	4.10±80.122c	4.20 ±0.122c	4.203 ±0.122c
Lycopene	1.574 ±0.234a	7.886 ±0.234b	1.851 ±0.234b	9.791 ±0.234b	2.22±0.234b	1.87±0.234b	2.300 ±0.111	2.32±0.111a	2.300 ± 0.111a	2.32 ± 0.111a	2.32±0.111a
α-carotene	1.462a ±0.020	1.159 ±0.020a	1.997 ±0.020a	1.258 ±0.020a	1.944 ±0.020a	1.669 ±0.020a	2.003 ±0.03	2.032 ±0.03a	2.002 ±0.03b	2.003 ±0.03b	2.003 ±0.03b
β-carotene	63.617 ±0.310a	55.892 ±0.310a	76.813 ±0.310a	59.807 ±0.310a	81.889 ±0.310a	28.537 ±0.310a	84.182 ±0.10	84.200±0.10	83.987±0.10	84.182±0.10	84.182 ±0.10
Lutein	3.092 ±0.30a	2.111 ±0.3.0b	3.663 ±0.3.0a	2.065 ±0.3.0b	4.246 ±0.3.0a	3.444 ±0.3.0b	4.816 ±0.15c	4.500 ±0.15c C	4.816 ±0.15c c	4.86 ±0.15c c	4.816 ±0.15c c
Zea-xanthin	4.271 ±0.027a	5.604 ±0.027b	6.865 ±0.027c	5.826 ±0.027b	8.168 ±0.027c	4.981 ±0.027a	9.3011±0.20c	9.400 ±0.20c	9.300 ± 0.20c	9.30 ±0.2c	9.301 ±0.20c
Antheraxanthin	2.745 ±0.278a	9.857 ±0.278b	3.769 ±0.278a	1.415 ±0.278c	4.105d ±0.278	3.201 ±0.278a	4.609 ±0.31d	4.610 ±0.31d	4.610 ±0.31d	4.609 ±0.31d	4.609 ±0.31d
Anstaxanthin	1.961 ±0.290a	1.033 ±0.290b	2.163 ±0.290a	1.670 ±0.290b	2.750 ±0.290a	2.233 ±0.290b	3.045 ±0.41c	3.050 ±0.41c	3.060 ±0.41c	3.045 ±0.41c	3.045c ±0.41c
Violaxanthin	4.065 ±0.310	2.328 ±0.310	2.328 ±0.310	4.988 ±0.310	2.364 ±0.310	1.690 ±0.310	2.350 ±0.310	2.350 ±0.06	2.350 ±0.06	2.500 ±0.06	2.350 ±0.06
Neoxanthin	4.065 ±3.00a	2.3283.00b	2.328 ±3.00b	4.988 ±3.00a	5.782 ±3.00b	4.08±3.00b	6.37±1.04c	6.37±1.04c	6.37±1.04c	6.37 ±1.04c	6.37±1.04c
Total carotene	89.621	90.1713	104.987	94.028	117.427	54.735	123.179	123.032	122.895	123.389	123.199

*Values are Means ± standard deviations of triplicate determinations. Values in the same row having the same superscript letters are not significantly different ($p < 0.05$).

CONCLUSION

Palm oil is a rich source of carotenoid. β -carotenoid making up to about 85% of the carotenoid. It is the richest natural source of carotene in terms of provitamin activity. β -carotenoid protects against blindness and carcinogens. Processing method has little effect on the carotenoid properties and physicohemical characteristics therefore choice of method should be based on the most efficient in terms of oil yield. The three different varieties varies slightly in both physicochemical properties and carotenoid characteristics, the commercially available oil samples (market samples) are the wildly grown varieties having just a little variation in physiochemical and carotenoid properties from the special varieties. Every part of the oil palm has economic and domestic values. The oils are useful for industrial, domestic and in pharmaceutical formulations.

CONFLICT OF INTEREST

All the authors declare no conflict of interest regarding this manuscript

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CHEMICAL SOCIETY OF NIGERIA (CSN) ABIA CHAPTER
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Full Length Research Paper

CHEMICAL ANALYSIS AND NUTRITIVE COMPOSITION OF ETHANOLIC LEAF EXTRACT OF THREE COMMON COMPONENTS OF AJU MBAISE, *(Cnestis Ferruginea, Argemone Mexicana, Polypodiophyta)* POLYHARBAL EXTRACT.

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ABSTRACT

Aju Mbaise Polyherbal Extract (APE) is widely used in Southeast Nigeria by many women to enhance labour, remove placenta after delivery and for Managing pains from postnatal and menstrual cramps. This study analyses chemically the ethanolic leaves extract of three major components of Aju Mbaise as well as their nutritional composition. The proximate analysis, mineral element determination and the quantitative phytochemical analysis of the ethanolic leaves extract of these constituent of Aju mbaise polyherbal extract was estimated using standard methods of analysis. In proximate analysis, the Ash content (4.433±0.252%), fiber content 1.520±0.20%, lipid content (8.540±0.046%) were higher in *Cnestis ferrugonea,* the protein content (11.980±0.020%) were observed to be higher on *Argemone Mexicana* whereas the moisture content (8.707± 0.0020%), the carbohydrate content was relatively higher in *phypodophyta*. For the mineral composition, it was found that *polypodiophyta* has relatively higher concentration of calcium (512.623± 0.006mg/kg), magnesium (6613.613± 0.344mg/kg), phosphorus (4672270 ± 0.113mg/kg) than the two other plant extracts. *Argemone Mexicana* showed higher concentration of sodium (6243.500±020mg/kg), potassium (4432.900±0.012mg/kg) compared to the other two plant extracts. These plant extract showed varied range of micro elements concentration. For phytochemicals, ethanolic leaf extract of *polypodiophyta* showed higher concentration of Alkaloid (40.502±0.003mg/kg), flavonoids (14.1855±0.120%), saponids (16.355±0.700%), Steroids (17.141± 0.001%), and cynnogenic glycosides (16.4775±0.117%) whereas *Cnestis ferruginea* has higher concentration of saponins (20.331± 0.326%). This study establishes the fact that ethanolic leaf extract of these postpartum plants has high nutritive values, minerals and are rich in phytochemicals.

Keywords: Aju-mbaise, postnatal, menstrual cramps, polyherbal extract, postpartum, phytochemicals.

INTRODUCTION

The substantial worldwide interest of herbal and polyherbal extracts in the treatment of diseases have been reported in different literatures. Several reports have revealed that the use of single herbs may have clinically insufficiency to the desired therapeutic roles. However. The use of optimized concentration and rations of different herbs offers more remedy with lower toxicity. (Benzile and Wachtel- Galor 2011).

These growing interest in herbal medicines have been underscored by their efficacies and role in alleviating extreme cases of ailments. Again, its exploration and utilization by inhabitant of developing and developed countries are factored on their affordability, accessibility, acclaimed non toxicity and as a natural healing agent (Ishtiaq 2017). However, the cost of procuring individual herbs against various microbial agents including antimicrobial, antifungal and inflammatory confirms the cost advantage of polyherbal remedy which may contain all in one of the aforementioned biological activities. Furthermore, herbs have shown promising therapeutic attributes in the treatment of plethora of ailments including arthritis, diabetes, livers, renal, obesity and cardiovascular diseases. For example, *cnestis farruginea* has been reported by, Adisa *et al* 2010) to show hypocholesterolemic and hypoglycemic effect against STZ-induced rodent. *Combretum racemosum* leaves have been reported by Kola and Benjamin (2002), to have anti-inflamatory, vasorelaxant and trypanocidal properties. *Commiphora* (myrrh) is a cough remedy among other herbal extract (Bent, 2008).

Aju Mbaise is an herbal therapy composed of combination of leaves, roots and trunk of different medicinal plants wrapped together. This herbal cocktail has its origin from Mbaise a sub-tribe of Igbo in Imo State, Nigeria. According Ijioma *et al,* (2020) the cocktail effectively detoxifies and sanitizes the womb as well as reduces the stomach to its original size and shape in good time when administered to women after child birth. According to Ugiomoh and Mbalewe, (2021), the cocktail is made up of *Polypodiophyta, Cnestic Ferruginea, Argemone Mexicana, Macaraanga Hurifolia, Ovaria Chamae, Trichsta Subcordeta, Polisota Hirsata, Trichsta subordeta, pterocarpus soyauxi, calichilia barteri* and *combretum racemosum etc.* These plants have shown their individual therapeutic effects against so many diseases. The efficacy and the therapeutic effect of these plants are based on their photochemical constituents and chemical characterization of their constituents. Therefore, this study examines the nutritional composition and chemical analysis of the ethanolic leave extract of three common components of Aju Mbaize polyherbal extract (APE), *Polypodiophyta, Cnestis Ferruginea and Argemome Mexicana plants*

COLLECTION OF PLANT MATERIALS.

Fresh samples of the three common plants, *Argemona Mexicana, Cnestis Peniginea* and *polypodiophyta* were collected at Ahiazu Mabise LGA of Imo State Nigeria. The plant was properly identified by botanist. The fresh sampled after collection was washed and dried. The dried samples were pulverized with a mechanical grinder. The powdered samples were used to determine the proximate analysis, mineral composition and the photochemical constituent of the plants extract.

PROXIMATE ANALYSIS

The proximate composition of *Argemona mexicna, cnestis ferruginea and polypodiophyta* was investigated with the standard methodology according the association of analytical chemist.

Estimation of Ash Content

Ash content was determined by the official AOAC (2019) method using muffle furnace (carbolite AAF1100, United Kingdom). Samples weighing 5g was placed in an empty dried platinum crucible of weight (w1). The weight of the sample and the weight of the of the platinum crucible were noticed (w2). The crucible containing the sample was subjected to ashing for 3 hours in a muffle furnace at a temperature 550^0c. The crucibles were removed and cooled in a desiccator and the final weight W3 was determined as follows.

$$\% \, Ash\ content = \frac{w3 - w1}{w2 - w1}\ x\ \frac{100}{1}$$

$$where\ w1 = weight\ of\ empty\ crucible$$

$$w2 = weight\ of\ empty\ crucible + extract\ before\ ashing$$

$$w3 = weight\ of\ empty\ crucible + Ash$$

Moisture Content

With a dried clean crucible of weight (w1) each samples weighing 5g was placed in it to make up w2 (weight of crucible + weight of sample). The crucible containing the sample was placed in an oven for drying at temperature 105^0c for about 24 hours. After the drying process, the weight (w3) of the crucible containing the dried sample was noticed. Thus, moisture content was determined as

$$moisture\ content\ (\%) = \frac{w2 - w3}{w2 - w1}\ x \frac{100}{1}$$

Estimation of crude fibre content:

A sample of weight 2g was defatted with petroleum ether, boiled under reflux for 30 mins with 200ml of 0.25m sulphuric acid (H_2S0_4) solution. It was filtered through a linen fabric and the insoluble matter was washed severally with hot water untill it was free of acid. The residue was then transferred to a beaker and boiled for 30 mins with 100ml of hot 0.31M sodium hydroxide (Na0H) solution. The process was done repeatedly and the final residue filtered through a thin but close pad of washed and ignited asbestos in a Gooch crucible. The sample was then dried in an electric oven weighed, incinerated, cooled and reweighed. The crude fiber content was determined as

$$\% \, crude\ fibre = \frac{weight\ of\ fibre}{weight\ of\ sampe}\ x \frac{100}{1}$$

Estimation of Crude Protein content of the extracts

Sample of weight 0.5g was gently placed in a 30ml kjeldahi flask. The content of the flask was digested by heating cautiously in the presence of sulphuric acid, anhydrous sodium sulphate and 0.5g of the Kjeldahi catalyst (copper) until a clear solution (Ammonia) appears. The clear solution was allowed to stand and cool. After cooling it was made up to 100ml with distilled water, which was added to avoid caking and them 5ml was transferred to the kjedahi distillation apparatus, followed by 5ml of 40% NaoH. A receiving flask containing 5ml of 2% boric acid and mixture of 5 drops of bromocresol blue and I drop of Methylene blue indicators was subjected to the distillation Apparatus such that the tap was about 20cm inside the solution. The distillation was initiated immediately and was titrated with 0.01M HCL to an end product. The percentage protein content was calculated as

$$\% \, protein\ content = \% \, Nitrogen\ x\ 6.25$$

This was repeated for the other samples. While the % Nitrogen was calculated thus

$$\%N = 1.4\ x\ \frac{(Vs - Vb)}{w}\ x\ M\ \ \propto DF$$

$\%N =$ $N\ content\ of\ sample\ expressed\ in\ \%\ by\ mass$

Vs $= volume\ of\ ml\ of\ the\ stnadard\ HCl\ used\ for\ the\ extract$

Vb $= volume\ in\ ml\ of\ the\ standard\ hydrochloric\ acid\ used\ for\ the\ blank\ test$

$M = molarity\ of\ the\ standard\ hydrochloric\ acide\ expressed\ to\ four\ decimal\ places$

$W = mass\ of\ test\ proteins\ in\ grams\ expressed\ to\ nearest\ 0.1mg$

Estimation of The Lipid Content

The lipid content was determined by the AOAC (2019) method using Soxhlet apparatus.

Approximately 5g (w3) of the extracts was placed into a thimble which was placed inside soxhlet extractor and n-haxane was poured into a pre-weighed round bottom flask (W2) used to extract the oil from the sample. This was carried out for about 6 hours. The solvent was removed from the extracted oil by distillation. The oil in flask was further dried in a hot air oven at 90^0 for 30 Minutes to remove residual organic solvent and moisture. This was cooled in a desiccator and flask and its content weighed (Wi) the quantity of oil obtained was expressed as percentage of the original extract used as thus;

$$\%\, lipid\ content = \frac{W2 - W1}{W}\ x \frac{100}{1}$$

Where $W = weight\ of\ plask$

$W2 = weight\ of\ plask + extracted\ fat$

$W = weight\ of\ extract\ used$

Total Carbohydrate Content (Using Difference Method)

Differential method of AOAC (2019) was adopted for the estimation of carbohydrate content. The carbohydrate content was calculated thus:

$$\%carbohydrate\ content = 100 - (\%\, protein + \%\, moisture + \%\, Ash + \%\, fat + \%\, fibre)$$

Estimation of the energy Values

The energy value of each of these sample extracts were determined by multiplying the protein content by 4, carbohydrate content by 4 and lipid content by 9 (AOAc 2019). Thus, energy value (kg/Joules) = 4.18 (% protein x 4) + (% CHO x 4) + (% lipid x 9)

DETERMINATION OF MINERALS IN THE EXTRACTS.

The AOAC official method 985.01 (2006) with little modification described by Chinedu, Onyeike and Ikewucho (2019) were used for the analysis of the following metals cupper, iron, lead, manganese, Arsenic, Aluminum, calcium, magnesium, nickel, mercury, molybdenum and cobalt, while flame photometer was used in the analysis of potassium and sodium. Using Atomic Absorption spectrophotometer (AAS) (Buch scientific model 210 VGP) The ash solution of the plant sample was prepared by weighing 5g of the powdered sample, this was ashed at 550^0c in muffle furnace for 5 hours, and the residues dissolved in 100ml of deionized water. Suitable salts of the metals were used to make their standards and suitable lamps were injected to calibrate the AAS using acetylene gas as the frame source. An aliquot of ash solutions was injected and the concentrations were extrapolated from the standard plots/curves of each metal.

QUANTITATIVE PHYTOCHEMICAL ANALYSIS OF THE EXTRACTS.

Alkaloids

1ml of the extracts was measured into a test tube, 5ml phosphate buffer was then added, and then 5ml of Bromocresol green was added to the test tube. After which, it was shaken for four minutes. Then 4ml of chloroform was added to the mixture and was separated using separatory funnel. The lower part was collected and was made up to 10ml mark with chloroform. The absorbance was read at 470nm using a spectrophotometer. The concentration of alkaloids was calculated using the formula:

$$\text{Alkaloids (\%)} = \frac{Conc.of\ standard\ x\ Abs.of\ sample}{Abs.of\ standard}\ x \frac{100}{1}$$

Tannin

The tannin content was determined according to the method described by Wintola and Afolayan (2011) with some modifications.

Into 1ml of the extracts, twenty milliliters (20ml) of distilled water containing 2.5ml of Folin-Denis reagent and 10ml of 17% Na_2CO_3 were added to the filtrate and properly mixed together. The bluish-green colour developed at the end of the reaction mixture, the absorbance of the tannic acid standard solution was measured after colour development at 760nm using spectrophotometer. The percentage of tannin in the sample was calculated using the formula:

Tannin (mg/100) = $\frac{Conc.of\ standard\ x\ Abs.of\ sample}{Abs.of\ standard\ x\ weight\ of\ sample}$

Flavonoids

Flavonoid was determined using spectrophotometric assay developed by Bao *et al.*, (2005), 0.2ml of the extracts was added to 0.2ml to 0.3ml of $NaN0_3$ at zero time. After 5min, 0.6ml 10% $AlCl_3$ was added and after 6min, 2ml of 1M NaOH was added to the mixture followed by the addition of 2.1ml of distilled water. Absorbance was read at 510nm against reagent bank and flavonoids content was calculated using the formula:

Flavonoids, (%) (Catechin) = $\frac{Conc.of\ standard\ x\ Abs.of\ sample}{Abs.of\ standard}\ x\ 100$

Saponin

The spectrophotometer method of Brunner, (1984) was used for the estimation of saponin in the samples.

0.5ml of the extracts was taken and 0.5ml of deionized water (blank) was added then 5ml of 8% vanillin in ethanol was added to the extracts and was mixed well. Then 5ml of 72% H_2S0_4 was added and mixed. After which it was heated in a shaking water bath for 60^0c for 10 minutes. The absorbance was read at 560nm in a spectrophotometer. The percentage saponin was calculated using the formula:

Saponin (%) = $\frac{Conc.of\ standard\ x\ Abs.of\ sample}{Abs.of\ standard\ x\ weight\ of\ sample}\ x\ 100$

Terpenoids

The procedure described by sofowora, (2011) was used with little modifications. 1g of extract was weighed into a 50ml conical flask, 20ml of chloroform/method (2:1) was added to the mixture, the mixture was shaken thoroughly and allowed to stand for 15mins at room temperature. The suspension was centrifuged at 3000rpm. The supernatant was discarded and the precipitate was rewashed with 20ml chloroform/methanol (2:1), and the centrifuged again. The precipitate was then dissolved in 10% SDS solution. 1ml 0.01m ferric chloride was added to the solution and allowed to stand for 30 minutes at room temperature before the absorbance was taken at 510nm. The terpenoids content was calculated using the formula below:

Terpenoids Content mg/100g = $\frac{Conc.of\ standard\ x\ Abs.of\ sample}{Abs.of\ standard\ x\ weight\ of\ sample}$

Steroids

1ml of test extract of steroid solution was transferred into 10ml volumetric flasks. 2ml of 4N sulphuric acid and iron (III) chloride (0.5%w/v, 2ml). the mixture was heated in a water-bath maintained at 70^0C for 30 minutes with occasional shaking and dilute to the mark with distilled water. The absorbance was measured at 780nm against the reagent blank. The steroids content was calculated using the formula:

Steroids Content, mg/100g Cholesterol = $\frac{Conc.of\ standard\ x\ Abs.\ of\ sample}{Abs.of\ standard\ x\ weight\ of\ sample}$

Cyanogenic Glycosides

1ml of the extracts was measured into a test tube. Alkaline picrate solution (4ml) was added on each sample, boiled for 5 minutes and allowed to cool. Absorbance was measured at 490nm. The Cyanide content was calculated using the formula below:

Cyanide Content mg/100g =

$$\frac{Conc.of\ standard\ x\ Abs.of\ sample}{Abs.of\ standard}$$

RESULTS AND DISCUSSION

Results

The results for chemical analysis carried out on the ethanolic extract of *Cnestis ferruginea*, *Argemone Mexicana* and *polypodiophyta* plant leaves.

TABLE 1: PROXIMATE COMPOSITION (mean = SD) of *Cnestis Ferruginea, Argemone Mexicana and polypodiophyta* ethanolic leaf extract

Pararuetermg/kg	Cnestis ferruginea	*Argemone Mexicana*	*polypodiophyta*
Ash%	4.433±0.252	3.813±0.012	2.930±0.030
Moisture %	5.647±0.038	4.613±0.015	8.707±0.020
Fibre %	1.520±020	0.907±0.058	0.413±0.015
Protein %	9.847±0.031	11.980±0.020	11.727±0.006
Lipid %	8.540±0.046	7.823±0.025	3.487±0.012
Carbohydrate %	69.923±0.235	70.863±0.067	72.737±000
Energy value (KJ/100g)	1657.409±3.37	1681.113±1.224	1545.610 ±1.002

TABLE 2 MINERAL COMPOSITION (MEAN ± SD**)** of *Cnestis ferruginea*, *Argemone mexicana* and *polypodiophyta* plants

parameter (mg/kg)	**Cnestis Ferruginea**	**Argemone Mexicana**	**Polypodiophyta**	**parameter (mg/kg)**	**Cnestis Ferruginea**	**Argemone Mexicana**	**Polypodiophyta**
Sodium	5214.283±0.011	6243.500±020	5628.173±0.043	Aluminum	0.110±0.011	0.901±0.011	0.104±0.001
Potassium	3216.33±0.025	4432.900±0.012	3426460±0.010	Cadmium	0.390±0.022	0.230±0.012	0.300±0.000
Calcium	3536.633±0.011	4146.200±0.046	5128.623±0.006	Copper	0.250±0.11	0.211±0.001	0.116±0.011
Magnesium	3972.440±0030	5269.200±0.020	6613.613±0.113	Cobalt	0.130±0.011	0.142±0.011	0.130±0.011
Phosphorus	3972.907±0012	2627.100±0.021	16.203±0.185	Lead	0.120±0.00	0.110±0.00	0.12±0.000
Iron	20.060±0.046	19.273±0.021	16.230±0.185	Manganese	0.240±0.00	0.0230±0.00	0.211±0.001
Arsenie	0.100±0.000	0.901±0.011	0.104±0.000	Mercury	0.090±0.000	0.086±0.00	0.093±0.00

DISCUSSION

The nutritional value of ethanolic extract *Cnestic ferruginea, Argemone maxicana and plypodiophyta* are presented in table one. The result obtained showed that *Cnestis Argemone mexicana and Polypodiophyta* respectively have high carbohydrate protein, lipid and moisture content with moderate Ash, fibre and mineral content. Nutrients such as carbohydrate, protein lipids, fibre are known to be required by the body in suitable proportions, to improve and maintain good health. The proximate analysis of the herbal cocktail (Aju Mbaise) revealed that the cocktail is rich in carbohydrate, crude protein, lipids, crude fiber, moisture and ash (Nnadiukwu, Monago-Igborodje and chukwu, 2020). According to Ajayi *et al* 2023, leaf extract of S.Jollyanum, which is another constituent plant of AJU Mbaise is rich in fat, moisture, protein, carbohydrate ash and fiber substance respectively with a great energy value. Dialium quineeuse another constituent plant of Aju Mbaise contains high concentration of protein, carbohydrate and moisture (Ayesson *et al* 2014). Thus, gave the herbal cocktail its high nutrient continent.

Table 2 revealed that *Ferruginea, Argemone Mexicana and polypodiophyta* contains high concentration of different minerals. Minerals are essential nutrients which the body needs in appropriate concentration to remain healthy. According to Belogum and Olatidoye (2012), these minerals serve as fundamental compactors and co-enzymes for some physiological and metabolic actions. Furthermore, they help most essential reactions at cell level (which includes glycolysis, tricarboxylic acid cycle and lipid and amino acid digestion), important for energy generation and maintenance of life. As indicated by (Imaghe, Malomo and Adebayo, (2009), mineral remain an important daily necessity for appropriate tissue functioning. The mineral and vitamine analysis of Aju Mbaise herbal cocktail revealed significant amount of minerals and vitamins. Nnadiukwu, manogo-Ighorodje and Chukwu (2020). This is in consonant with the report of Ezejinfu, (2017) that Aju Mbaise contained appropriate concentration of mineral, (Potassium, calcium, magnesium, sodium, iron, zinc, phosphorus, copper, manganese and chromium).

Ibironke and Olusola (2013) revealed the presence of micro and macro element in seeds and leaves of S. Jollyanum (Another component) plant of the herbal cocktail) making the plant and the cocktail an important component in building solid bones, productions of energy and carrying out some metabolic reactions in the body. According to Ayesson, (2004) *Dialium quineense* another constituent plant of ‘Aju Mbaise” contains appreciable concentration of iron, magnesium, sodium calcium, potassium and reasonable amount of Ascorbic acid. It can be scientifically deduced that utilization of this herbal cocktail can help fight against minerals and vitamins deficiencies and improve health and growth in women after child.

TABLE 3 Shows the photochemical constituents of *cnestis ferruginea, Argemone Mexicana and polypodiophyta*. It was revealed that these constituents of Aju Mbaise are rich on phytochemicals. The Alkaloids, Tanins, Flavonoid, Saponin, Terpenoids, Steroids and Cyanogenic glycosides at different concentration. Alkaloids support its medical use as analgesic for for head and backache, joint swelling and pain in arthritis. The existence of alkaloids in the extracts shows that they may have potential antimicrobial activity. Plants that are rich in alkaloid are known for reducing blood pressure and have anti-malaria properties; therefore, the plant extracts can be used as antimalaria. (Okwu and Okwu, 2004).

The tannis and terpenoids content in the leaf extract support the use of the plants leaf extract for the treatment of swellings, wounds and as hip bath for postpartum bleedings. Tannins have been found to be anti-parasitic, anti-viral and antibacterial agent and help to hasten the healing of inflamed mucous membrane and wound (Paul *et al*, 2012).

Flavonoids are used as anti-inflammatory agent (Bohan and Kocipai, 2014). Saponins exhibits cardio protective measure by binding cholesterol to form insoluble complexes thus preventing cholesterol reabsorption and accumulated in serum (COE and Arderson, 2016) Saponins potentiate the hemolytic and antimicrobial properties of plants. Saponins prevent cancer by preventing DNA damage. The significant level of saponin in the ethanolic extracts support their uses in traditional medicine. Saponins aids in eliminating viruses, bacteria, and fungi infection and have shown to compliment the potency of some Vaccines (Agoha 2021). Therefore, the leaf extracts may be useful in treating come infection like sexually transmitted diseases. According to (Hudson, 2016) the steroids phytochemicals are currently used for treating symptoms of uterine cramps, abdominal colic and menstrual irregularity while topical progesterone in pharmacological doses is used to treat a variety condition including premenstrual syndromes, anovulary cycles, dysfunctional uterine bleeding and menopausal symptoms, cyanogenic glycosides are generally food, reducing the bioavailability of trace metals. Hence the widely use of Aju Mbaise and its constituents as a postpartum plant in southeast.

TABLE 3: PHYTOCHEMICAL COMPOSITION OF *Cnestis Ferruginea, Argemone mexicane and polypodiophyta*

Parameters	*Cnestic ferruginea*	*Argemone Mexicana*	*Polypodiophyta*
Alkaloids %	16.49±0.057	15.585±0.0064	40.502± 0.0030
Tannins (mg/100g)	5.895±0.053	62.065±0.488	13.905±0.0180
flavonoids (%)	6.860±0.326	14.46±0.041	16.355± 0.120
Saponins (%)	20.331±0.361	0.070±0.042	12.978± 0.700
Therpenoids (mg/100)	9.945±0.361	0.070±0.042	12.998± 0.125
Steroids (mg/100)	1.978±0.039	12.930±0.311	17.141±0.001
Cyanogenic glycosides (mg/100)	0.831±0.029	14.470±0.410	16.4775± 0.117

CONCLUSION

The study has shown that these constituents of Aju Mbaise polyherbal Abstract (APA*) (Cnestis Ferruginea, Argemone Mexicana and polypodiophyta*) contains numerous essential nutrients that play very important biological roles in the human system that helps to maintain good health and promote quality healthy living.

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CHEMICAL SOCIETY OF NIGERIA (CSN) ABIA CHAPTER
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Conference Proceedings

Full Length Research Paper

PHYTOCHEMICAL AND NUTRITIONAL COMPOSITIONS OF ELEPHANT GRASS WASTE (*Pennisetum purpureum*)

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ABSTRACT

Elephant grass waste has been used in the past for yam pepper soup. This research is aimed at finding out how nutritious it is so as to know if its continual use by humans in this wise is advisable. The phytochemical and nutritional compositions of the sample were determined using standard procedures. The results of the phytochemical screening of the sample revealed the presence of Saponins (++), Flavonoids (++), Alkaloids (+), Cardiac glycosides (+) and absence of Tannins (-). While its quantitative analysis showed it contains saponins (888.2µg/g), flavonoids (104.2µg/ml), alkaloids (32.2µg/ml), cardiac glycosides (1.89%) and tannins (0.38%). The proximate analysis results showed that the waste contain 23.87% Ash, 21.94% total carbohydrate, 11.5% moisture, 6.95% crude protein, 0.65% fat and 811.80k/100g total metabolizable energy. This result suggests that Elephant grass waste is safe for medicinal, livestock grazing and cement production purposes.

Keywords: *Phytochemicals, Nutritional compositions, Elephant grass waste, quantitative analysis*.

INTRODUCTION

Elephant Grass (*Pennisetum purpureum)* is also known as Napier grass, or Uganda grass. It is a tall grassy perennial plant in the poacene family. It is native to subtropical Africa (Ibibia *et al.*, 2020; Clark *et al.*, 2023). The apical ends of the stems of Elephant grass plants usually have whorled tender young leaves before flowering. It is widely cultivated in tropical and subtropical regions as a weed or forage crop (Clark *et al.,* 2023). Elephant grass in Nigeria is one of the most recommended soup ingredients eaten by the Igbo tribe of Abia State. It is called Achara by the Ibos. Elephant grass is generally used as animal food, an ornamental plant and for erosion control (Okaraonye and Ikewuchi, 2009).

While preparing Elephant grass for soup the outer coats are usually removed and thrown away as wastes. Those outer coats were used by our elders for hot yam pepper soup in the past. Based on such usage, this research is designed to find out if Elephant grass wastes have some nutritive and medicinal values and if it is safe for human consumption so as to educate the public about such.

MATERIALS AND METHODS

Materials: Analytical weighing balance, Electric blender, knife, round bottom flask, thermometer, measuring cylinder, 250ml and 500ml conical flasks, pH meter, oven, refrigerator, beaker, hand glove, filter paper, masking tape, nylon bags etc.

Reagents: N-Hexane, 0.1M NaOH, 0.1M Oxalic acid, chloroform 1.25% NaOH, 10% HCl, 0.5M HNO_3, Conc. NH_4OH, distilled water etc.

Method

Preparation of Elephant grass waste

The bark (Outer coats) of Elephant grass purchased from Umungasi Market in Osisioma LGA, Aba was washed with clean water, cut into small pieces and dried in the oven at 80^0C for hours in chemistry/Biochemistry Laboratory of Abia State Polytechnic Aba. When fully dried it was ground into fine particle size with an electric blender and stored in an air tight sample bottle. Thereafter, 100g of the powered sample was extracted by marceration in $300cm^3$ of absolute alcohol (98%) in a $500cm^3$ beaker for three (3) days. It was filtered with a white cotton cloth and concentrated using rotor evaporator. The concentrated extract was partitioned in 1:1 chloroform water (boiled at 100^0C) in a separatory funnel. The lower chloroform layer was collected and allowed to cool at room temperature. When cold it was decanted into a reagent bottle sealed with aluminum foil and stored in a refrigerator until required.

Phytochemical Screening of the Elephant Grass Waste

Qualitative phytochemical tests were done to find out if the following phytochemicals were present, using standard methods (AOAC, 1990). The phytochemicals screened of were Alkaloids, flavonoids, glycosides, Tannins and Saponins. Quantitative phytochemical Analysis of the Elephant grass waste was done by using AOAC (1990) to determine the concentrations of Saponins, Flavonoids, Tannins, Alkaloids and Cardiac glycosides in it.

Proximate Analysis of Elephant Grass Waste

Proximate composition of Elephant grass waste was assayed using standard methods (AOAC, 1990) The major constituents of the Elephant grass waste assayed for are moisture, Ash, Fat, crude fiber, crude protein and total carbohydrate.

RESULTS AND DISCUSSION

Results

Phytochemical profile of Elephant Grass (*Pennisetum purpureum)* waste.

Table 1: Phytochemical Screening Results

Phytochemicals	Concentration
Saponins	++
Flavonoid	++
Alkaloids	+
Cardiac Glycoside	+
Tannins	-

Key: ++ Moderately present, + slightly present, - Absent

Table 2: Quantitative Phytochemical Analysis of Elephant Grass waste (*Pennisetum purpureum)* waste

Phytochemicals	Concentrations
Saponins (µg/g)	888.52
Flavonoids (µg/ml)	104.4
Alkaloids (µg/ml)	32.2
Cardiac Glycosides (%)	1.89
Tannins (%)	0.38

Table 3: Proximate composition of Elephant Grass waste (*Pennisetum purpureum)*

Parameter	Concentration
Ash content (%)	23.87
Total carbohydrate k/100g	21.94
Moisture content (%)	11.537
Crude protein (%)	6.95
Fat content (%)	0.6
Energy value (K/100g)	811.80k/100g
Crude fibre (%)	35.103

DISCUSSION

The phytochemical screening of *Pennisetum purpureum* (Elephant grass) waste revealed that Elephant grass waste still contains a reasonable amount of Saponins, (++) and flavonoids, (++) little amounts of Alkaloids (+) and cardiac glycosides (+) and does not contain tannin (-) at all as shown in (Table 1). However, the quantitative analysis showed the following results; Saponins (888.52µg/g), Flavonoids (104.4µg/ml), Alkaloids (32.2µg/ml), Cardiac glycosides (1.89%) and Tannins (0.38%) respectively (Table 2).

Saponins are glycsoidic and triterpenoidic compounds found in plants. They have pharmacological properties like anti-inflammatory and antipyretic activities (Atangwho *et al.,* 2010). Saponins reduce the uptake of some nutrients such as glucose and cholesterol at the gut by intraluminal physicochemical interaction in the elephant grass waste (Okaraonye and Ikewuchi, 2009). Flavonoids are polyphenolic compounds found in vegetables, fruits and beverages like tea, coffee and fruit drinks (Oboh and Masodje, 2009). They possess antibacterial, antioxidant, anticancer, anti-inflammatory, antipyretic and analgesic properties (Okwu, 2004). Alkaloids have been said to have a wide range of pharmacological activities such as antimalarial (e.g quinine), anticancer (e.g homoharrintonine), antibacterial (e.g chelerythrine) and antihyperglycemic activities (e.g piperine) (Namadina *et al.*, 2019). When compared with the results of the work done by Okaraonye and Ikewuchi (2009) on the inner fresh tender edible portion of Elephant grass it is seen that the Elephant grass waste still contains exploitable phytochemicals.

Table 3 shows the proximate compositions of Elephant Grass waste (*Pennisetum purpureum)* as stated. From the table, it is clear that the elephant grass waste still contains an appreciable amount of nutrients: Ash (23.87%) Total carbohydrate (21.94k/100g), Moisture (11.537%), Crude protein, (6.95%), Crude fiber, (35.103%), Energy (811.80k/100g) and a little quantity of fat (0.6%). Since the Elephant grass waste contains such a high level of Ash

(23.87%), it then means that it contains more minerals than the inner parts of the main Elephant grass used in soup making which was said to contain 10.09% Ash (Singh, 2004). The value of the total carbohydrate content of elephant grass waste worked on here is higher (21.94k/100g) than that reported by (Singh, 2004) of the main elephant grass itself (17.16k/100g). This observation shows that Elephant grass waste contains more energy nutrient than that of the Elephant grass. Hence most of the carbohydrates found in the waste of the Elephant grass can be used as a good source of meal for the grazing of livestock (Aldeham *et al.,* 1994). The moisture content of Elephant Grass waste as shown in Table 3 was high (11.53%). The moisture content of any food is an index of its water activity and is used to measure its stability and susceptibility to microbial contamination (Scott, 1980). The elephant grass waste analyzed contained low protein (6.95%) as shown. This value is quite low compared with the amount got by (Okaraonye and Ikewuchi (2009); Osabor *et al.,* (2008); Ojowundu *et al.,* (2008)) from the Elephant grass itself which was 14.99%. The relative proportion of protein in elephant grass waste can be increased by dehydrating the waste. The protein content of the Elephant grass waste can serve as a good source of nutrient in grazing of livestock (Pyke, 1979).

CONCLUSION

From the discoveries of this study, Elephant grass waste can be used for medicinal purposes, grazing of livestock and for the production of cement due to the numerous bioactive compounds found in it, and its high ash content. When utilized in this way there will not be any adverse effects.

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CHEMICAL SOCIETY OF NIGERIA (CSN) ABIA CHAPTER

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Conference Proceedings

Full Length Research Paper

SORPTION ISOTHERM STUDIES OF MONOCROTOPHOS PESTICIDE ADSORPTION USING ACTIVATED AND UNACTIVATED BOILER FLY ASH AND MAIZE COB WASTE BIOMASS

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ABSTRACT

The adsorptive removal of monocrotophos pesticide from aqueous solution using boiler fly ash (BFA) and maize cob (MC) waste biomass was studied. Boiler fly ash and maize cob, which are agricultural wastes, were obtained from an oil mill and refuse dump respectively. They were washed, ground and milled and the mill retained on 250 µm mesh was used for investigation of effect of initial concentration on the sorption capacity of the adsorbents. The adsorbents were divided into two parts, one part was activated -activated boiler fly ash (Act-BFA) and activated maize cob (Act-MC) while the other parts were left unactivated - unactivated boiler fly ash (Unact-BFA) and unactivated maize cob (Unact-MC). UV/vis spectroscopy was used to measure the residual pesticide concentration in a batch system and the equilibrium data was treated according to various isotherm models. The result showed that the adsorption capacity depends on the initial concentration of pesticide solution, as adsorption capacity increased with increase in initial pesticide concentration. Activation of the adsorbent improved the sorption capacity of the adsorbent. The maximum amount adsorbed for initial concentration of 1000mg/L was 410mg/g for Act-BFA and the lowest was 113.18mg/g for Unact-MC. The trend of the sorption capacity was Act-BFA >Unact-BFA > Act-MC >Unact-MC. Among the isotherms-Langmuir, Freundlich, Dubinin-Radushkevich (D-R), Temkin and Harkins-Jura (H-J), used to model the equilibrium sorption data, from the R^2 values, the Langmuir isotherm gave a better fit for maize cob with R^2 values of 0.9980 and 0.9977 forAct-MC and Unact-MC, respectively while Freundlich isotherm gave a better fit for boiler fly ash with R^2 values of 0.9970 and 0.9988 for Act-BFA and Unact-BFA respectively. The trend for the fitness of the isotherms obtained was Freundlich>Langmuir>Temkin > Harkins-Jura > Dubinin-Rasushkevich. Therefore, activated and unactivated boiler fly ash and maize cob biomass can be used to remove monocrotophos pesticide from aqueous solution.

Key words: Adsorption, agricultural by-products, Environmental management, Isotherms, Pesticides.

INTRODUCTION

Environmental pollution is one of the serious predicaments of the modern world. Both natural and anthropogenic activities result in accumulation of wide range of toxic xenobiotics compounds in the environment and thus cause global concern (Igwe *et al.*, 2014; Menezes *et al.*, 2017). Principal xenobiotics includes pesticides, fuels, solvents, polyaromatic hydrocarbons (PAHs), etc. Pesticides are any substance or mixture of substances used or applied for the prevention, destruction, repelling or mitigation of any kind of pest. The impact of pesticide release into the environment is increasing as a result of rapid urbanization, industrial and technological expansion, over application run off and waste generation from domestic, industrial and agricultural sources. Extensive usage of pesticides is accountable for water contamination because of their leaching and run off losses (Mathanakeerthi *et al*., 2021; Vaikosen *et al*., 2023). Inappropriate discarding of empty bottles, washing of spray instrument and unfettered discharge from manufacturing industries are further sources of water resources contamination. Therefore, the consequences of these pesticides' contamination affect food security (Eun *et al*., 2021).

When pesticides are released into the environment, they are either: (1) Broken down or degraded by the action of solar energy, water or other chemical or microorganism such as bacteria; or (2) They might resist degradation and thus remain unchanged in the environment or ecosystem for a long period of time. The ability of these pesticides to remain unchanged is called pesticide persistence and is measured by the pesticide half-life and the soil adsorption coefficient (Koc) (Deer, 2004). The larger the Koc the more strongly the pesticide is held to soil organic matter and the less likely it will leach. Also, a volatile pesticide gets into the atmosphere easily and hence causes much environmental hazard (Nader & Elkhatib, 2018)

Many methods have been developed for the decontamination of pesticides such as leaching, chromatography, volatilization, precipitation, etc., to ensure proper removal of these pesticides' contaminants (Iizuka *et al*., 2013; Rasolonjatovo *et al*., 2017). Many pesticides tend to adsorb strongly to the soil, hence strong sorption, low water solubility and low vapour pressure makes leaching, precipitation and volatilization insignificant pathways for pesticide dissipation. Adsorption has been reported as one of the unit operations used in waste decontamination and very effective technique in which adsorbates are attached on adsorbent's surface and therefore removal from wastewater (Mihajlovic *et al*., 2015; Ajiboye *et al*., 2020; Marton *et al*., 2020; Göktepeli, *et. al*., 2021). Adsorption is one of the most important factors that affects the fate of pesticides in soil and determines their distribution in the soil/water environment (Mihajlovic *et al*., 2015; Nader & Elkhatib, 2018; Alacabey, 2022). Activated carbon have been reported as the major conventional adsorbent used in adsorption. Adsorption of pesticides from aqueous solutions using activated carbon has been reported (Igwe *et al*, 2009; González-Garcia, 2018; McGinley *et al*., 2022; Murtala *et al*., 2022; Harabi *et al*., 2024). Conventional activated carbon adsorption has been reported to be very expensive (Igwe *et al*., 2011). Hence, the search for low cost, readily available agricultural by-products such as maize cob and boiler fly ash for pesticide decontamination, hence, a form of waste to wealth.

Therefore, in this research, the adsorption of Monocrotophos pesticide using boiler fly ash and maize cob was investigated. The effect of initial concentration of pesticide was investigated. Comparison of the sorption capacity of the adsorbents for activated and unactivated was also investigated and the experimental results fitted to some isotherm models.

MATERIALS AND METHODS

Materials

The boiler fly ash was obtained from an oil mill located at Uturu, Abia State, while maize cob was obtained from a refuse dump site at Eke market, Okigwe, Imo state. All reagents used were of analytical grade, purchased and used without further purifications. Monocrotophos (Dimethyl (1E)-1-methyl-3-(methylamino)-3-oxoprop-1-en-1-yl phosphate) ($C_7H_{14}NO_5P$), 400 g/L, manufactured by Sabero organic Gugarat Ltd and formulated by Afcott Nigeria Plc, Lagos was purchased and used without further purification. Doubly distilled-deionized water was used in all dissolutions and dilutions. The chemical structure of the monocrotophos pesticide is shown in Figure 1 (Vaikosen*et al*., 2023), while the properties of the pesticide are shown in Table 1 (NCBI,2024). Doubly distilled-deionized water will be used in all dissolutions and dilutions.

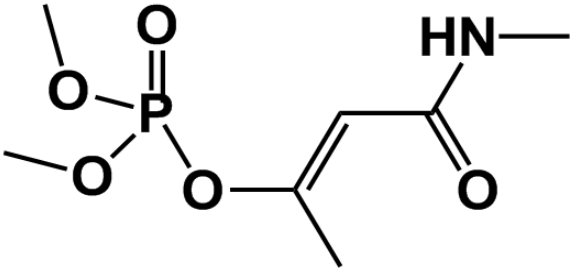

Figure 1: Chemical structure of Monocrotophos pesticide

Table 1: Properties of Monocrotophos pesticide

Chemical formula	Molar mass	Appearance	Odor	Density	Melting point
$C_7H_{14}NO_5P$	223.2 g·mol^{-1}	Colorless to reddish-brown	Mild, ester-like.	1.33 g/cm^3	120 °C

Methods

Preparation of adsorbents and adsorbates

The maize cob was washed thoroughly with water and then with de-ionized water, ground to powdered form and air dried. Big lumps in the boiler fly ash was removed and both maize cob and boiler fly ash were sieved separately using a test sieve shaker (EFL IMK3 model made by Endecotts England). The meal that was retained on the 250 µm was used. The adsorbents were divided into two parts each. One part each was dissolved in 2% (v/v) nitric acid for 24hrs, filtered and air dried. These were stored as activated boiler fly ash (ABFA) and activated maize cob (AMC) for experimental studies. The remaining part each was left unactivated and labeled as unactivated boiler fly ash (UBFA) and unactivated maize cob (UMC).

Stock solutions of known concentrations of monocrotophos were prepared. Different concentrations were obtained from the stock solutions by serial dilutions. A 200 – 960 nm wavelength UV/vis spectrophotometer was used to determine concentrations in the solution after adsorption. A calibration curve using Beer Lambert principles was used to obtain residual monocrotophos concentrations.

Effect of initial concentration

About 100 mL of different concentrations (400 mg/L to 1000mg/L) of monocrotophos pesticide solutions were put in reagent bottles and 1.0 g each of ABFA, UBFA, AMC and UMC of 250 µm size were separately added to different reaction mixtures and were agitated in a constant temperature rotary shaker at 100 rpm, temperature of 30°C and pH of 7.5 for 1 hr. After 1 hr, the reaction mixtures were centrifuged and the supernatants were filtered rapidly through a Whatman No. 41 filter paper. The pesticide concentration in the filtrates were determined using a UV visible absorption spectrophotometer model SP-300.

RESULTS AND DISCUSSIONS

The amount adsorbed as the initial concentration of monocrotophos pesticide was increased is shown in Figure 1. It was observed that as the initial concentration of the pesticide increased, the amount adsorbed also increased. This is attributed to the fact that as the concentration of the pesticide increases, there became available more pesticides for adsorption. Also, activation of the adsorbent, improved the sorption capacity of the adsorbent and that BFA gave better sorption capacity than MC. Similar results have been reported (Maingi *et al*., 2017; Lazarotto *et al*., 2021; Murtala *et al*., 2022; Luttah *et al*., 2023; Harabi *et al*., 2024).

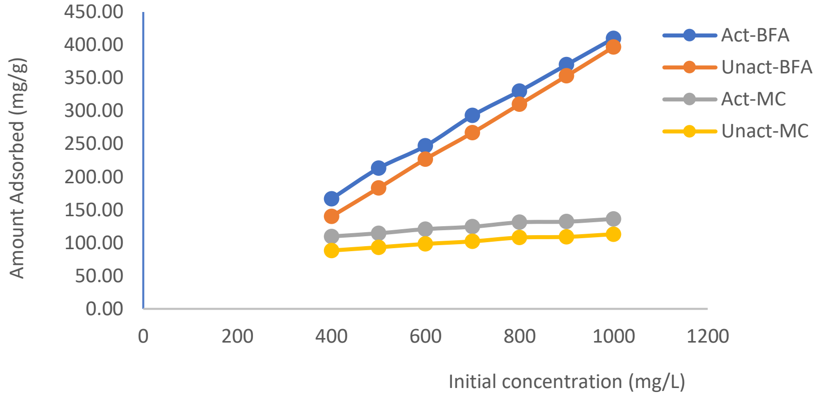

Fig 1: Amount adsorbed against initial concentration for adsorption of Monocrotofos pesticide using activated and unactivated boiler fly as and maize cob

The adsorption isotherm models used for this study are Langmuir (Guo and Wang, 2019) (Eq. 1), Freundlich (Al-Ghouti and Da'ana, 2020) (Eq. 2), Dubunin-Radushkevich (Wang and Guo, 2020) (Eq. 3), Temkin (Eq. 4) Harkins and Jura (H-J) (Eq. 5), (Hu *et al*., 2023) isotherms:

Langmuir: $q_e = \frac{q_m K_L C_e}{(1+K_L C_e)}$ (1)

Freundlich: $q_e = K_F C_{e^{\frac{1}{n}}}$ (2)

Dubunin-Radushkevich:

$$q_e = qDexp\left(-\beta\left[RT\ln\left(1+\frac{1}{C_e}\right)\right]^2\right) \quad (3)$$

Temkin: $q_e = K_T C_{e^b}$ (4)

Harkins and Jura: $q_e = \left(\frac{A}{B\log C_e}\right)$ (5)

The results for the adsorption isotherms for the adsorption studies are shown on Figure 2 for unactivated boiler fly ash; Figure 3 for activated boiler fly ash; Figure 4 for unactivated maize cob and figure 5 for activated maize cob. The constants for the isotherms and R^2 values are shown on Table 2.

From the R^2 values, it could be seen that the Freundlich isotherm, gave the best fit to the sorption data, comparing favourably with the experimental plots. The trend of fitness of the isotherms isFreundlich>Langmuir> Temkin>Dubinin-Radushkevich>Harkins-Jura.

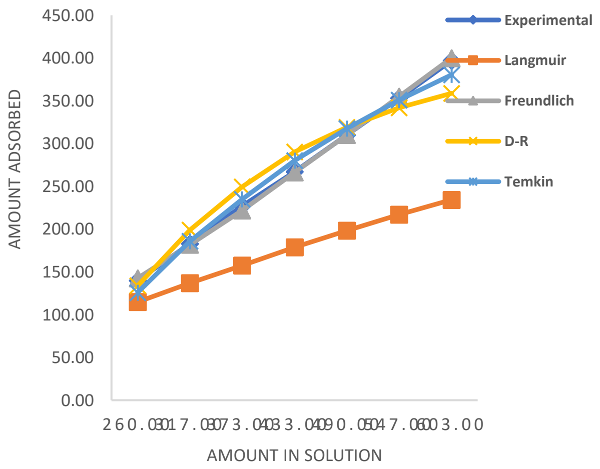

FIG 2: ADSORPTION ISOTHERM PLOTS AGAINST EXPERIMENTAL FOR ADSORPTION OF MONOCROTOFOS PESTICIDE USING UNACTIVATED BOILER FLY ASH

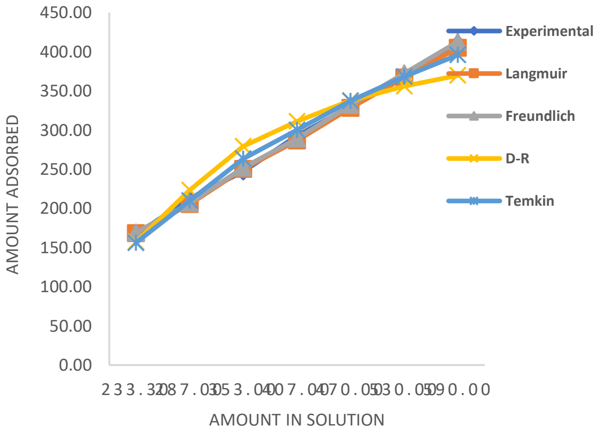

FIG. 3: ADSORPTION ISOTHERM PLOTS AGAINST EXPERIMENTAL FOR ADSORPTION OF MONOCROTOFOS PESTICIDE USING ACTIVATED BOILER FLY ASH

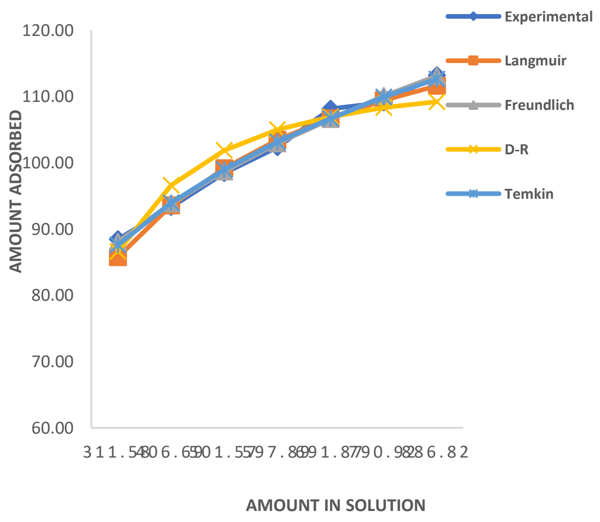

FIG. 4: ADSORPTION ISOTHERM PLOTS AGAINST EXPERIMENTAL FOR ADSORPTION OF MONOCROTOFOS PESTICIDE USING UNACTIVATED MAIZE COB

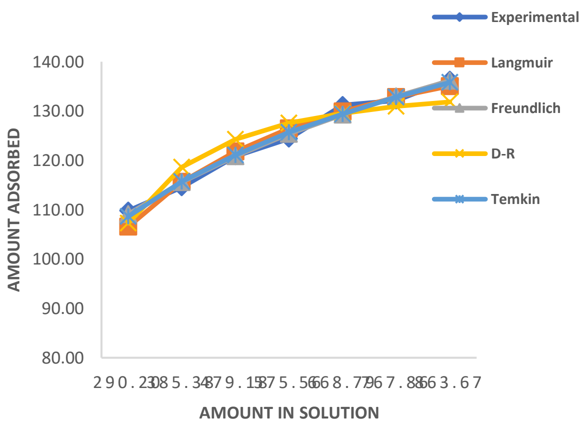

FIG 5. ADSORPTION ISOTHERM PLOTS AGAINST EXPERIMENTAL FOR ADSORPTION OF MONOCROTOFOS PESTICIDE USING ACTIVATED MAIZE COB

Table 2: Adsorption isotherm parameters for the adsorption of monocrotophos pesticide onto Unactivated BFA, Activated BFA, Unactivated MC and Activated MC

S/N	*Isotherm/Constants*	*Boiler fly ash (BFA)*		*Maize Cob (MC)*	
		Unactivated BFA	Activated BFA	Unactivated MC	Activated MC
1.	Langmuir				
	q_m (mg/g)	1111.11	5000.00	133.33	156.25
	K_L (L/mg)	4.4313 E-4	1.4946 E-4	5.7854 E-3	7.3843 E-3
	R^2	0.9024	0.4656	0.9977	0.9980
2.	Freundlich				
	1/n	1.2266	0.9608	0.2393	0.2031
	K_F (mg/g)	0.555	0.8987	22.2844	34.4905
	R^2	0.9988	0.9970	0.9923	0.9887
3.	D-R				
	B (mol^2/J^2)	0.0134	0.0089	0.0042	0.0032
	q_D(mg/g)	449.62	432.51	112.84	135.36
	R^2	0.9581	0.9429	0.8993	0.8810
	E	7.50	6.11	12.50	10.91
4.	Temkin				
	A	5.83 E-3	7.85 E-3	0.1243	0.2698
	B	302.52	256.32	23.949	24.912
	R^2	0.9846	0.9849	0.9892	0.9853
5.	H-J				
	A	10000.00	14285.71	10000.00	16666.67
	B	3.00	2.86	4.00	3.33
	R2	0.9001	0.9212	0.9910	0.9899

Adsorption isotherm models have been employed to model equilibrium sorption data (Al-Ghouti and Da'ana, 2020; Alacabey, 2022; Murtala *et al*., 2022; Harabi *et al*., 2024; Sunartaty, *et al*., 2024) and many authors have found Freundlich isotherm as giving a best fit to sorption experimental data (Kowanga *et al*., 2016;Li *et al*., 2022).The Freundlich isotherm has been reported to be used to describe non-monolayer adsorption that occurs on the non-uniform surface of the adsorbent(Afroze *et al*., 2016; An *et al*., 2017).Also, the low values of the mean sorption energy (E) of monocrotophos adsorption on UNACT-BFA (6.11); ACT-BFA (7.50); UNACT-MC (10.91) and ACT-MC (12.50); showed that the forces of attraction were Van der Waal and not chemical bonding; hence, the sorption processes involved was physical adsorption (physisorption),

CONCLUSIONS

Therefore, this work has shown that activated and unactivated boiler fly ash and maize cob, can be used to remove monocrotophos pesticide from aqueous solution. Also, isotherm models were successfully used to model the sorption equilibrium data and Freundlich isotherm was found to give best fit to the sorption data.

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CHEMICAL SOCIETY OF NIGERIA (CSN) ABIA CHAPTER

A paper presented at the maiden AbiaChem conference held at COLPAS Old Building, Michael Okpara Universisity of Agriculture, Umudike, Abia State between 23rd and 25th July, 2024. **Article Number: AbiaChem1-041-ORG; Pages 270-278.**

Conference Proceedings

Full Length Research Paper

ANTI- NOCICEPTIVE ACTIVITIES OF *Allium sativum* (GARLIC) AND *Curcuma longa* (TURMERIC) ESSENTIAL OIL ON WISTAR ALBINO RATS (*Rattus norvegicus).*

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ABSTRACT

The current study assessed the analgesic and anti-inflammatory properties of turmeric and garlic essential oils. The essential oils were hydro distilled from the rhizomes of turmeric and bulbs of garlic in a yield of 0.80% (w/w) and 0.75% (w/w) respectively. The anti-nociceptive activity was not fully displayed in essential oils of *C. longa* until the 90th and 120th minute ($p<0.05$ top >0.01) for only the 400 mg dose. The activity increased steadily between the 90th and 120th minute. Statistically, the essential oil of *A. sativum* was non-significant at confidence level of $p>0.05$. The anti-inflammatory activity of the oils was only significant ($p>0.001$) for the 100 mg per administration and shows a very high inhibition rate between the 1st to the 3rd hr. The activities of the 200 mg/kg of the essential oils were only active at the 4th hour. Activity observed could be attributed to effect of absorption rate and inflammation mediators' modulations. There is evidence showing that these plants have anti-inflammatory and anti-nociceptive potency. This review concludes with emphasis on dietary consumption of these plants, if not contraindicated may be effective for different pharmacological effect. This research work will also help other researchers and new drug developers in the preparation of new combination of these active constituents with other herbal formulation.

Keywords: *Allium sativum, curcuma longa,* essential oils, anti-inflammation, anti-nociceptive, carrageenan and ibuprofen

INTRODUCTION

Medicinal Plants include plants that have biological (medicinal) activities used in traditional medicine utilized by over 3.3 billion people in the less developed countries (Ahvazi et al., 2012; Moges & Moges, 2020; Salmerón-Manzano et al., 2020; Oteng Mintah et al., 2019). These medicinal plants are rich in biological active components which can be used in drug development. The use of medicinal plants in traditional medicine of most developing countries for the maintenance of good health, has been widely observed. Furthermore, during the past decade, the preparation of medicine and development of several drugs and chemotherapeutics from these plants as rural herbal remedies have become a topic of global importance (Sofowora et al., 2013; Chaachouay & Zidane, 2024; Ekor, 2014; Fawzi Mahomoodally, 2013; Kazantseva et al., 2022).

Essential oils are the volatile and water immiscible compounds extracted from plants and composed of aromatic odors, aliphatic hydrocarbons, and fatty acids. Essential oils are enormously used in phytomedicine and aromatherapy and also in pharmaceuticals as antibacterial, antioxidant, antiviral, insecticidal, anti-inflammatory, anticancer, etc. (Nazir & Ahmad Gangoo, 2022; Hamid et al., 2011; de Sousa et al., 2023; Mohamed & Alotaibi, 2023; Ramsey et al., 2020).

The health benefits of essential oils include brighten (whitens) and *takes care of skin* problems such as moisturizes dry skin, keeps the skin young and free from wrinkles, *including problems* caused by stress and chicken pox, elevates mood, lower anxiety (keep body and mind fit), easing heartburn, easing aches and pains (Orchard & van Vuuren, 2017; Gao et al., 2023; Khakham, 2023).

Essential oils act as decongestant by providing a short-term relief for blocked nose (nasal congestion) in colds and flu, hay fever, catarrh and sinusitis by reducing the swelled blood vessels in the nose thereby opening airways and also decreases plaque formation in respiratory mucosal cell lines (NHS, 2023; Chang et al., 2013; Lizogub et al., 2007).

Natural essential oils have played an essential role since ancient times, as antimicrobial and antibacterial agent in human pathogens against gram-negative bacteria (*Escherichia coli*, *Klebsiella pneumoniae*, *Pseudomonas aeruginosa*, *Proteus vulgaris*) and two gram-positive bacteria *Bacillus subtilis* and *Staphylococcus aureus,* reduce microbial contamination *(*Bachir & Benali, 2012; Amini et al., 2016; Prabuseenivasan et al., 2006; Sienkiewicz et al., 2012; Nuñez & Aquino, 2012; Chouhan et al., 2017; Man et al., 2019*)*.

Essential oils were found exhibit a strong analgesic and anti-inflammatory activities in various severe cases of inflammation by inhibit the production of cyclooxygenase (COX), the enzyme that makes prostaglandins (PGs). These essential oils provide relief from joint pain and other body pains (Ricciotti & FitzGerald, 2011; Miguel, 2010; Chahal et al., 2023; Chandrakanthan et al., 2020; Chahal et al., 2023; Xiao et al., 2014).

Essential oils are used in food industries to season or condiment dried and cured meats, soups, ice- cream, cheese. They are also used in the alcoholic and nonalcoholic beverages and in making of sweets and chocolate (oranges, lemon, mint and fennel). Also, to extend the shelf life of foods as a preservative (Marshall, 2018; Snyder, 2019; Ameh & Obodozie-Ofoegbu, 2016).

In pharmaceutical industry they are used flavour toothpaste in dentistry (mint, eucalyptol and fennel essences), and as analgesics. They are used in many medicines to neutralize unpleasant tastes. Cosmetic industries use essential oils to make cosmetics, soaps, scents, perfumes and make- up (Sarkic & Stappen, 2018; Sharma et al., 2023).

To balance up the increasing free radical production in organism and food products the problems oxidative stress and the attendance chronic sickness and contamination and oxidation of foodstuffs, the chemistry development has favored the appearance and application of new chemical substances such as essential oils that is generally considered as safe. (Konfo et al., 2023; Inobeme and Adetunji, 2024; Preedy, 2015; Rao et al., 2019). The antimicrobial properties of essential oils medicinal plants have been reported to be effective as a chemical preservative in foods against strains of *Staphylococcus aureus*, *Listeria sp*, *Escherichia coli* and *Salmonella sp.* that contaminate food and cause Foodborne Diseases (FBD) (de Almeida et al., 2023; Pinto et al., 2024; Abdi-Moghadam et al., 2023; Bava et al., 2023; Fournomitiet al., 2015; Omidbeygi et al., 2007).

The veterinary industries use the essential oil of the *Chenopodium ambrosoides*, which is highly prized for its ascaridole (worm-killer) content. Limonene, menthol, menthe spicata (spearmint) and tanacetum pennyroyal against ant; garlic, coriander, aniseed, basil against aphids; lavender, mints, lemongrass against fleas; rue, citronella, mint against flies; menthaspicata, basil, rue against lice; mints, hisopo, rosemary, dill against moths; tanacetum, cumin, wormwood and thyme against cockroaches; and tagetes, salvia, calendula, asparagus, etc. against nematodes essences are used to make insecticides (Nerio et al., 2010; Regnault-Roger et al., 2012;). There are certain substances used as biocides such as thymes, cloves, salvia, mint, oregano, pine with bactericidal properties (Russo & Palla, 2023; Macchia et al., 2022; Raveau et al., 2020).

The essences different plant origin is used to disguise (as deodorant) the unpleasant smell of industrial products like rubber, plastics (such as toys), textile industry, paper manufacture (such as notebooks, toilet papers and face wipes are scented), and paints (Sousa et al., 2022; Rowe, 2005; Johansen, 2008). Menthol is used in tobacco industry for the mentholated cigarette (Lee & Glantz, 2011; Anderson, 2011; Kreslake et al., 2008).

MATERIAL AND METHODS

Plant sample collection

Fresh rhizomes of *Curcuma longa* (turmeric) and bulbs of *Allium saliva* (garlic) were collected from local market lyana-Iba Market Ojo, Lagos State of Nigeria on 12th of May 2022 and was identified by Yebunji, 0.0. of the University of Lagos Herborium under herbarium number LUH 7631 and LUH 7633 respectively.

Drugs and reagents

Ibuprofen and diclofenac Injection, , Distilled water, Acetylsalicylic, Saline solution, Hexane, and Carrageenan.

Preparation of plant materials

The plant samples were air-dried at room temperature for three weeks and ground using mortar and pestle into powdery form to increase the surface area hauling the oil particles.

Isolation of essential oil

The leaves sample (200g) were packed into the round bottom flask, and was adequately filled with distilled water. The grounded samples was then subjected to hydro distillation, the oil was collected over hexane and kept in a air tight tube called beer Lambert tube, kept in a cool and dry place until analysis.

Anti-nociceptive Activities of *Curcuma longa* (Turmeric) and *Allium sativum* (Garlic)

Study Design

Adult Wistar albino rats (Rattus norvegicus) weighing between (100-180g) of either genders were used. Animals were kept in cages in temperature-regulated either genders w house and had good access to water and standard laboratory diet. They were allowed to acclimatize to the laboratory conditions for a period a two weeks.The animals were kept fasting for 12h prior to the time of experiment. Rats were grouped into five groups (A-E)consisting five rats each. The first group (A) receive standard diclofenac, while the second group (B) is used as control. Third (C), fourth (D) and fifth group (E) were given extract from turmeric and garlic in a different dosage of 100 mg, 200 mg, and 400 mg.

Anti -nociceptive activities

Anti -nociceptive activities of the extracts were carried out using hot plate method. Time in seconds between placing threat on the radiant heat source at 55°C and sharp withdrawal upon licking of the paws or jumping was recorded as "reaction time". After doseing with the prepared extt:act and placing on the radiant heat source at 55°C an increase in reaction time was indicative of analgesia. Maximum possible analgesic was calculated from increase in time.

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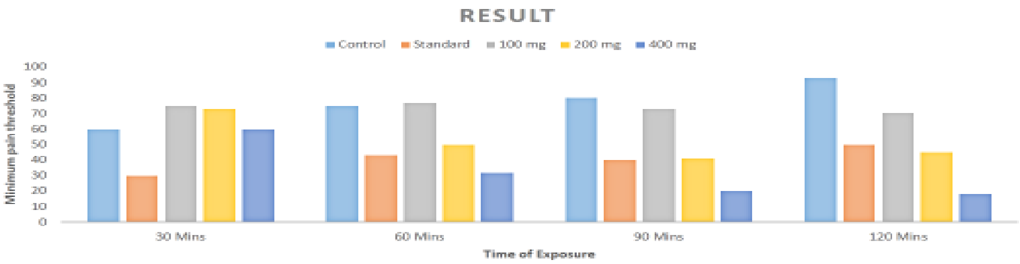


A bar chart showing anti-noiciceptive activity of essential oil of *C. longa* on hot plate test.

Effect of C.longa on heat induced pain. Control, Standard, and C.Longa represent 1mL saline solution, 100 mg/kg of Aspirin injection and 100, 200, and 400 mg of C.longa respectively. *P<0.5, * *P<0.01, * * * P<0.001 statiscally compared to control.

Anti- inflammatory activities of *Curcuma longa* (turmeric) and *Allium sativum* (garlic) Carrageenan Activities

Paw edema was induced by an intradertnal injection of 0.1 ml of carrageenan (1% in normal saline solution) into the plantar surface of the lett hind paw of rats. The acute phase of inflammatory reaction, i.e. edema volume of left hind paw was determined using a digital venial caliper prior to and 30, 60 and 120mins after carrageen in injection. All the drugs were administered one hour prior to carrageenan.

Percentage inhibition of paw edema was calculated using the following formula:

$$\% \text{ inhibition} = \frac{V_c - V_t}{V_c} \times 100$$

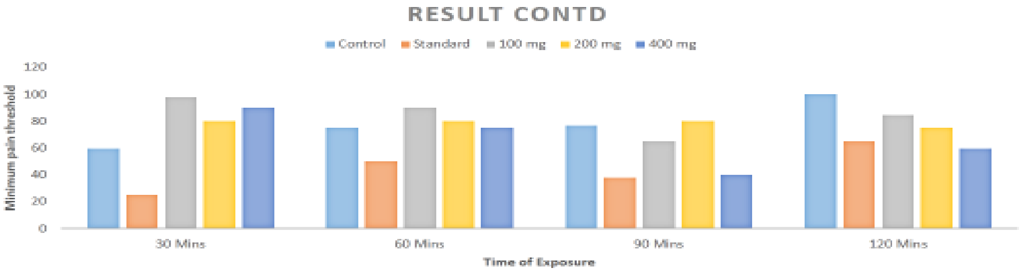
V_c= mean paw edema volume in control group

V_t = mean paw edema volume of treated group

RESULT AND DISCUSSION

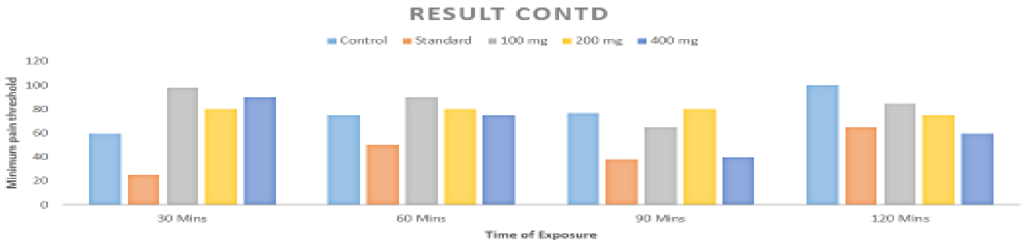
Results

The results of the experiments are as follows.



A bar chart showing anti-noiciceptive activity of essential oil of *A. sativum* on hot plate test.

Effect of A. *sativum* on heat induced pain. Control, Standard, and A. *sativum* represent 1mL saline solution, 100 mg/kg of Aspirin injection and 100, 200, and 400 mg of A. *sativum* respectively. *P<0.5, * *P<0.01, * * * P<0.001 statistically compared to control.



A bar chart showing anti-noiciceptive activity of essential oil of *A. sativum* on hot plate test.

Effect of A. *sativum* on Carragenean-induced inflammation. Control, Standard, and A. *sativum* represent 1mL saline solution, 100 mg/kg of Aspirin injection and 100, 200, and 400 mg of A. *sativum* respectively. *P<0.5, * *P<0.01, * * * P<0.001 statistically compared to control.

DISCUSSION

In carrageenan-induced inflammation, the essential oils of *Allium sativum* induced time dependent in paw edema is summarized in figure 4.13. The anti-inflammatory activity of the oils was only significant ($p<0.001$) for the 100mg per administration and shows a very high inhibition rate between the 1st to the 3rd hr. The activities of the 200mg/kg of the essential oils were only active at the 4th hour. At this hour, the inhibition was more pronounced than the ibuprofen injection. The carrageenan model is a time-dependent tri-phasic process. The 1st phase which involves the liberation of histamine serotonicn (0-2h), the 2nd is cytokines (3rd h), and he the 3rd phase is prostaglandin (4h). *Curcuma longa* have been potentially active within the 4th hour inhibiting the cyclooxygenanse (COX) responsible for the prostaglandin synthesis. Activity observed could attributed to effect of absorption rate and inflammation mediators' modulation. Earlier investigations by [62],65] showed that xylene-induced ear edema using acute exudative and chronic proliferative (cotton pellet granuloma) inflammation models. Xylene-induced ear edema model is useful for the evaluation of anti-inflammatory topical steroids and non-steroidal antiphlogistic agents, especially those phospholipase A2. Application of xylene induces acute neurogenous edema, which is partially associated with the substance P. Substance P is widely distributed in the central and peripheral nervous system and its release from sensory neurons in the periphery causes vasodilatation and plasma extravasations, leading to swelling of the ear, suggesting the role of xylene in neurogenous inflammation.

Analysis performed on four anti-inflammatory sulfur containing compounds from garlic indicated that sulfur compounds inhibited the production of nitric oxide (NO) and prostaglandin E2 (PGE2) and the expression of the pro-inflammatory cytokines tumor necrosis factor-α, interleukin-1β in lipopolysaccharide (LPS)-activated macrophages.

Activites carried out utilized acute (Carrageenan induced paw edema) and chronic (Cotton pellet induced granuloma) inflammatory models. Allocated to the control, standard (Piroxicam) and test (Garlic) drug groups. The effect of the test drug in terms of present inhibition was found to be about 50% in acute and 21% in chronic models. Also, the acute effect was similar to standard drug (Prabuseenivasan et al., 2006; Lizogub, et al., 2007; Bachir, R. G., and Benali, M. 2012; Sienkiewicz et al., 2012; Amini et al., 2016)

In the hot plate nociception test, the essential oil reduced the paw licking time in all phases is summarized in fig. 4.12. The anti-nocieptive activity was not fully displayed in the essential oils of *C. longa* until the 90th and 120th minute

($p<0.05$ to $p<0.01$) for only the 400mg dose. The activity increased steadily between the 90th to the 120th minute. Statistically, the essential oil of *A. sativum* was non-significant at confidence level of $p>0.05$.

A previous experimental study done in the laboratory setting of the department of Clinical Pharmacology and Therapeutics, Koirala Institute of Medical Sciences, Dharan, Nepal (BPKIHS). Hot plate test, Tail flick test and Writhing test were used for evaluating the antinociceptive effects. A probability level less than 0.05 ($p<0.05$) was considered significant. Significant effects in comparison to vehicle were observed in all the three antinociceptive test models at 200mg/kg test dose of aqueous extract of purified *Curcuma longa.* No significant effect as compared to vehicle was observed at 50mg/kg and 100mg/kg test doses of *C. longa*. This study showed that *C. longa* possesses antinociceptive effect (Nuñez and Aquino, 2012; Chouhan et al., 2017)

CONCLUSION

This research shows that oils from turmeric possess anti-nociceptive properties on rats Garlic show non-significant for anti-nociceptive. Turmeric was active at 100mg for long term pain. Based on the data in literature regular dietary consumption of garlic and turmeric, if not contraindicated may be effective for different pharmacological effect.

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CHEMICAL SOCIETY OF NIGERIA (CSN) ABIA CHAPTER
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Conference Proceedings

REVIEW

WASTE MANAGEMENT AND SUSTAINABLE CHEMISTRY AS A SOLUTION TO NIGERIA'S UNDERDEVELOPMENT

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ABSTRACT

Waste management has been erroneously perceived to be the sole responsibility of local authorities but the operational effectiveness and efficiency of the management of waste lies upon the active participation of both the citizens and the municipal agency. This study investigates waste management and sustainable chemistry as a solution to Nigeria's underdevelopment. The study uses a review approach to examine this subject matter. The review is based on existing literature to discuss waste management. The study reveals that about 50% of generated solid waste in many Nigerian cities has remained unattended, thus, giving rise to unhealthy conditions especially in crowded regions. More so, this study reveals that paucity of funds and unhealthy implementation of waste management policies and programs are among the factors that have hindered waste management in Nigeria. This study concluded that illnesses and deaths can be prevented if both the citizens and local authorities jointly ensure that waste and chemicals usage do not pollute the environment nor contaminate water, air and soil, thus, helping to solve the problem of underdevelopment in Nigeria.

Key Words: Waste Management, Sustainable Chemistry, Waste Disposal, Incineration, Underdevelopment,

INTRODUCTION

Wastes arise through the uncontrolled activities of human beings. The geometric rise in human population coupled with urbanization and large communities' growth have triggered waste generation. Many negative effects have emanated from the lackadaisical management of waste and these include, among others, the contamination of the atmosphere, soil and water, thus, causing a major impact on public health. This paper seeks to address waste management and sustainable chemistry as a panacea to Nigeria's underdevelopment problems.

In virtually all the activities of man (agricultural, chemicals, water purifiers, medicines, among others), chemicals play a key role. More so, the chemical industry contributes significantly to the gross domestic product (GDP) and job creation of national economies. However, any mismanagement of chemical poses a big risk to poor communities in developing economies (including Nigeria). This is due to their conditions of living, occupations and lack of access to hygienic food and water (UNDP, 2015).

A good use and application of pesticides and fertilizers can make fertile agricultural lands on which poor and rural communities depend for survival. On the contrary, when agricultural chemicals are poorly managed and handled, they can pose big risks to the health of humans and can also lead to land degradation, impacting livelihoods in agricultural sector, fisheries and other sub-sectors (UNDP, 2015).

GENERATION OF WASTE

Many researchers have identified some stakeholders, persons, organizations or institutions that may have interests in sufficient waste management. These include the government (both local and national), municipal authorities, non-governmental organizations (NGOs), city corporations, private contractors, households, recycling companies and Ministries of Finance, Health and Environment (Guerroro et al., 2013).

Furthermore, some writers and scholars have identified some important factors that affect the elements of the waste management systems. These factors include family size, education level and monthly salary, among others (Sajauddin et al., 2008). Also, households' attitudes, which are related to the separation of waste are influenced by the active investment and support of a real estate company, community residential committees' inclusion for public participation and collection service fee based on the weight and volume of the waste (Sheinberg, 2011). In addition to the above factors are land size, peer influence, gender, household location and membership of environmental organization (Ekere et al., 2009).

According to Hazra et al. (2009), it has been discovered that the collection, transfer and transport or movement practices are being affected by insufficient information on collection schedule, poor route planning and improper bin collection systems, inadequate infrastructure and bad roads. Notwithstanding the organization of the informal sector and the promotion of micro-enterprises are some of the effective ways to extend affordable waste collection services (Sharholy et al., 2008).

The incessant migration of people from rural to urban cities and towns in Nigeria has been trending over the years. This uncontrolled growth of urban cities has left many cities in Nigeria deficient in infrastructural services like pipe-borne water, sewage disposal and solid waste management (Singh et al., 2018). About 50% of generated solid waste in many Nigerian cities has remained unattended to. This has given rise to unhealthy conditions especially in crowded regions, thus, resulting in a rising morbidness especially due to microbial and parasitic infections across the population with the urban dwellers and waste controllers being worst hit. Waste management is part and parcel of public health and sanitation.

WASTE GENERATION, DISPOSAL AND HEALTH

Associated with the handling, disposal and treatment of waste either directly or indirectly are health issues. Directly by recovering and recycling activities in the waste management industry through exposure to poisonous substances in the waste or to emissions from landfill site, incinerators, odors, noise and indirectly through ingestion of contaminated food, soil and water (Ministry of Health, 1995).

As remarked by Viel et al. (2008), despite the advancements in technology, improved legislation coupled with regulatory systems in waste management field and health surveillance, the acceptance of the public on the new waste disposal and treatments facilities is still insignificant. This is due to lack of concern about adverse effects on the environment and human health. Studies have shown that incinerator's emissions are linked to respiratory illnesses. Serious and chronic symptoms of respiratory failure are also connected to incinerator emissions, likewise the association between the development of certain cancers' symptoms in person who are living very close to incinerator sites.

Crowley et al., (2003) identified the following specific cancers: laryngeal cancer, excess of bladder, liver cancer, soft-tissue sarcoma and cancer of the lung, stomach cancer and leukemia. More so, there is a gradual rise in risk of negative health effects close to landfill sites and real risks linked to residence close to certain landfill sites.

INCINERATION OF WASTE

Waste incineration can help decrease the quantity of disposed waste by up to 90% (Singh, 2018). These significant quantity reductions can be found only in waste streams that have high amounts of packaging materials, paper, horticultural waste and plastics. Because of costs and pollution, incineration without energy recovery is not a chosen option.

Waste incineration is a very costly and it poses problems of air and ash pollution. Incineration needs wastes kept outside for gathering to be put in containers in order to stay dry and much of the waste stream is not inflammable. However, it can be used to bring down the original volume of combustibles by 80-95% (Urban Development Series, 2012).

WASTE DISPOSAL, RECYCLING AND MANAGEMENT

On factors influencing household waste disposal decision-making, Tedesse et al. (2008) listed the supply of waste facilities, insufficient supply of containers and longer distance to these containers, inadequate funds, lack of legislation, among others. As regards waste recycling, Gonzalez-Torre et al. (2005) discovered some factors as being the reasons why some communities build and develop strong recycling habits. These factors include among others, social influences, beneficent and regulatory factors.

These authors also reported that persons who go to the bins frequently to dispose of general refuse are more likely to recycle some products in their homes. Again, in most cases, the shorter the distance to the recycling, the bigger the number of fractions that citizens separate and take at home. According to Matete et al. (2008) and Asase et al. (2009) respectively, factors that affect the management of environmental aspect of solid waste in developing countries (including Nigeria) are lack of environmental control systems and real impacts evaluation, among others.

Municipalities have not been able to handle solid waste as a result of financial factors. The delivery of proper waste management services has been hindered by the following factors: big expenditure required to provide the service, lack of zeal on the part of the users to pay for the service and inadequacy of proper use of economic instruments (Sharholy et al., 2007).

The management of waste has been regarded generally as the sole responsibility and duty of local authorities and the public is not supposed to participate. Meanwhile, the operational effectiveness and efficiency of the management of solid waste lies upon the active participation of both the citizens and the municipal agency, therefore, societal dislike for contributing in solutions, people's participation in decision-making and community awareness are some of the socio-cultural aspects enlisted by some scholars. More so, waste management workers are always associated with low social status. This situation is as a result of low motivation among the employees of solid waste. Even some politicians do not give high priority to solid waste compared to other municipal activities. These lead to limited trained and skilled personnel in the municipalities.

On the contrary, support from municipal authorities and strategic plans for the management of waste that create room for the annual monitoring and evaluation of the system are among the positive factors that improve the system. Some researchers (Asase et al., 2009) have gone further to point out that adequate and strong legal framework positively contribute to the growth and development of the integrated waste management system. This notwithstanding, the absence of lack of satisfactory policies coupled with weak regulations are hindrances to the development of the integrated waste management system (Seng et al., 2010).

SUSTAINABLE CHEMISTRY

The subject of sustainable chemistry gives a holistic view with the inclusion of relevant tasks of waste management. Sustainable chemistry guides and approaches can be very useful for waste management if and only if more outputs are recycled and more products regained for further use on a high level.

Friege (2016) identifies the following as the benefits of sustainable chemistry in waste management:

- Lower hazardous waste and lower risks for operational health.
- Better use of secondary raw-materials.
- Better quality of resources arising from necessary waste.
- Better use of renewable resources based on separated chemicals from industrial waste.
- Waste reduction as a result of better process in the chemical industry.

GOALS AND IDEAS BEHIND THE SUSTAINABLE CHEMISTRY

1. Making available value-creating products and services through new products and technologies.
2. Raising the use of substances, products and processes with minimal adverse effects.
3. Ensuring recycling concepts.
4. Natural resources conservation.
5. Evading damage and destruction to the ecosystems, resources and human beings.

UNDERDEVELOPMENT

According to Tamuno (2009) in Ukpabia (2019), development means a process of transformation that is usually seen or felt in the occurrence of some desirable changes in different aspects of life of the society. At any point in time these changes are absent in a society, that society can be said to be underdeveloped. Such changes include:

1. Fall in the level of absolute poverty.
2. Rise in the level of employment.
3. Decrease in the extent of personal and regional inequalities.
4. Increase in real output of goods and services plus improvements in production techniques.
5. Improvements in government services, housing conditions, health services and literacy.
6. Improvements in the level of political and social consciousness of the people.
7. Higher ability to draw on local resources (material and human) in order to meet local needs.

For Okowa (2005), the main goals of development are economic, political and social empowerments. Development must entail building the capacity of a nation technologically in order to exploit its environment to attain its existential needs (Ohale, 2018).

FINDINGS FROM THE STUDY

The following findings were made from the study:

1. The application of hazardous chemicals in products and in productive sectors and sub-sectors, their usage and the dumping of commodities or products that contain them, can lead to the release of poisonous chemicals causing pollution that affects the quality of water and makes it unsafe for drinking.

2. Surface waters released from sectors like industry, agriculture, mining, among others, can pollute the seas, oceans, waterways, nutrients and oceans' food chain.
3. The wastes which end up in rivers, oceans or other waterways can cause the yearly death of hundred thousands of sea turtles, fishes and other water animals and sea birds.
4. The use, production and management of chemicals and wastes, if not handled properly can lead to serious environmental degradation, water, air and soil contamination and the disruption of the ecosystem (UNDP, 2015).
5. The management of wastes involves a significant number of different stakeholders, who have different fields of interest. These people are key players in shaping the system of a city or town. However, it is wrongly to be the sole responsibility of the local authorities.
6. There is a cost attached to solid waste services as any other services that are provided but the expenditures are not recovered in general.

RECOMMENDATIONS

Based on the findings of this study, the following recommendations are made:

1. There should be a production of reliable data and the creation of proper information channels between and within municipalities.
2. Decision makers who are saddled with the responsibility of planning and policy making should be well-informed on the cities' situation so as to make positive and rewarding changes, develop good integrated waste management instruments that will be congruent with the needs of the citizens bearing in mind their ability and willingness to pay for the services.
3. Our Universities and other research centers have a significant role to play in preparing and equipping professionals and technicians in the field of environment.
4. We must ensure that wastes and chemicals usage do not pollute the environment nor contaminate water, air and soil, but rather protect the health of humans, thereby preventing illnesses and deaths.
5. Improving and rehabilitating the management and disposal of wastes and the reduction in the release of harmful chemicals is a bold step in the protection of world's seas, oceans and marine raw-materials.

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Conference Proceedings

Full Length Research Paper

EVALUATION OF ANTI-ALZHEIMER'S DISEASE PHARMACOLOGICAL ACTIVITIES OF CURRY (*Murruya keonigii*) PLANT LEAF

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ABSTRACT

Alzheimer's disease (AD) is an old age disease identified in 1906 with progressive neurodegenerative disorder shown by impairment in learning and memory loss, followed by cognitive deficits and behavioural disturbances.The pathology of AD is complicating and multi-factorial which include inflammatory cascade, oxidative stress, senile plague deposition and cholinergic deficit. Recent studies have revealed that plants possessing antioxidant, anti-inflammatory and memory enhancing properties are more effective in the treatment of the disease. This study evaluated the Anti-Alzheimer's disease properties of antioxidant and anti-inflammatory activities of *Murruya keonigii* curry plant leaf using DPPH, FRAP,Hydroxyl radical scavenging techniques, and reduction of egg induced plant oedema respectively. At different concentrations range of 15.63 mg/dl, -1000mg/dl the percentage DPPHH inhibition activity ranges from 73.68± 0.68 - 65.29±4.74 % whereas that of ascorbic acid used as standard ranges from 64.39 +0.48- 62.61±1.97 %. The result of percentage inhibition of hydroxyl radicals of *M.koenigii* at concentration range of 15.63 - 1000mg/dl gave 6.62 ± 0.02% -49.36 ± 2.82% while gallic acid used as standard gave a range of 19.17 ± 2.04% - 93.16 ± 2.49%.The result of FRAP using concentration range of 0.2 mg/ml- 1.0 mg/ml afforded absorbance range of $0.2137\pm0.0058-0.2157\pm0.0000$. Vitamin C used as standard gave lower absorbances of 0.1753±0.0068 - 0.1913±0.0021. The result of the anti-inflammatory study shown by the effect of methanol extract of *Murraya keonigii* on egg albumin induced rat paw oedema indicated that all the doses showed significantly higher inhibitory effects on inflammation than diclofenac sodium ($P < 0.05$). The leaf extract presented strong Anti-Alzheimer's disease pharmacological activities which could be exploited for pharmaceutical formulations.

Keywords: Anti-Alzheimer, antioxidant, anti-inflammatory, *Murraya keonigii*, DPPH, FRAP

INTRODUCTION

Old age is a blessing when it comes with good health but when riddled with diseases it becomes challenging. Alzheimer's disease is one the ailments associated with aging, it is a progressive neurodegenerative disease that is characterized by server memory loss, unusual behaviour, personality changes and a decline in cognitive function. Of the neurodegenerative disorders Alzheimer's disease (AD) is considered to be responsible for about 60% of all dementia in people aged 60 and above (Francis *et al*, 1979). The symptoms are shown by impairment in learning and memory loss, followed by cognitive deficits and behavioural disturbances such as depression, agitation and psychosis. Alzheimer's disease (AD) was identified in 1901by a German psychiatrist and neuropathologist. Alois Alzheimer in a fifty year woman called August Deter, he followed her case until 1906 when she died and the disease was publicly reported (Berchtold and Lotman, 1998). The disease is diagnosed in people above 65 year of age but can also occur much earlier. In 2006 there were about 2.6

million victims or sufferer's world over. (Brookmeyer *et al.,* 2007; Amaducci *et al.*, 1986).

The pathology of AD is complex and multifactorial which include inflammatory cascade, oxidative stress, senile plague deposition and cholinergic deficit. Drugs that have been introduced to manage and treat the disease. have been found to be less effective and with side effects. Hence ethnopharmacological screening of plants may provide useful leads in the discovery of new drugs for Alzheimer's disease.

Recently WHO estimated that about 80% of people world-wide rely on herbal medicine for some part of their primary health care. In Germany about 600 to 700 plant-based medicines are available and prescribed by some 70% of German physicians (Erlich, 2015). This goes a long way to underscore the importance and use of medicinal plants. There is a resurgence of the use and demand for medicinal plants as they play important roles in prevention and management of some health disorders such as diabetes, cancer, arthritis, degenerative challenges like Parkinson and Alzheimer's diseases (Kaur *et al*., 2015). The medicinal value of some natural resources, plants inclusive have not been fully discovered and tapped. Investigations on plants are on-going to discover novel drugs or templates for development of new therapeutic agents.

Murraya keonigii (Linn) Spreng commonly called curry plant, family Rutaceae, is a medicinal plant that is native to India, Sri Lanka and some Asia countries (Harish *et al*., 2012). It is usually found in tropical and subtropical regions and cultivated in China, Australia, Nigeria, South Africa etc. The plant is highly valued for its leaf which is used for spicing and flavouring of food. Curry leaves possess the qualities of an herbal tonic. The medicinal value of this *Murraya keonigii* is as a result of the chemical constituents of the plant. The curry leaves are believed to have several pharmacological and medicinal properties such as anti-diabetic, antioxidant, anti –inflammatory, anti-carcinogenic, anti-ulcer, anti-microbial, anti-hypercholesterol and hepato-protective properties (Patil 2015; Negi *et al*., 2008). Other pharmacological activities of the plant include cardiovascular protection, cytotoxic activity, antidiarrheal activity and phagocytic activity. The carbazole alkaloids, triterpenes and constituents of the volatile oils isolated from the plant may account for these medicinal properties (Bhandari 2012; Disegha *et al*., 2014),

The antioxidant and anti-inflammatory properties of the plant leaves have been linked to the management of Alzheimer's disease. Anti-oxidant activity has to do with substances that prevent damage to cells caused by free radicals. Free radicals are molecules that have unpaired electrons which cause the said molecule to become unstable very reactive. Free radicals in the body have been implicated as major causative agents of some degenerative disorders such as Parkinson and Alzheimer diseases and cause pre-mature aging of skin. They have been linked to causing some age-long diseases such as diabetes, cardiovascular disease, Parkinson and Alzheimer's diseases as they induce oxidative stress (Oboh and Rocha, 2007). AD is seen as being caused by multiple factors, oxidative stress caused by imbalance between production and detoxification of reactive oxygen species (ROS) by the antioxidant defense is taken as one of the important factors in the development of this neurodegenerative disease. Therefore, medications that can reduce oxidative stress through prevention of oxidation of cells will mitigate the effect of neurological orders. Plants with antioxidant properties will be useful in treatment of Alzheimer disease. Hence, this work seeks to evaluate the Anti-Alzhemier's disease properties of antioxidant and anti-inflammatory activities of the plant.

MATERIALS AND METHODS

SAMPLE COLLECTION: *Murraya keonigii* plant leaves were purchased from New Market in Aba South local government of Abia State. The plant was identified and authenticated by The Forrestry Department, Michael Okpara University of Agriculture Umudike, Umuahia Abia State, Nigeria.

SAMPLE PREPARATION: The fresh *M. keonigii* plant leaves were washed with clean water and air-dried on the laboratory bench for a period of three weeks. The leaves were ground with electric blender.

Exactly 700 g of the plant sample was percolated in 1.5 litres of methanol and allowed to stand for 72 hrs , It was then filtered with Whatman filter paper no 42. The filtrate was concentrated with rotary evaporated set at 45C to get a mass of 28 g which was used for the analysis.

DETERMINATION OF ANTIOXIDANT ACTIVITY

The antioxidant activity potential of *M. keonigii* was assayed using DPPH (2,2-diphenyl-1-picrylhydrazyl) and hydroxyl radical scavenging and FRAP (Ferric reducing activity power) techniques

DPPH free radical scavenging assay

The DPPH (2,2 -Diphenyl-1-picrylhydrazyl) free radical scavenging activity of the sample was determined using the method described by Mensor *et al.* (2001). Briefly a 0.1 mM solution of DPPH in alcohol was prepared. The sample extract 1 ml was added to 2 ml ethanolic DPPH solution until the color of sample became purple. Then the mixture was shaken using a vortex and left to stand at room temperature for 30 minutes in a dark place. After, it was stirred again using a vortex. The absorbance of the solution was measured at 517 nm. The degree of the decolouration of the solution effectively indicates the scavenging efficiency of the sample. blank with reagent was prepared and absorbance of it was read. Ascorbic acid was used as control. The percentage inhibition of DPPH activity was calculated using this formula:

$$\frac{A_0 - A_1}{A_0} \times 100\%$$

Where A_0 = Absorbance value of the blank sample or control

A_1 is the absorbance value of the test sample.

Hydroxyl radical scavenging activity assay

Deoxyribose assay was used to determine the hydroxyl radical scavenging activity in an aqueous medium. This was done by measuring the competition between deoxyribose and the fractions of hydroxyl generated from Fe3+/ ascorbate/EDTA/H_2O_2 system according to the method described by Barry *et al.* (1987). The reaction mixture containing $FeCl_3$ (100 mM) EDTA 104 M H_2O_2 (I mM) 1.0 ml of reagent 3.0mM deoxyribose, 0.1mM EDTA, 2mM H_2O_2 and 0.1 L-ascorbic acid, 0.1mM $FeCl_3.6H_2O$ in 10 mM phosphate buffer pH 7.4 and various concentration of the extract 50-350 µg/ml. The reaction mixtures were incubated at 37 °C for 1hr followed by addition of 1.0ml of 1% (w/v) TBA (0.25 N HCl) 1.0 ml 10%(w/v) TCA. The reaction mixture heated in a boiling water bath 100°C for 20 min and the pink chromogen (malondialdehyde –TBA adduct) was extracted into 1.0 ml of butan-1-ol for the absorbance to be read at 532nm against reagent blank. Ascorbic acid was taken as the positive control. (Tijaani *et al.,* 2018). The percentage inhibition was calculated using the expression.

$$\frac{\text{Abs (control)} - \text{Abs(Sample)}}{\text{Abs (control)}} \times 100$$

Ferric reducing activity potential (FRAP) assay

The reducing power activity of sample extract was assayed according to the method of (Yen and Dun-Chen (1995) modified from the method of Oyaizu (1986). Sample extract was mixed with phosphate buffer (2.5 ml), 2m, pH

6.6) and potassium Ferricyanide [$K_3Fe(CN)_6$] (2. 5ml, 1%). The mixture was shaken using a vortex and incubated at 50°C for 20 mins. Then it was cooled. Trichloroacetic (TCA) acid 2.5ml, (10%) was added to the mixture which was then stirred using a vortex and centrifuged at 300 rpm for 10 mins. The solution (2.5ml) was mixed with distilled water (2.5ml) and ferric chloride ($FeCl_3$) (0,5ml, 0.1%). Then the mixture was shaken again using a vortex and the absorbance of the solution was measured at 700nm.

ANTI-INFLAMMATORY ACTIVITY ASSAY BY EGG-ALBUMIN-INDUCED INFLAMMATION IN RATS

Adult albino rat (23-28g) of either sex randomized into different groups of 6 mice, each was used for the experiment. The leaf extract (27, 54 and 81mg/kg i.p) and ASA (100m/kg orally) was administered to mice 1 hr before the induction of inflammation. Control group received 10,l/kg of distilled water orally. Inflammation was induced in mice by the injection of 0.1ml of fresh egg-albumin into the subplantar tissue of the right hind paw . The linear circumference of the injected paw was measured before and after 0.5,1,2,3,4 and 5hrs after the administration of the phlogistic agent. Edema (inflammation) was assessed as the difference in paw 5hrs after the administration of the phlogistic agent (Hess and Milonig, 1972). All the animals were fasted for 24 hours before the commencement of the experiment. The average (mean) oedema was assessed by measuring with vernier calipers

RESULTS OF ANTIOXIDANT ACTIVITIES OF *M. keonigii* PLANT LEAF

Results of DPPH (2,2-dipheny-1- picryl-hydrazyl) percentage DPPH inhibition (Figure 1); percentage inhibition of hydroxyl radicals (Figure 2) and ferric reducing assay potential (FRAP) are as shown below.

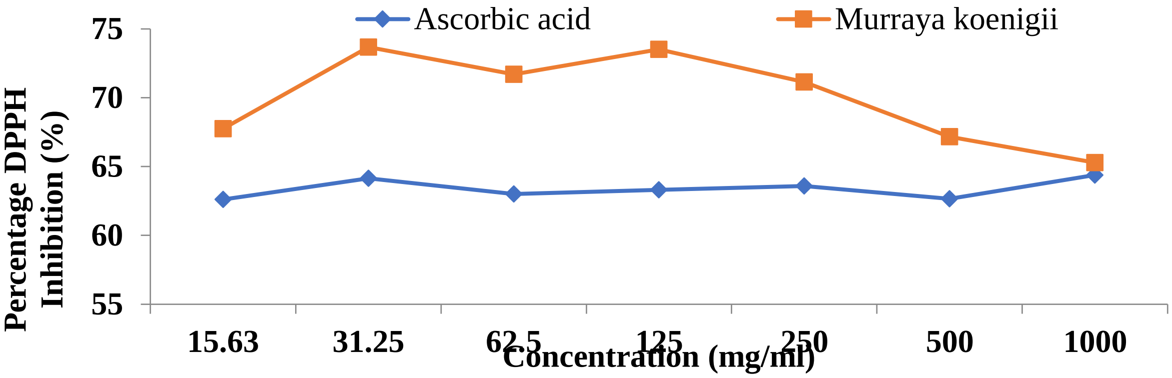

Figure 1: Graphical representation of percentage DPPH inhibition

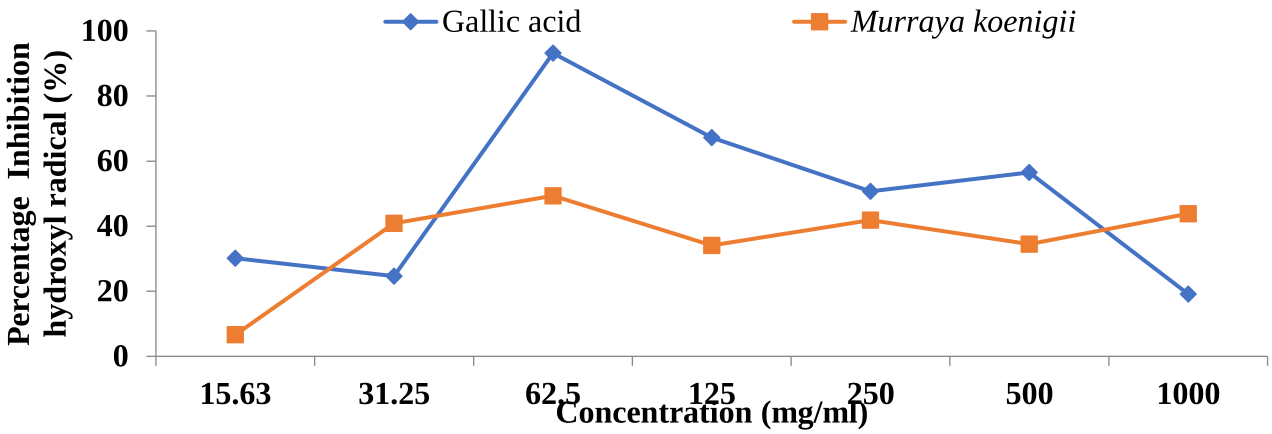

Figure 2: Graphical representation of percentage hydroxyl radical inhibition

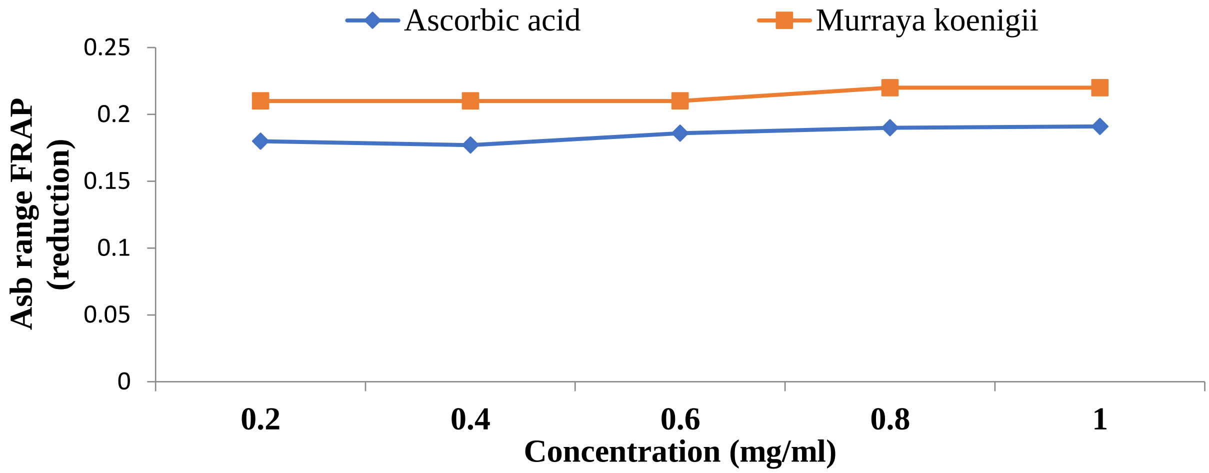

Figure 3: Graphical representation of FRAP assay

RESULT OF ANTI-INFLAMMATORY ANALYSIS

The results of anti-inflammatory analysis are shown in Table 1 below.

Table 1: Effect of methanol extract of *Murraya keonigi* on egg albumin induced rat paw oedema

Treatment (mg/kg b. w)	Mean increase in paw size (mm)					% decrease in Paw size at 4 hrs
	0 hr	1 hr	2 hrs	3 hors	4 hrs	
NCR	0.11± 0.01*	0.11± 0.00*	0.11± 0.01*	0.11± 0.00*	0.11± 0.01*	
EAIORAT	0.40 ± 0.00	0.35± 0.07	0.35± 0.07	0.35± 0.07	0.32± 0.00	20
EAIORAD	0.35±0.06	0.37± 0.02	0.29± 0.01	0.21± 0.05	0.22± 0.02	37
EAIORA100E	0.35± 0.07*	0.22±0.02*	0.25±0.00*	0.23±0.04	0.20±0.04	43
EAIORA200E	0.40 ± 0.01*	0.23 ± 0.04*	0.23 ± 0.04*	0.21 ± 0.14	0.19± 0.00	53

Data expressed in Mean ± SD: *Significant at $P < 0.05$ compared with EAIOAT
NCR: Normal control rats
EAIOAT: Egg albumin induced oedema rats administered 20% tween 80
EAIORAD: Egg albumin induced oedema rats administered Diclofenac
EAIORA100E: Egg albumin induced rats administered 100 mg/kg b. w. of MK extract
EAIORA200E: Egg albumin induced rats administered 200 mg/kg b. w. of MK Extract

DISCUSSION

The result of 2,2-diphenyl-1- picrylhydrazyl (DPPH) antioxidant property of *Murraya keonigii* methanol (MKME) extract as shown in Fig. 1 revealed that the extract compared favourably with the standard reference vitamin C. At low concentrations of 15.63, 31.25 and 62.5 mg/dL the MKME was found to show high percentage inhibition 67.76 %, 73.68 % and 71.70 % when compared to the standard. At high concentration of 500 and 1000 mg/dL the percentage inhibition of the extract reduced while percentage of the standard increased but still lower than that of the extract. From the result so far, the MKME has more antioxidant potentials than the standard ascorbic acid. The antioxidant assay using DPPH inhibition revealed that it has a potent antioxidant activity comparable to vitamin C which was used as a reference standard. 2, 2-diphenyl-1-picrylhydrazyl (DPPH) is a dark-coloured crystalline powder composed of stable free radical molecules. In laboratory, it is used to monitor chemical reactions involving radicals, most notably antioxidant assay (Sharma and Bhat, 2009; Onoja and Anaga, 2013). The antioxidant compounds neutralize the free radical character of DPPH by transferring either electrons or hydrogen atoms to DPPH thereby changing the colour from purple to the yellow-coloured stable diamagnetic molecule diphenyl-picryl-hydrazine. (Naik, *et al*., 2003). The degree of discoloration indicates the scavenging potential of the extract or antioxidant in terms of hydrogen donating ability (Mosquera *et al*., 2007). Absorbance increases with concentration of plant extract indicating the concentration of hydrogen donating compounds in the extract also increased which also implies high reducing power. Antioxidants are generally compounds that terminate the attack of free radicals and thus reduce the risk of these degenerative diseases like neurological disorders, cancer, emphysema, cirrhosis. atherosclerosis, arthritis, Alzhemer’s disease. Antioxidant supplements or dietary antioxidants protect against the damaging effect of free radicals.

The result of the percentage inhibition of the hydroxyl radical is graphically shown in figure 2. At concentration of 1000 mg/dL, the percentage inhibition of MKME was observed to be 43.82% while that of the reference standard (gallic acid) was recorded as 19.17%. At this concentration, the MKME showed a higher percentage than the reference standard gallic acid. At 500 mg/dL the percentage of MKME decreased to 34.49% while that of the reference standard increased to 56.51%. At 125 mg/dL the percentage inhibition MKME remained at 34.10% while that of Gallic acid increased to 67.20%. At concentration of 62.5 mg/dL MKME showed a peak inhibition of 49.36 % while that of the reference standard gallic acid was recorded as 93.16 % at the same concentration. At the least concentration of 15,63 mg/dL there were significant reductions in the percentage inhibitions of MKME and the reference standard gallic acid which were observed to be 6.62% and 30.13 % respectively. At concentration of 62.5 mg/dL the *Murraya keonigii* methanol extract MKME and the standard reference showed their peaks. The result has also demonstrated that *M. koenigii* possesses strong antioxidant potentials which can also give account of its use in herbal medicine for treatment of diseases, Alzheimer disease inclusive.

The result of ferric reducing activity potential (FRAP) of methanol extract of leaf of *Murraya keonigii* plant is shown in Fig 3. Ferric assay measured direct reduction of F^{e3+} to Fe^{2+} resulting in formation of Prussian blue complex. The increase in absorbance of the reaction mixture indicates greater reduction capability. The result is dose concentration dependent. Ascorbic acid was used as the standard. 0.2 mg/mL of the sample gave an absorbance of 0.213+0058 while the same concentration of the standard gave an absorbance of 0.1753+0058. At concentration of 0.4 mg/mL the absorbance increased to

0.2140+0.0058 whereas the standard absorbance increased also to 0.1770 +0.0020. At a concentration of 1.0 mg/mL, the absorbance of the sample increased to 0.2157+0.0000 while that of the standard increased to 0.1913+0.0021. The above values show that the result of FRAP assay is dose concentration dependent. The reducing capacity of the methanol extract of *M. keonigii* leaf could be on its ability to donate electrons to the ferric ions thus reducing it to ferrous ions. This invariably demonstrates the antioxidant potential of *M. koenigii* plant leaf. The presence of flavonoids, phenolics, vitamins A, C and E may be responsible for this antioxidant potential of the leaf as these are strong antioxidants.

All the doses showed significantly higher inhibitory effects on inflammation than diclofenac sodium ($P < 0.05$) which showed 37% as shown in table 1. The leaf extracts present anti-inflammatory properties with respect to time.

Within 4 hours of egg albumin administration after treatment with 100mg/kg of leaf extract, 43% inhibition of inflammation was achieved. The 200mg/kg dose presented 53% inflammatory inhibition within 4 hours of egg albumin administration to the rat's right pairs. This indicates that 200mg/kg dose has the highest inflammatory inhibition and may be attributed to the dose of leaf extract and the anti-inflammatory property of the leaf. This, therefore means that more dose of the extract can achieve a 100% inflammatory inhibition.

CONCLUSION

Studies have shown that natural products from plant have been involved in treatment and management of diseases. This is as result of the pharmacological activities which include, antioxidant, anti-microbial, anti-inflammatory, anticancer, anti-diabetic, hepato-protective and cholesterol lowering, the plant resources possess. Alzheimer's disease is a senile and degenerative disorder which its pathologies are complex and multifactorial. These include oxidative stress, inflammatory cascade, cholinergic deficit etc. Oxidative stress and anti-inflammation have been implicated as major causative agents of old age-related ailments. Plants with antioxidant capacities reduce oxidative stress caused by presence of free radicals

This work has shown that *Murruya keonigii* plant has strong antioxidant and anti-inflammatory potentials which it demonstrated by inhibition of DPPH, FRAP and hydroxyl scavenging ability and reduction of oedema. With this, the extract from the plant can suppress some of pathological factors of Alzheimer's disease. Therefore, the plant *M. keonigii* could be incorporated in diets and pharmaceutical formulations to treat and manage Alzheimer's disease.

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CHEMICAL SOCIETY OF NIGERIA (CSN) ABIA CHAPTER
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REVIEW

GREEN CHEMISTRY AND ITS APPLICATION IN THE AGRICULTURAL, PHARMACEUTICAL, ENERGY AND POLYMER INDUSTRIES.

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ABSTRACT:

Today, the world faces the challenges of climate change and environmental pollution. Statistics have shown that the world generates over 400 million metric tons of plastic waste annually, of which 60% ends up in the natural environment or landfills, having detrimental impacts on human health, marine wildlife, and the health of our ecosystems. The agricultural industry has also become the leading source of pollution in many countries, as pesticides, synthetic fertilizers, and other toxic farm chemicals can poison freshwater, marine ecosystems, air, and soil. These substances can also remain in the environment for eons of years without decaying or decomposing. Pharmaceutical active compounds released through wastewater treatment plants in natural waters have been recognized as emerging contaminants. The use of fossil fuels releases large amounts of gases such as $CO_{2,}$ CO, NO_X, and SO_X into the air, which causes global warming, also oil spillages during crude oil exploitation, and petroleum products custody transfer, renders arable lands unfit for agricultural purposes, and as well as destroys aquatic lives. Recognizing the negative impact of activities emanating from these industries, hence this study seeks to explore how green chemistry which involves activities, design of chemical products, and processes that reduces or eliminates the use and generation of hazardous substances from these industries. Therefore, this review provides an overview of green chemistry, recent advances, challenges, and its application in four key industries: agriculture, pharmaceuticals, energy, and polymeric industries, to foster an eco-friendly environment.

Keywords: Green chemistry, Sustainability, Waste, Eco-friendly, 3Rs.

1.0 INTRODUCTION

Today, more than 98% of all organic chemicals are still derived from petroleum, and this has raised much environmental concern, therefore demanding industries such as the pharmaceutical, agricultural, polymeric, and petroleum industries to “go green” while maintaining their bottom line. The key themes of green chemistry are the eradication of toxic substances and pollution prevention (U.S. Environmental Protection Agency, 2021). Green chemistry emerged from various existing ideas and research efforts (such as atom economy and catalysis) in the period leading up to the 1990s. Since the 1940s, environmental issues began to emerge with the growth of industrial activities (de Marco, *et al*., 2019).

2.0 GREEN CHEMISTRY (GC) AND ITS RECENT ADVANCES

Green Chemistry (GC) is the use of chemical skills and knowledge to reduce or eliminate the use or generation of hazardous substances during the planning, manufacturing, and application of chemicals to minimize threats to the health of operators and the environment (Anastas & Warner, 1998). It is a fundamental approach to developing chemical products in a very safe environmental practice. For example, making a drug product without using ingredients that are toxic or solvents that are toxic. In general, green chemistry creates alternatives to hazardous substances, it aims to reduce waste by designing new chemical processes and products. In 1998, Paul Anastas & John Warner published the first manual of GC, in which they proposed 12 principles for the theme (Anastas & Warner, 1998; Constable, 2021) which are listed below:

- It is better to prevent waste than to treat or clean up waste after it is formed through designing reactions that leave less waste or none at all.
- Maximize Atom Economy: When developing synthetic processes, efforts should be made to ensure that as many materials as possible are included in the finished product. As a result, there will be a decrease in waste production.
- Design less hazardous chemical synthesis: Create reactions with the least amount of hazardous chemicals used and produced.
- Create goods and chemicals that are safer: Design chemicals that can perform the same actions as those that exist, but with less toxicity; for example, using paint that contains soy oil rather than fossil fuel reducing the hazardous risk by 50%
- Use safer chemicals and products: When using auxiliary chemicals, try to stay away from them as much as possible and make sure they're not too harmful.
- Increasing Energy Efficiency: create reactions that can be done at room temperature, and standard temperature whenever possible.
- Use Renewable feedstock: Feedstock are starting material used for many reactions. Use starting materials from renewable resources rather than limited ones like fossil fuels.
- Avoid or reduce Chemical derivatives: Eliminate the use of blocking groups or protecting groups whenever possible, as it generates additional waste.
- Use catalysts, not stoichiometric reagents: In principle, catalysts are not consumed meaning that can be regenerated and reused within the reaction. For example, Catalytic aerobic oxidation is much faster than of aerobic oxidation without catalysts.
- Create Products and Chemicals That Break Down After Use: develop products that will naturally degrade in the environment rather than remain and cause more pollution.
- Evaluate immediately to stop pollution: Monitor all reactions to ensure they are creating as few unwanted byproducts as possible.
- Minimize Potential for Accidents: Design chemicals and reactions that have the smallest possible risk for an accident. Practice lab safety to prevent spills or other harmful accidents.

2.1 Importance of GC across Industries.

Application of GC is pivotal in the environmental, economic, and social well-being of society. Green chemistry has improved public health and well-being, enhanced quality of life, and improved worker safety and conditions. It cost savings through waste reduction, increased resource efficiency, and reduced liability for environmental damage. It creates job opportunities in the green sector and increases investor confidence. It decreased greenhouse gas emissions, reduced environmental toxicity, and climate change mitigation (Sharma, et al., 2020; de Marco, *et al*., 2019; Constable, 2021).

3.0 APPLICATION OF GREEN CHEMISTRY IN THE AGRICULTURAL, PHARMACEUTICAL, ENERGY, AND POLYMERIC INDUSTRIES

3.1 Green Chemistry in Agriculture

Sustainable agricultural practices using green chemistry aim to minimize environmental impacts while maintaining or improving crop yields and quality. According to Velisek *et al*. (2007), sustainable agriculture seeks to achieve three goals: farm profitability; community prosperity, and environmental stewardship. An estimated 140 billion tons of agricultural biomass are produced annually worldwide. By employing environmentally friendly production techniques to create high-value goods, we may be able to cut our reliance on non-renewable resources and greenhouse gas emissions by about 50 billion tons of fossil fuels. (Forster *et al*., 2013). Brazil is a global pioneer in the use of Green Chemistry in agriculture and was the first nation to include biofuels into its energy mix on a big basis. Crop variety and ecological balance are two further benefits of biodiversity that increase the resilience of farming systems. (Chojnacka, 2024). Consumer preferences have a major influence on the adoption of sustainable farming techniques, as they have a direct impact on agricultural operations. The goal of agricultural sustainable chemistry, which is mostly based on green synthesis, is to minimize or get rid of dangerous chemicals. Bio-based chemicals, derived from renewable resources, are used in this industry and are often less harmful than synthetic counterparts. Utilizing bio-based fertilizers made from organic waste is a significant use of this, as it gives crops the necessary nutrients with lower carbon emissions and soil pollution (Kuma *et al*., 2021).

3.1.1 Development and use of Eco-friendly pesticides and fertilizers

The development and use of eco-friendly pesticides are very important aspect of green chemistry in Agriculture. Pesticides are recognized worldwide as the real means of controlling pests, at the same time such chemicals are highly toxic or poisonous to other species in the environment (Kuma *et al*., 2021). The pollution caused by heavy metals such as lead and mercury or chlorinated organic compounds (pesticides) can have severe health consequences. Both groups are associated with various cancers, especially those of the reproductive system, immune system, depression, birth defects, sterility, and neuro-behavioral problems. The need to produce a greater quantity and quality of food by pest control resulted in intensive use of pesticides over the last 50 years (Chavarri *et al*., 2000; Kuma *et al*., 2021). Concerns over the hazards and potential harm to the public's health, the environment, and the economy have been raised by the growing usage of these compounds and their poor treatment. of lessen the usage of dangerous synthetic pesticides, alternative approaches of pest management have been created, along with goods. Biopesticides come from naturally occurring sources such as fungus, bacteria, plants, and insects; neem oil, pyrethrin, and spinosad are some substitute sources (Mansour, 2004). In order to reduce the amount of chemicals used, Integrated Pest Management also integrates biological, cultural, chemical, and physical controls. While successfully controlling pests, these options put human safety, environmental sustainability, and ecosystem benefits first (Kuma *et al*., 2021).

3.2 Green Chemistry in Pharmaceutical Industries.

The establishment of the ACS Green Chemistry Institute Pharmaceutical Roundtable whose members include AstraZeneca, Bayer, Lilly, GlaxoSmithKline, Merck & Co., Novartis, Pfizer, and Takeda, among others by the ACS Green Chemistry Institute in 2005 (Bryan et al.,2023) has encouraged innovation while catalyzing the integration of green chemistry and green engineering in the pharmaceutical industry. Application of green chemistry in the development of pharmaceuticals is vital as it can lead to a reduction in waste generation, lessen energy consumption, and play an important role in eliminating health-related issues caused by the use of organic solvents or processes resulting in the production of toxic compounds (Srivastava, 2023, Mohammed, 2023; Yadav & Dubey, 2024). In the pharmaceutical industry, green chemistry involves the use of computational methods, artificial intelligence, green solvents and experimental conditions that applies advanced techniques or state-of-the-art techniques such as flow chemistry to mitigate waste production and develop molecules with less toxic effects (Constable, 2021; Mishra et al., 2021). In pharmaceutical Industries, the principles of green chemistry (GC) can be thoroughly applied in the eco-friendly synthesis of pharmaceuticals by choosing non-toxic solvents but rather using green solvents (ideally water), considering green reaction media, single pot synthesis, etc (Supratik *et al*., 2022). The US Environmental Protection Agency has honored a number of pharmaceutical businesses for their exceptional contributions to the use of green chemistry in the pharmaceutical sector. These companies include: (i) Merck and Company, Inc. was honored for inventing a more environmentally friendly method of producing LAGEVRIOTM (molnupiravir), an antiviral medication used to treat COVID-19 (Kimata et al., 2023; U.S. Environmental Protection Agency, 2024), (ii) Amgen was honored for developing a more environmentally friendly manufacturing process that made it possible to produce LUMAKRAS (sotorasib) (Hoshiyama, 2023), a novel medication used to treat some non-small cell lung cancer (U.S. Environmental Protection Agency, 2024) .

3.3 Green Chemistry in the Energy Industry (Petroleum)

The world's concerns about the environment have grown dramatically during the last ten years. The internal combustion engine (ICE) uses a lot of gasoline fuel, which indicates that it is not ecologically friendly. Effects of gasoline consumption on the environment include ozone depletion, acid rain, greenhouse impact, and climate change (Sindhu *et al*.,

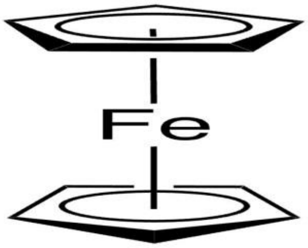

Figure 1: Ferrocene

2017). The use of octane-boosting chemicals in gasoline fuel may be one factor contributing to its environmental unfriendliness. Since gasoline itself has a low octane value, these chemicals are added separately to the fuel. Gasoline contains octane-boosting chemicals because engines need a minimum amount of octane to function properly and prevent knocking. Nonetheless, some octane-boosting substances are investigated because of their environmental issues. Tetra-ethyl-lead, or TEL, was first added to gasoline as an octane booster. According to Elfasakhany (2005), 1 g of TEL is needed for every gallon of gasoline to raise the octane rating by around ten times. TEL additives, however, contaminate catalytic converter catalysts and cause hazardous air pollution (Agarwal, 2007). However, new methods are being employed for a cleaner and environmentally friendly fuels (Gasoline). Gasoline which is one of the petroleum products widely used and its exhaust emissions of CO, CO2 gases and other harmful materials into the atmosphere imposes environmental hazards. New technologies have been adopted to help reduce the harmful substance emissions by burning of cleaner fuels, this has brought about a paradigm shift in the choice of gasoline additives for blending. The octane rating of gasoline can be increased by using ferrocene [Fe(C5H5)2] (**Error! Reference source not found.**) as an octane enhancer. Petroleum refineries utilize ferrocene instead of TEL because it is less expensive than MMT. The ferrocene-derived iron-containing deposits have the potential to create a conductive layer on the spark plug surfaces (Hjeresen, & Gonzales, 2002; Stratiev & Kirilov, 2009; Patil *et al*., 2014). Ferrocene (Dicyclopentadienyl iron (II)) an organometallic compound, being the representative of the sandwich compounds class, is known worldwide for its antiknock properties. Thanks to simplicity of application, environmental friendliness and high efficiency, this fuel additive became very widespread.The substance is insoluble in water, but is easily soluble in gasoline and diesel fuel, benzene, ether and other organic solvents. The commercial use is based on the property that ferrocene undergoes homolytic decomposition under the conditions of fuel combustion. Ferrocene lowers the formation of soot particles upon combustion of diesel and ordinary fuel. Oxygen containing compounds (oxygenates) such as methyl tert-butyl ether (MTBE), tert-amyl ethyl ether (TAEE), tert-amyl methyl ether (TAME), amongst others have proven to help give a smother combustion and less emission of harmful substances. But the alcohol based oxygenates like Methanol (CH_3OH), Isopropyl alcohol or Iso-Propanol ($CH_3CHOHCH_3$), Iso-Butanol $(CH_3)_2CHCH_2OH$, n-Propanol ($CH_3CH_2CH_2OH$), tert-Butanol $(CH_3)_3COH$ have shown in recent researches to be about the best method of improving gasoline quality and limit harmful emissions.

3.3.1 Spillage effects and Agricultural application for remediation

The successful application of the well-known medicinal plant, *Costus afer*, in the restoration of petroleum hydrocarbon-contaminated soil adds to the list of what green plant can potentially do to rid the environment of harmful chemical compounds to enhance human and environmental health. According to Emeka *et al* (2023) the efficacy of the plant is so pronounced that after 30 days of treatment, the polluted soil total petroleum hydrocarbon (TPH) concentration level dropped, thereby showing the improvement in the soil health. *Costus afer* is just one out of many plants that can and should be employed in soil remediation for restoration of oil damaged lands for farming and other industrial uses.

3.4 Green Chemistry in the polymer Industry.

According to the United Nations Environmental Protection, the world generates over 400 metric tons of plastic waste annually (Mutlu & Leonie, 2022) in which about 60% ends up in natural environments such as landfills. Common plastic waste found in the environment includes plastic bottles, plastic bags, plastic food packages, etc. Various approaches have been adopted in applying green chemistry in polymeric industries which include the production of alternatives to plastics.

3.4.1 Production and utilization of Biodegradable and Bio-based polymers

Due to the surge of undegradable plastics in the environment, industries are now moving in to bio plastic production which are not only degradable but as well as eco-friendly (Maraveas, 2020; Hatti-kaul, 2020). Today agro-waste from different sources such as tomato pomace, wheat straw, palm oil fibers, coconut husk, etc are utilized to produce biodegradable bags, electrical gadgets, plates, bowls, tanks, food packages wrapping films, etc. The interesting thing about bio-based polymer is that it is cost-effective and also the raw materials are abundant in nature. Despite the economic and environmental benefits accrued with Bio-based polymer, global statistics show that bio-based polymer production is still low as about 2.1 million tons were produced in 2018. Notwithstanding the advantages bio-based polymers provide for the economy and environment, worldwide data reveal that the production of bio-based polymers is still very low, with just 2.1 million tons produced in 2018 (Hatti-Kaul, 2020).

4.0 CONCLUSION AND RECOMMENDATION

Application of green chemistry principle in these key industries (Agricultural, Pharmaceutical, Polymer, and petroleum industries is paramount as it will create an eco-friendly environment for all to live. Green strategies will yield high-value products that have the potential to reduce the need for about 50 billion tons of fossil fuels, which will significantly reduce greenhouse gas (GHG) emissions and our reliance on non-renewable resources. Most importantly, however, is the potential to reduce the tons of plastics, which are known to be a major environmental pollutant that negatively affects aquatic and human life. Therefore, we conclude by reminding everyone the need to adopt the 3R (Reduce, Reuse, and Recycle) in our daily activities as to save our lives and environment

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REVIEW

CATALYSIS OF NOXIOUS GASES PRODUCED DURING THE SYNTHESIS OF BIOFUELS: A REVIEW

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ABSTRACT

One of the leading types of research in the area of energy supply is biofuels. This is because, biofuels are discovered to have the potential to replace fossil fuels which are currently and widely recognized as unsustainable because of depleting supplies and increasing demand. And the environmental concerns regarding the emissions responsible for climate change, including the released of other harmful substances such as COx, SOx, NOx and methane released during the production and utilization of fossil fuel have led to global environmental degradation effects such as greenhouse effect, acid rain, ozone depletion and climate change. Thus, the need for a biodegradable, sustainable, nonpolluting, locally available, accessible, and a reliable fuel obtained from renewable sources. And such fuel is referred as biofuels and is classified into biodiesel and bioethanol. The “biofuels” in this work are referred to the energy enriched chemicals generated through the biological processes or derived from the biomass of living organisms, such as microalgae, plants and bacteria. There are several technologies for the conversion of biomass into biofuels, biopower and bioproducts. Biomass can be processed through two major conversion pathways: biochemical and thermochemical. The appropriate biomass conversion process is determined by the type and quantity of the biomass feedstock and the desired form of energy (end-use requirements, economic considerations, environmental standards, and product specification). It was discovered that the gasification reaction of the biomass can yield the following: $CO(g) + H_2(g) + CO_2(g) + CH_4(g) + Tar(l) + H_2O(l) + H_2S(g) + NH_3(g) + C(s)$ + trace-species. Some of these gases are noxious, causing environmental pollution, especially in the case when they are misconducted after a heavy use of them. They are dangerous and can cause serious damages to the health. Catalysis has been useful in the prevention of pollution by avoiding formation of waste (unwanted byproducts) and can be adopted for the catalysis of these noxious gases into useful and less harmful chemicals thereby making the production and utilization of biofuels more environmentally friendly.

Key words: Biofuels, Biomass, Catalysis, greenhouse gases, Environmental pollution,

INTRODUCTION

The biggest challenge modern industrial society is facing today is the decline and exhaustion of the fossil energy resources. The primary sources of energy that power our civilization are those of fossil fuels. The combustion of fossil fuels such as coal, oil and natural gas for the conventional method of producing transportation fuels, chemicals, and power, has been established for many years (Andres et al. 2012; Maximino et al. 2008). Globally, the economy of the world depends on the energy generated from coal, petroleum and natural gas. And the continuous use of petroleum-sourced fuels is now widely recognized as unsustainable because of depleting supplies and increasing demand. Presently the twin crises that are confronting the world are that of the fossil fuel depletion and environmental degradation (Maximino *et al.* 2008; Sippy and Anuradha, 2011). Environmental concerns have increased significantly in the world over past decades, particularly after the Earth Summit-92.

The emissions responsible for climate change, including the released of other harmful substances such as SOx, NOx and methane released during the production and utilization of fossil fuel have led to global environmental degradation effects such as greenhouse effect, acid rain, ozone depletion and climate change. In addition, the combustion of the fossil fuels used is considered as the major factor responsible for global warming due to large-scale carbon dioxide emissions. This method is a significant global concern as it releases greenhouse gases (GHG) particularly carbon dioxide (CO_2) into the atmosphere. According to Cannon & Sperling, petroleum consumption for road transportation was the largest source of CO_2 emissions (2009). It accounts for 23% of CO_2 emissions worldwide and 59.5% of CO_2 emissions in Nigeria (Saboori et al. 2014; Tajudeen, 2015). According to Maxinimo et al (2008), the atmospheric concentration of CO_2 was about 383 parts per million (ppm) by volume. Future CO_2 levels were expected to rise due to ongoing burning of these fossil fuels and land-use change. The IPCC Special Report on Emissions Scenarios gives a wide range of future CO_2 scenarios, ranging from 541 to 970 ppm by the year 2100. Fossil fuel reserves are sufficient to reach this level and continue emissions past 2100, if coal, tar sands or methane clathrates are extensively used (IPCC, 2007).

Due to the environmental problems caused by the use of fossil fuels, considerable attention has been made to biodiesel production as an alternative to petro diesel and is an eco-friendly, alternative diesel fuel prepared from domestic renewable resources i.e. produced from vegetable oils and animal fats (Sippy and Anuradha, 2011).

The fuels of bio-origin can provide a feasible solution to this worldwide petroleum crisis. Scientists around the world have explored several alternative energy resources like biomass, biogas primary alcohols, vegetable oils and biodiesel. These alternative energy resources are highly environment-friendly but need to be evaluated on case-to-case basis for their advantages, disadvantages and specific applications. Some of these fuels can be used directly, while some others need to be formulated to bring the relevant properties closer to conventional fuels.

Biomass is a renewable energy resource which comprises carbon, hydrogen, oxygen, traces of nitrogen and some minerals. Biomass utilization has an advantage over other renewable sources such as solar energy, wind energy and hydroelectric power because of its low dependence on site and climate as diverse biomasses can grow in varied conditions. Moreover, biomass can be easily stored and transported (albeit with a lower energy density than fossil fuels) (SikarwarVineet et al. 2017).

Globally, biomass fuel is becoming ever more attractive as suitable substitute for fossil fuels due to the increasing demand for clean energy, declining fuel reserves, and its contribution towards reducing dependence on crude oil (Juliet et. al. 2016). Recent studies showed that biomass provides more than 10% of the global energy supply making it one of the leading potential viable renewable energy resources (Saidur et al 2011, Miao & Wu 2004, Heidenreich & Foscolo 2015). An extensively explored research area is the development of clean and sustainable technologies to utilize biomass feed stocks to produce biofuels (Tilman et al 2009).

MEANING OF BIOFUEL

The term biofuel refers to as solid, liquid or gaseous fuels that are predominantly produced from bio-renewable or combustible renewable feed stocks (Demiras, 2007). They are biodegradable and contribute to sustainability (Puppan, 2002). Biofuels are nonpolluting, locally available, accessible, and sustainable, and are a reliable fuel obtained from renewable sources. More so, they are classified into bioethanol and biodiesel (Sylvia, 2019).

Here "biofuels" are referred to the energy enriched chemicals generated through the biological processes or derived from the biomass of living organisms, such as microalgae, plants and bacteria, which are predominantly employed in the transportation sector. They are also used to generate heat and electricity or can be used as the feedstock to the synthesis of important chemicals. Gaseous biofuels are normally used for heat and power production, whereas liquid biofuels are generally employed in the transportation sector. Biofuels, in general, include bio-methanol (MeOH), bio-ethanol (EtOH), bio-dimethyl ether (DME), synthetic natural gas (bio-methane), Fischer Tropsch (FT) fuels and H_2 (Rodionova 2016, SikarwarVineet *et al.* 2017).

Biofuels may be classified into two categories: primary and secondary biofuels. The primary biofuels are the natural biofuels directly produced from firewood, plants, forest, animal waste, and crop residue. The secondary biofuels are directly generated from plants and microorganisms and may be further divided into three generations (Rodionova 2016). The first generation of biofuels is the production of ethanol from starch rich food crops like wheat, barley, corn, potato, sugarcane, or biodiesel from soybean, sunflower and animal fat. While the second generation of biofuels is the production of bioethanol and biodiesel from several species of plants such as jatropha, cassava, miscanthus, straw, grass and wood. The third generation of biofuels is the production of biodiesel from microalgae and microbes (Abdelaziz et. al. 2013).

There are several technologies for the conversion of biomass into biofuels, bio-power and bio-products (Juliet et. al. 2016). Biomass can be processed through two major conversion pathways: biochemical and thermochemical (Damartzis & Zabaniotou 2011). The appropriate biomass conversion process is determined by the type and quantity of the biomass feedstock and the desired form of energy (end-use requirements, economic considerations, environmental standards, and product specification) (Simonyan & Fasina, 2013). Furthermore, biomass conversion efficiency is dependent on the feedstock particle size and shape distribution and the type of reactors (Juliet *et. al.* 2016).

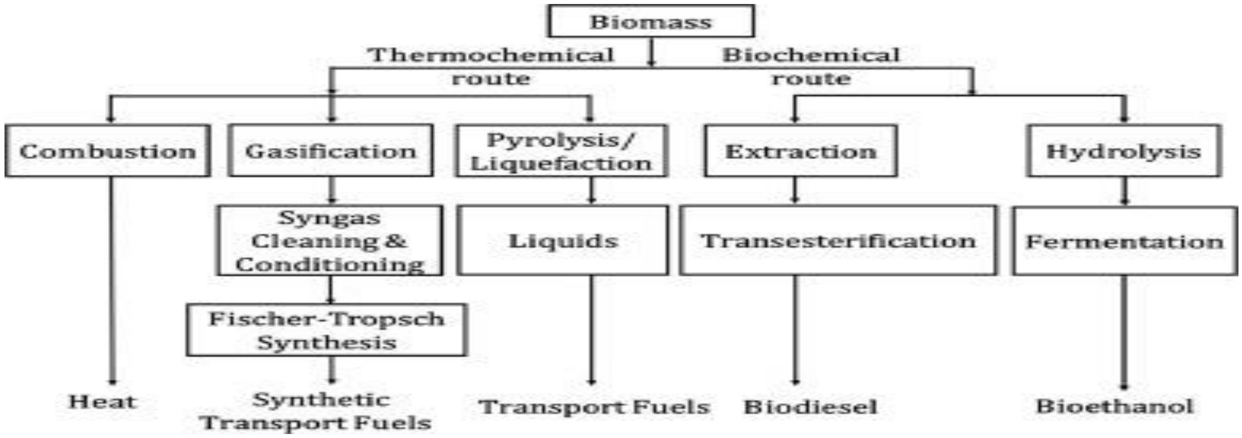

Fig.1: Thermochemical and biochemical conversion routes for biomass to biofuels (Damartzis & Zabaniotou 2011).

Biomass-derived syngas, which acts as a raw material for different biofuels production, contains many contaminants such as tars, particulates (PM), alkalis, nitrogen, sulphur, halides and traces of some other elements. Cleaning of these contaminants prior to their feeding in catalytic reactors for biofuel generation is a crucial step (SikarwarVineet et al. 2017).

Biofuels are global bio-renewable liquid transportation fuels that might replace gasoline and diesel fuel. Bioethanol is good alternate fuel that is produced almost entirely from food crops (Sippy and Anuradha 2011). Biodiesel has advantage over petroleum diesel when compared. For example, biodiesel produces lower exhaust emissions, biodegradable, non-toxic, renewable and essentially free of sulfur; thereby, making biodiesel a renewable energy and environmental friendly towards sustainable resource. Also, they are economical and efficient (Sylvia 2019). And as such has become more attractive recently because of its environmental benefits. There are several reasons for biodiesel to be considered as relevant technologies by both developing and industrialized countries. They include energy security reasons, environmental concerns, foreign exchange savings and socioeconomic issues related to rural sector (Sippy and Anuradha 2011).

NOXIOUS GASES PRODUCED DURING THE SYNTHESIS OF BIOFUELS

Noxious gases are the volatile and toxic gases that result from the manufacturing fields such as automobile, chemical industry, textile, pharmaceuticals, the production and consumption of fossil fuels etc. They cause environmental pollution, especially in the case when they are misconducted after a heavy use of them. They are dangerous and can cause serious damage to the life health, for example, causing the symptoms such as fatigue and nausea in humans and animals, and can even induce cell canceration in the body (Ruilin 2018, Wang et al, 2017; Dudynski, 2018). Examples of these harmful gases are COx, CH_4, NH_3, SOx, NOx, H_2S, Volatile Organic Compounds (VOCs) and volatile organic gases (trichloroethylene, carbon tetrachloride, acetone and formaldehyde) (Sadeghian 2019; Vellingiri et al. 2016, Tsai 2016, Ruilin 2018). They pose a high environmental risk.

Net GHG emissions from biofuels are significantly lower than the combustion of conventional petroleum-derived fuels (Rothenberg 2015). However, biofuel synthesis also generates GHGs in every step in the supply chain, from the raw feedstock production, to transport, conversion, to biofuels distribution and end application, as depicted in the figure below. Therefore, lifecycle assessment (LCA) should be considered a vital factor in ascertaining the amount of the noxious gases released during the production and consumption of biofuels.

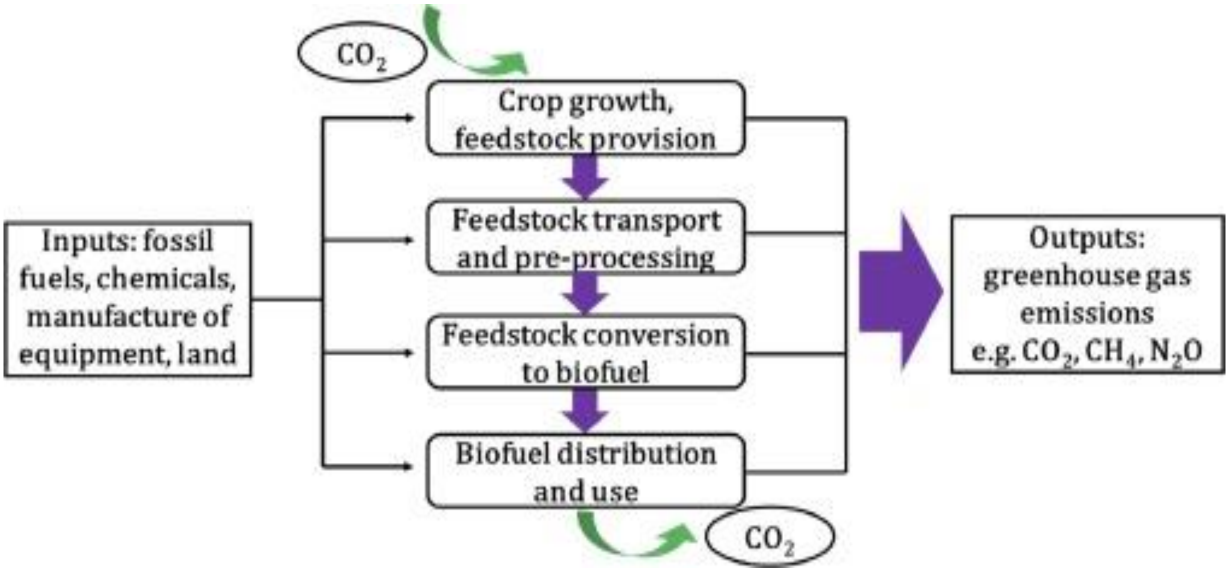

Fig.2 GHG emissions in biofuel synthesis supply chain (SikarwarVineet *et al*. 2017).

Gasification is the thermochemical transformation of solid or liquid biomass into a mixture of carbon monoxide, hydrogen, carbon dioxide, methane, tar, water vapour, hydrogen sulphide and other trace species whose fractions are determined by operational variables such as raw material characteristics, gasifying media (steam, air, O_2, CO_2), temperature and pressure inside the gasifier, and catalysts (if used). The heat supplied can be intrinsically produced via exothermic combustion reactions or can be supplied from outside sources. A simplified gasification reaction can be represented below:

Biomass → $CO(g)+H_2(g)+CO_2(g)+CH_4(g)+Tar(l)+H_2O(l)+H_2S(g)+NH_3(g)+C(s)$+traces pieces

(Lange 2007; Hrdlicka et. al. 2008; Sikarwar Vineet *et al*. 2017).

CATALYSIS OF NOXIOUS GASES

Catalysis is the phenomenon of changing the rate of reaction by the addition of a substance which by itself remains unchanged chemically (Chorkendorff & Niemantsverdriet 2007). This change in the rate of reaction results from adding a catalyst to the reaction. A catalyst makes a reaction to occur faster, without being consumed in the process. Since the catalyst is not consumed in the process, each catalyst molecule can participate in many consecutive cycles, so we need only a small amount of catalyst relative to the substrate. There are many different types of catalysts. They range from the proton, H+, through Lewis acids, organometallic complexes, organic and inorganic polymers, all the way to enzymes (Carberry 2001).

The science and technology of catalysis is of great significance as it affects our daily life. Catalysts are the workhorses of chemical transformations in the industry. Approximately 85–90% of the products of chemical industry are made in catalytic processes. Four major sectors of the world economy; petroleum and energy production, chemicals and polymer production, food industry and pollution control, involve catalytic processes. Catalysts are indispensable in

- ❖ Production of transportation fuels in one of the approximately 440 oil refineries all over the world.
- ❖ Production of bulk and fine chemicals in all branches of chemical industry.

- Prevention of pollution by avoiding formation of waste (unwanted byproducts).
- Abatement of pollution in end-of-pipe solutions (automotive and industrial exhaust) (Chorkendorff & Niemantsverdriet 2007).

Catalysts are used to produce fuels such as gasoline, diesel, heating oil, fuel oil etc. Production of plastics, synthetic rubbers, fabrics, cosmetics etc. involve catalytic processes. The production of clean energy from renewable energy sources, such as hydrogen for fuel cells and transportation fuels from non-edible biomass are also catalyst dependent processes. Automobile emission catalysts are used to reduce emissions of CO, NOx and hydrocarbons from mobile vehicles (Carberry 2001).

The catalyst offers an alternative path for the reaction, which is obviously more complex, but energetically much more favorable. The activation energy of the catalytic reaction is significantly smaller than that of the un-catalyzed reaction; hence, the rate of the catalytic reaction is much larger. The overall change in free energy for the catalytic reaction equals that of the un-catalyzed reaction. Hence, the catalyst does not affect the equilibrium constant for the overall reaction of a given reaction. Thus, if a reaction is thermodynamically unfavorable, a catalyst cannot change this situation. A catalyst changes the kinetics but *not* the thermodynamics. The catalyst accelerates both the forward and the reverse reaction to the same extent (Chorkendorff & Niemantsverdriet 2007).

Categories of Catalysis

Catalysis is divided into three categories: homogeneous catalysis, heterogeneous catalysis, and bio-catalysis. Although the catalysts and the process conditions in each category can be very different, the principles of catalysis are the same. Once you understand these principles, you can apply them in all three categories. The main advantages of catalysis is that you get the desired product faster, using fewer resources and generating less waste (Chorkendorff & Niemantsverdriet 2007, Carberry 2001, Riikka 2018).

Bio-Catalysis

Enzymes are nature's catalysts. Enzymes allow biological reactions to occur at the rates necessary to maintain life, such as the buildup of proteins and DNA, or the breakdown of molecules and the storage of energy in sugars. An example is the breakdown of alcohol to acetaldehyde inside the body by the enzyme alcohol dehydrogenase. The acetaldehyde in turn is converted into acetate by aldehyde hydrogenase. Some people cannot tolerate alcohol (as revealed by facial flushing after drinking a small amount) because they lack the form of the enzyme that breaks down acetaldehyde.

Homogeneous Catalysis

In homogeneous catalysis, both the catalyst and the reactants are in the same phase, i.e. all molecules are in the gas phase, or, more commonly, in the liquid phase. One of the simplest examples is found in atmospheric chemistry. Ozone in the atmosphere decomposes, among other routes, via a reaction with chlorine atoms. Ozone can decompose spontaneously, and also under the influence of light, but a Cl atom accelerates the reaction tremendously. As it leaves the reaction cycle unaltered, the Cl atom is a catalyst. Because both reactant and catalyst are both in the same phase, namely the gas phase, the reaction cycle is an example of homogeneous catalysis. (This reaction was historically important in the prediction of the ozone hole.) Oxides of nitrogen serve as catalysts for the oxidation of sulfur dioxide in the lead chamber process for producing sulfuric acid, an instance of homogeneous catalysis in which the catalyst and reactants are gases. Traces of water vapor catalyze some gas reactions—for example, the interaction of carbon monoxide and oxygen, which proceeds only slowly in dry conditions.

In homogeneous catalysis, often aimed at the production of delicate pharmaceuticals, organometallic complexes are synthesized in procedures employing molecular control, such that judicious choice of ligands directs the reacting molecules to the desired products.

Heterogeneous Catalysis

In heterogeneous catalysis, solids catalyze reactions of molecules in gas or solution. As solids (unless they are porous) are commonly impenetrable, catalytic reactions occur at the surface. To use the often expensive materials (e.g. platinum) in an economical way, catalysts are usually nanometer-sized particles, supported on an inert, porous structure.

Catalysis of Carbon mono oxide (CO)

An example of heterogeneous reaction is the cleaning automotive exhaust, the catalytic oxidation of CO on the surface of noble metals such as platinum, palladium and rhodium. To describe the process, we will assume that the metal surface consists of active sites, denoted as "*" The catalytic reaction cycle begins with the adsorption of CO and O_2 on the surface of platinum, whereby the O_2 molecule dissociates into two O atoms (X* indicates that the atom or molecule is adsorbed on the surface, i.e. bound to the site *). The adsorbed O atom and the adsorbed CO molecule then react on the surface to form CO_2, which, being very stable and relatively un-reactive interacts only weakly with the platinum surface and desorbs almost instantaneously.

$2CO\ (g) + O_2\ (g) \rightarrow 2CO_2\ (g)$

The reaction above occurs in the presence of catalyst and can be adopted for the removal of CO produced during the production of biofuels.

Catalysis of Carbon di Oxide (CO_2)

Catalytic conversion of CO_2 into chemicals and fuels has been noted as a viable method to reduce carbon emissions and achieve carbon neutrality (Gao et al 2022). CO_2 is mainly converted into C_1 compounds (methane, methanol, formic acid, etc.), C_2 compound (ethane, acetic acid, ethanol, formate, etc.), cyclic carbonate, dimethyl carbonate, carbonate, decanoate, salicylic acid and other chemical products. Through thermal catalysis, electrocatalysis, and photo(electro)catalysis, catalytic conversion, electrochemical conversion, enzymatic conversion, plasma conversion, and bioconversion (Gao et al 2022, Xing et al, 2020). According to Xing et. al. (2020), the most-studied technology for CO_2 conversion is catalytic conversion technology. In this method, technologies such as photocatalysis, electrocatalysis, plasma catalysis, and conventional thermal catalysis are widely studied.

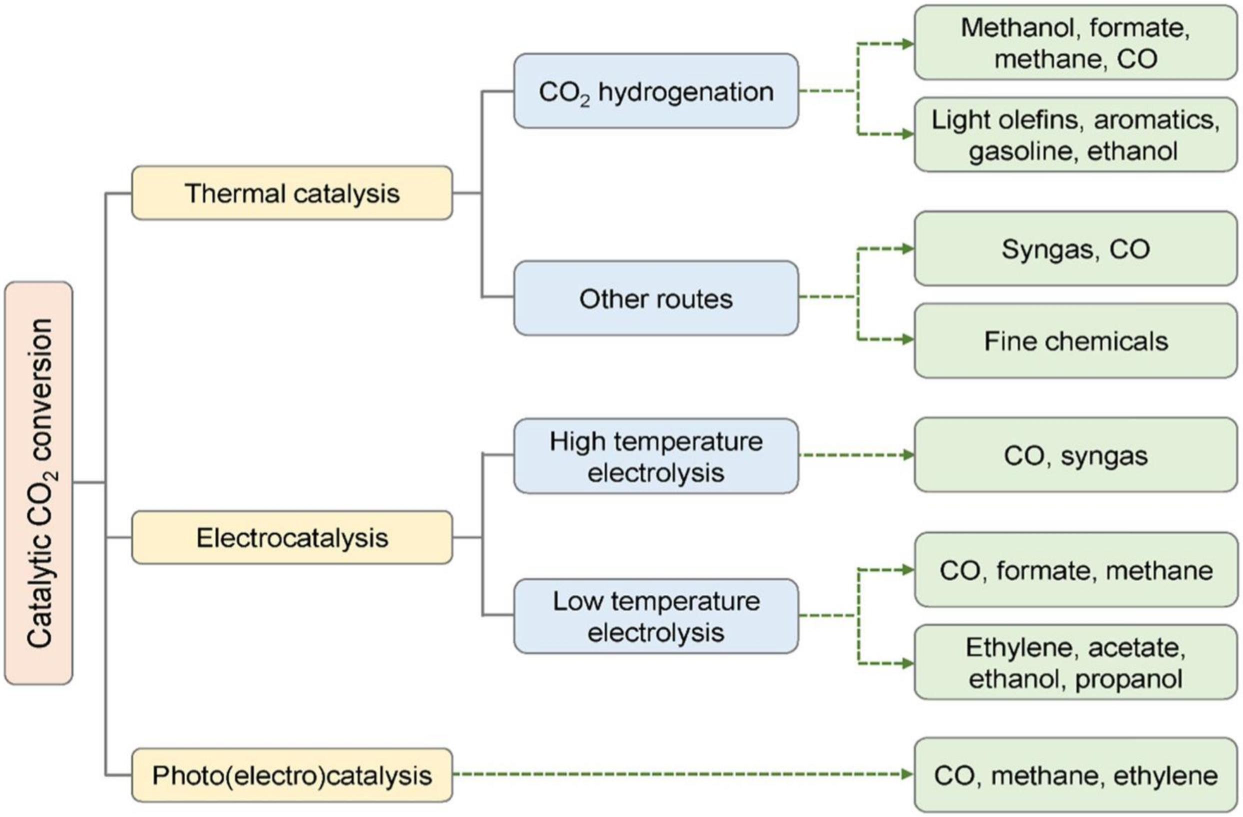

Fig. 3: Heterogeneous catalysis routes for CO_2 conversion into chemicals and fuels (Gao *et al* 2022)

Photo-Catalytic of CO_2

The photo-catalytic reduction of CO_2 is achieved by simulating photosynthesis of plants. The essence is that semiconductor photo-catalysts generate photo-generated electron-hole pairs under light conditions, and promote the oxidation-reduction reaction between CO_2 and H_2O to generate hydrocarbons. In the process of photo-catalytic reaction, when the energy of light radiation is higher than its own forbidden band width, the electrons will be excited to transition from the valence band to the conduction band, thereby forming holes having oxidizing ability and electrons having the reducing ability required for catalytic reaction. Subsequently, the electrons react with H_2O to reduce CO_2 to hydrocarbons such as methanol, methane, formaldehyde, and formic acid; while photo-generated holes with strong oxidation ability oxidize H_2O to release O_2. Catalysts are essential for photocatalytic processes. Here are three photo-catalyst materials used commonly: semiconductor materials, graphene-based nano-materials and MOFs-based heterogeneous catalysts (Xing et. al 2020).

Electrocatalysis of CO_2

Electrocatalytic reduction is a technology that converts CO_2 into carbon monoxide (CO), hydrocarbons, alcohols, esters, carboxylic acids and other new substances, through the cathode and anode in aqueous or non-aqueous solvents (O'Toole, et al, 1985). The products obtained are usually mixtures of carbon compounds, such as CO, formic acid (HCOOH), methanol (CH_3OH), formaldehyde (HCHO), methane (CH_4), Ethylene (C_2H_4), etc. (Karamad *et al*, 2015; Gao *et al* 2022)

Plasma Catalysis of CO_2

Plasma is considered to be a fourth material form which is different from solid-liquid-gas. When the temperature of other particles such as ions and gas molecules in the plasma is much lower than the electron temperature, it is called non-thermal plasma (NTP). NTP occurs in the presence of high-energy electrons. It is caused by the inelastic collision between high-energy electrons and CO_2 gas molecules under the action of an electric field. The C=O bond dissociation energy of CO_2 molecules is 5.5eV, and the electron energy in low temperature plasma is mostly between 1–20eV (Xing et al, 2020). The addition of Ni / TiO_2 catalyst can increase the CO_2 conversion rate from 14% to 28% (Chen et. al 2017).

Thermal Catalysis of CO_2

At present, the fuel products converted by CO_2 catalysis include methane, methanol, formic acid, dimethyl ether, and syngas, etc. CO_2 methanation refers to the strongly exothermic reaction process of H_2 and CO_2 to form CH_4 and H_2O under the action of 150–500 _C, 0.1–10 MPa, and a metal catalyst (Chang et al, 2003). The Ru nanoparticle Ru/TiO_2 catalyst supported by TiO_2 yield 100% CH_4 at 160°C (Xing et al. 2020).

Catalysis of Oxides of Nitrogen (NOx)

The quantities of nitrogen generated during the production of biofuels depend on the intrinsic characteristics of the raw biomass along with operational parameters (SikarwarVineet *et al*. 2017). During the pyrolysis phase of Biomass gasification, nitrogen leaves the feedstock in the form of ammonia or hydrogen cyanide (Hannson et al. 2004). Normally, ammonia is the dominant nitrogen species and is produced during primary reactions (from biomass) or in the secondary gas phase reactions (from HCN). With increasing temperature, fractions of ammonia and HCN rise considerably during secondary reactions. Eventually HCN also reacts with hydrogen to form ammonia. However, almost 75% of ammonia produced during gasification is converted to elemental nitrogen at operational temperature (Becidan et al. 2007, Espinal et. al. 2007, SikarwarVineet *et al*. 2017).

Hot gas cleaning of nitrogen (present in the form of ammonia) in syngas is carried out via selective oxidation or thermal degradation in the presence of catalysts (Woolcock & Brown 2013). Tar cracking catalysts such as nickel-based, iron-based, dolomite, etc., are also effective in ammonia cracking. They are cost-effective and, therefore, suitable substitutes to Ru, W, nitrides, oxy-nitrides and carbides (Torres et. al. 2007). Commonly employed nickel-based catalysts decompose ammonia up to 75% (Mojtahedi 1995).

Catalysis of Sulphur

Sulphur is present as hydrogen sulphide, carbonyl sulphide and carbon disulphide in syngas and sulphur dioxide (in combustion by-products). The percentage of this contaminant is dependent upon the composition of the biomass feedstock (Gupta 2001). Usually biomass contains low amounts of sulphur (0.1 to 0.5 g kg^{-1}) as compared to coal (50 g kg^{-1}), except for a few feedstocks such as black liquor (> 1 g kg^{-1}) and some types of grasses (Torres et. al 2007; Leibold 2008).

Metal oxides are the most promising sorbents on account of their high removal efficiency, high thermal tolerance and regeneration potential. Westmoreland and Harrison (1976) presented a comprehensive evaluation of potential metals vis-à-vis desulphurization potential and free energy minimization. Vamvuka *et al*. (2004) have reduced their list to Fe, Zn, Mn, Cu, Co, Mo, V as most effective oxides for the removal of sulphur.

A blend of metal oxides have been discovered to have better characteristics for desulphurization than individual metal oxides in terms of removal efficiency, regeneration capacity, heat tolerance and other contaminant removal potential. For example, a blend of Mn, V and Cu displayed high sulphur removal even at elevated temperatures of 600 °C and above (Torres et al 2007). In addition, a mixture of CuO and ZnO had very high removal efficiency of above 99%. ZnO is readily available and is one of the most prevalent regenerable sorbents (Tamhankar et al. 1986).

Recovery of sulphur during syngas cleaning is the key consideration for all the removal techniques. Sulphur is usually recovered as elemental sulphur or as sulphuric acid via previously discussed physical and chemical processes. The acid is usually employed as a reagent in catalytic processes such as petroleum alkylation, methyl methacrylate synthesis, etc. or in leaching processes such as mining or synthesis of hydrofluoric acid, phosphate, etc. (Rappold & Lackner 2010).

CONCLUSION

From this review, it is observed that the heterogeneous catalysis of some noxious gas during the synthesis of biofuels can lead to the capture of these noxious gases like CO, CO_2, NH_3, H_2S. Thereby, presenting the synthesis and the utilization of biofuels as environmentally friendly fuel. Also contributing to the reduction of pollution of the environment by the synthesis of biofuels. The catalytic oxidation of CO on the surface of noble metals such as platinum, palladium and rhodium is adopted in the cleaning of automotive exhaust and can be adopted in the catalysis CO produced during the production of Biofuels. Catalytic conversion of CO_2 into chemicals and fuels is a viable method to reduce carbon emissions and achieve carbon neutrality. Through thermal catalysis, electrocatalysis, and photo(electro)catalysis, CO_2 can be converted into a wide range of valuable products, including CO, formic acid, methanol, methane, ethanol, acetic acid, propanol, light olefins, aromatics, and gasoline, as well as fine chemicals.

Ammonia is the dominant nitrogen species and is produced during primary reactions (from biomass) or in the secondary gas phase reactions (from HCN). But can be cleansed by hot gas cleaning of nitrogen (present in the form of ammonia) in syngas via selective oxidation or thermal degradation in the presence of catalysts such as nickel-based, iron-based, dolomite, and so on. It is seen from the review that a blend of metal oxides have better characteristics for desulphurization than individual metal oxides in terms of removal efficiency, regeneration capacity, heat tolerance and other contaminant removal potential. A blend of Mn, V and Cu displayed high sulphur removal even at elevated temperatures of 600 °C and above, and a mixture of CuO and ZnO had very high removal efficiency of above 99%.

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PHYTOCHEMICAL SCREENING AND ANTI-HYPERGLYCEMIC ACTIVITIES OF THE METHANOLIC EXTRACTS OF WHITE GARLIC (*Allium sativum*) AND PURPLE GARLIC (*Allium ophioscorodon*)

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ABSTRACT

Garlic is a bulbous plant used as flavour in food and also as herb in the treatment of wide range of diseases. It has two major types, the white garlic (*Allium sativum*) and the purple garlic (*Allium ophioscorodon*). The purpose of this research was to investigate the phytochemical constituents of the methanolic extracts of both the white garlic (*A. sativum*) and purple garlic (*A. ophioscorodon*) as well as their anti-hyperglycemic activities on alloxan-induced diabetic albino rats. Cold maceration was used to extract the phytochemicals of both samples using methanol as a solvent. The qualitative and quantitative phytochemical analyses carried out showed that both extracts contain alkaloids, saponins, flavonoids, tannins, phenols, steroids and glycosides in appreciable amounts. However, the purple garlic extract contain more phytochemicals than the white garlic extract. 15 Albino rats were used to carry out the anti-hyperglycemic activity and were grouped into five; A, B, C, D and E. Groups B - E were diabetically induced by alloxan and their blood glucose levels were measured using a glucometer while Group A was used as a control. Rats with postprandial blood glucose above 250 mg/dl were considered as diabetic and were used for the experiment. Glibenclamide, a conventional anti-diabetic drug was used as a reference standard. Both white and purple extracts exhibited anti-diabetic activities, though, Glibenclamide showed more activity than the extracts, yet, the garlic extracts are recommended due to their availability and affordability with little or no side effects. The purple garlic contains higher phytochemicals and exhibited higher anti-hyperglycemic activity than the white garlic and therefore, will be of higher medicinal value in folklore medicine.

Keywords: White garlic; Purple garlic; phytochemicals; Anti-hyperglycemia; Albino rats

INTRODUCTION

Garlic, scientifically known as *Allium sativum,* a tropical medicinal bulbous blooming plant in the *Amaryllidaceae* family and genus of *Allium is* used in herbal medicine and cookery as a flavour. The onion, shallot, leek, elephant garlic (*Allium ampeloprasum*), chive, Welsh onion, and Chinese onion are among its near relatives. In Igboland, it is known as garlic but spelt "galiki" because of a little variance in the language. In Hausa, it is known as tafarnuwa, while in Yoruba, it is known as ata ile (Block, 1985; Begum and Nath, 2000; Ayaz and Alposy, 2007). It has a special smell, pungent-smell, which is attributed to numerous sulphur compounds which it contains and which are believed to account for most of its medicinal properties.

It has been reported that garlic contains numerous bioactive compounds and also possesses so many activities, like, anticoagulant, antioxidant, antibiotic, hypocholesterolaemic, etc. (Augusti *et al*., 1996; Bordia *et al*., 1996). It is indigenous to South Asia, Central Asia, and Northern Iran, and people have been consuming and using it for at least a few thousand years. It has been used as a food flavouring and a conventional medicine since the time of the ancient Egyptians. 76 % of the world's supply of garlic comes from China (Amagase and Milner, 1993; Block, 2010).

It is a perennial flowering plant which grows from a bulb. It features a one-meter-tall, upright blooming stem (3 ft). The leaf blade has an acute apex, is flat, linear, and solid, and is 1.25–2.5 cm (0.5–1.0 in) in width. In the Northern Hemisphere, the plant can produce pink to purple flowers from July through September (Rader and McGuinness, 2019). The odoriferous bulb has an inner sheath that encloses the clove and outer layers of thin sheathing leaves. Frequently, the bulb contains 10 to 20 asymmetrically shaped cloves, with the exception of those closest to the centre.

There are two main types of garlic. They are; white garlic (*Allium sativum*) and purple garlic (*Allium ophioscorodon*). The white garlic (*A. sativum*) which is also known as softneck variation is a foreign garlic, usually imported from other countries and cannot be seen in open markets but frequently seen in supermarkets and shopping malls because, it's very expensive and considered to be superior to purple garlic. Softneck species do best in milder climates with warmer winters. Moreover, they mature earlier than hardneck species and they have the best storage life, between 7 - 9 months (Colleen, 2022). Purple garlic (*A. ophioscorodon*), also known as hardneck, has big, easy-to-peel cloves with a stronger flavour than softnecks; it has stronger smell and spicy. Typically, purple garlic produces a single ring with 6–10 cloves (the segmented parts). The shelf life is just four to five months due to the loose, easy-to-peel epidermis or scales (Kamenetsky, 2007). It is the local garlic that can be found easily in an open market; it is available and affordable, unlike the white garlic that is imported and expensive.

Phytochemicals are the bioactive chemical components of plants. They are the major ingredients in medicinal plants which give them the potentials to be used in herbal medicine (Lambert *et al*., 1997; Igwe and Mgbemena, 2014; Chikezie *et al*., 2015). These bioactive components include; alkaloids, tannins, phenols, flavonoids, saponins, antioxidants, etc. (Sofowora, 1993; Hoareau and DaSilva, 1999, Igwe and Okwu, 2013). Phytochemical screening is the process of analyzing, investigating, extracting and determining the bioactive constituents present in different parts of medicinal plants to validate their claims in herbal medicine (Edeoga *et al*., 2005). Phytochemical screening involves both qualitative and quantitative analysis. While qualitative analysis deals with the presence or absence of a chemical constituent, quantitative analysis deals with the composition or concentration of the chemical constituent present in the plant sample.

Diabetes is a chronic illness that develops when the body either cannot use the insulin that the pancreas makes properly or does not create enough of it. (Insulin is the hormone that controls blood sugar levels) (De-Silva *et al*., 2018; Bommer *et al*., 2018). Globally, diabetes is currently ranked as the sixth most common cause of mortality. The WHO published its most recent figures in 2024, indicating that diabetes is responsible for around 422 million deaths annually, of which an estimated 1.5 million are attributable to either inadequately or untreated diabetes (Atkinson and Eisenbarth, 2001; WHO, 2024; NIDDKD, 2024). General symptoms of diabetes mellitus include thirst, weight loss, polyuria, blurred vision, etc., which, if left untreated, could lead to cardiovascular diseases, organ failure, and even death (Thomas and Philipson, 2015; SMCD, 2018).

Antidiabetic drugs like insulin, metformin, glibenclamide, pramlintide, alpha-glucosidase inhibitors, dopamine, etc., are the synthetic drugs use to combat diabetes. These drugs are in short supply, very costly, with huge side effects. Since medicinal plants have few or no negative effects and are widely available, they have become a valuable tool in the fight against diabetes mellitus, and garlic is one of them.

MATERIALS AND METHODS

Samples Collection and Identification

The fresh bulbs of purple garlic (*Allium ophioscorodon*) were purchased from Ogbete Main Market, Enugu, Enugu State, and the white garlic (*Allium sativum*) bulbs were purchased from Shop rite, Abia Mall, Umuahia, Abia State, Nigeria, both on the 26th November, 2019 and were identified and authenticated at the Taxonomy Unit of the Department of Forestry, Michael Okpara University of Agriculture, Umudike, Abia State, Nigeria.

Samples Preparation

The scales of the bulbs of both the purple garlic (*A. ophioscorodon*) and the white garlic (*A. sativum*) were carefully removed and the bulbs were separated into cloves (segmented parts) respectively. The cloves were thoroughly washed, chopped and air-dried in a well-ventilated room for five (5) months in order to remove moisture. The dried cloves of both purple garlic (*A. ophioscorodon*) and white garlic (*A. sativum*) were pulverized with Thomas Wiley milling machine and then stored separately in an air tight bottle for analyses.

Extraction of Phytochemicals

Cold maceration method was used for the extraction and 500 g of each of the samples was percolated in a glass jar with 2.0 litres of 95 % methanol each and was kept for four (4) days without shaking to avoid froth (air bubbles) (JohnBull and Afolabi, 2011; Igwe and Echeme, 2013; Kwekowe *et al.*, 2021). Each of the percolate was filtered through Whatmann No 1 filter paper and each filtrate was concentrated under reduced pressure using digital Heidolph Rotary evaporator (4000 series). Each concentrate was exposed for evaporation to dryness in order to get the crude samples of both white and purple garlic.

Phytochemical Screening

This includes both the qualitative and quantitative analyses of both white garlic (*A. sativum*) and purple garlic (*A. ophioscorodon*) methanolic crude extracts.

Qualitative Analysis

The qualitative analysis of phytochemicals such as alkaloids, saponins, tannins, flavonoids, phenols, steroids and glycosides in both white and purple garlic was carried out using standard methods. Alkaloids and phenols were qualitatively analyzed using the method described by Ejikeme *et al*. (2014). The method described by Harborne (1999) and Ejikeme *et al*. (2014) was used to analyze for saponins, while the method described by Edeoga *et al*. (2005) was employed for tannins and flavonoids and Salkowski test was used to detect the presence of steroids (Rahman *et al*., 2010). Moreover, the experimental procedure as suggested by AOAC (2000) and reported by Ejikeme *et al*. (2014) was used to detect the presence of glycosides in both samples.

Quantitative Determination of Phytochemicals

The quantitative determination of phytochemicals such as alkaloids, saponins, tannins, flavonoids, phenols, steroids and glycosides in both white and purple garlic was also carried out using standard methods. The method described by Onwuka (2005) was used to determine alkaloids and the method described by Obadoni and Ochuko (1998) was used to determine saponins while Folin Dennis colorimeteric method as described by Edeoga *et al*. (2005) was employed for the determination of tannins. Flavonoids were determined using the method of Baham and Kocipai (1974), as described by Onwuka (2005) and phenols determined using AOAC method (2000) as described by Edeoga *et al*. (2005). Also, steroids were quantitatively analyzed by the method described by Okeke and Elekwa (2003) and glycosides were determined by calorimetric method as described by Ejikeme *et al*. (2014).

Anti-hyperglycemic Activity of White and Purple Garlic Extracts on Alloxan-induced Diabetic Rats

Evaluation of the anti-diabetic effects of aqueous extracts of both white and purple garlic in alloxan-induced diabetic rats was done by employing the method described by Moradabati *et al.* (2013). The rats were obtained from the laboratory of the Animal Production Unit, Department of Zoology and Environmental Biology, Michael Okpara University of Agriculture, Umudike. Fifteen (15) albino rats of an average weight of between 203 and 238 g were randomly divided into five groups of three rats each. Diabetes was induced through intraperitoneal administration of 150 mg/kg body weight of alloxan in all the animal groups except one.

Group A = Normal control, non-diabetic, no treatment

Group B = Diabetic without treatment

Group C = Diabetic treated with the 1st extract (purple garlic)

Group D = Diabetic treated with the 2nd extract (white garlic)

Group E = Diabetic treated with the conventional drug (Glibenclamide) 5 mg/kg body weight. Parameters monitored were fasting blood glucose using glucometer and body weight

Induction of Diabetes into the Experimental Rats

Alloxan monohydrate was used to induce diabetes in the test animals (rats). 1 g of the salt was dissolved in 100 ml of citrate buffer solution (pH = 4.5) as described by Kumar *et al.* (2008). The resulting solution has a concentration of 10 mg/ml. The alloxan solution was administered subcutaneously (under the skin) to the animals. The rats were made to fast overnight before the administration of an equivalent dose of 100 mg/kg body weight each. They were allowed to eat commercial food and drink water at liberty while being observed for one to seven days. At the end of the seven days, their respective blood sugar levels were measured with the aid of a glucometer.

Animals with postprandial blood glucose above 250 mg/dl were considered to be diabetic and were used for the tests. The selected rats were randomly grouped into four designated groups, corresponding to groups B to E above. Separate non-diabetic rats were confined in a different group, A. The animals in groups C and D were given the two extracts at a daily dose of 250 mg/kg body weight and observed for 21 days, while those in group E were given the reference drug (glibenclamide) at 5 mg/kg body weight daily for the same period. The blood glucose levels of all the rats in groups A–E were measured weekly and recorded accordingly.

RESULTS AND DISCUSSION

Qualitative Phytochemical Screening of Both White and Purple Garlic Extracts

The table below shows the qualitative screening of both white and purple garlic. The parameters that were screened include; alkaloids, saponins, flavonoids, tannins, phenols, steroids and glycosides.

Table 1: Qualitative Phytochemical Screening of Both White and Purple Garlic Extracts

	Alkaloids	Saponins	Flavonoids	Tannins	Phenols	Steroids	Glycosides
Purple garlic	+++	+	++	++	+	+	+++
White garlic	++	++	+	++	+	+	++

+++ = Highly Abundant, ++ = Abundant, + = Low Abundant

The qualitative phytochemical analysis displayed in Table 1, showed that the above mentioned parameters were all present in both white and purple garlic. However, some parameters appeared in abundance more than others: alkaloids and glycosides having +++ showed that they are the most abundant bioactive compounds present in purple garlic, followed by flavonoids, tannins and saponins, having ++, which indicated that they are moderately present, then, followed by phenol and steroids, having one +, which indicated that they are the least in abundance.

Quantitative Phytochemical Determination of both White and Purple Garlic Extracts

The Table below shows the quantitative phytochemical determination of both white and purple garlic crude extracts.

Table 2: Quantitative Phytochemical Determination of both White and Purple Garlic Extracts

	Alkaloids	Saponins	Flavonoids	Tannins	Phenols	Steroids	Glycosides
Purple	4.98±0.22	1.73±0.11	2.03±0.06	2.87±0.05	1.05±0.11	0.45±0.03	4.23±0.05
White	3.21±0.05	2.07±0.07	1.32±0.02	3.56±0.09	0.83±0.02	0.17±0.01	2.78±0.10

Table 2 shows the quantitative phytochemical analysis of both white and purple garlic. The quantitative analysis showed significant variations in some phytochemical content of the two garlic extracts, in which alkaloids, steroids, flavonoids, phenols, and glycosides were higher in the purple garlic extract while saponins, and tannins were higher in the white garlic extract. The contents of alkaloids and glycosides were 4.98 % and 4.23 % in the purple garlic extract as against 3.21 % and 2.78 % in the white garlic extract respectively. The corresponding values for Phenols and steroids were 1.05 % and 0.54 % respectively for the purple garlic extracts. Saponins and tannins contents in the white garlic extracts were 2.07 % and 3.56 % as against 1.73 % and 2.87 % of the purple garlic extracts.

Comparatively, the overall phytochemical constituents of the purple garlic extract showed higher concentrations than that of white garlic extract. These phytochemical constituents are attributed to all the health benefits accrued to garlic and the reason why it is considered an important medicinal plant worldwide.

Anti - Hyperglycemic Activity of Purple and White Garlic

The Table below shows the results of the anti-hyperglycemic activity of both white and purple garlic methanolic crude extracts on alloxan-induced diabetic rats.

Table 3: Anti-hyperglycemic Activity of Garlic Extracts on Diabetic Albino Rats

RAT BLOOD GLUCOSE LEVEL (mg/dl)

	INITIAL	WEEK 1	WEEK 2	WEEK 3	WEEK 4
NORMAL CONTROL	92.67 ± 4.16	93.33 ± 3.06	93.00 ± 2.00	93.00 ± 3.60	93.67 ± 3.22
DIABETIC CONTROL	319.33 ± 34.39	329.67 ± 31.94	337.00 ± 21.93	0.00±0.00 (DEAD)	0.00±0.00 (DEAD)
PURPLE GARLIC EXTRACT	366.33 ± 13.80	269.33±12.66	211.33 ± 10.02	189.67 ± 7.10	175.33 ± 7.51
WHITE GARLIC EXTRACT	344.33 ± 45.80	272.00 ± 36.10	215.00 ± 23.81	193.67 ± 20.03	181.00 ± 24.27
GB	362.00 ± 29.51	243.66 ± 34.50	194.00 ± 6.25	164.00 ± 06.25	107.33 ± 05.03

Table 3 shows the result of changes in the blood glucose level of diabetic albino rats treated with crude extracts of both white and purple garlic, standard drug, glibenclamide (GB) and the control. From the result above, there was no significant difference in the blood glucose levels of the diabetic rats which recorded mean glucose level between 319.33 mg/dl to 366.33 mg/dl. However, they all differed significantly from the mean blood glucose, 92.67 mg/dl recorded in the control (non-diabetic rats). The blood glucose levels of the treated rats was a confirmation of the state of diabetes, since all were above 250 mg/dl.

During the 28 days assessment period, the blood glucose of the rats fluctuated between the baseline concentration of 92.69 and 93.67 mg/dl. The diabetic control rats increased from 319.33 mg/dl at the baseline stage to the 3rd week (21 days) and the 4th week (28 days) as all were dead of the diabetes. In the garlic crude extracts administered on the test rats, there was a steady reduction in the blood glucose of the rats tested with purple garlic extract from 366.33 to 211.33 mg/dl by the 2nd week (14 days) and eventually, blood glucose level of 175.33 mg/dl at the end of the 4th week (28 days). Similarly, the white garlic crude extract treated rats had reduced blood glucose level from 344.33 mg/dl at the baseline to 215 mg/dl after 14 days and eventually 181.00 mg/dl at the end of the 28 days. The result also showed that the standard drug, glibenclamide (GB) was able to bring the blood glucose of the diabetic rats within normal having a mean level of 107.333 mg/dl.

CONCLUSION

The phytochemical screening of methanolic crude extracts of both white garlic (*A. sativum*) and purple garlic (*A. ophioscorodon*) has shown that both extracts contain some important chemical constituents, such as alkaloids, saponins, flavonoids, tannins, phenols, steroids, and glycosides, in appreciable amounts, which is the reason why garlic is held in high esteem in folklore medicine. Comparatively, the phytochemical constituents of purple garlic are higher than those of white garlic.

The anti-hyperglycemic activity of both white and purple garlic methanolic crude extracts carried out on alloxan-induced diabetic rats showed that the garlic extracts were able to put the blood glucose level outside the diabetic range after the trial weeks of oral administration as compared to a normal sugar level below the 250 mg/dl mark for diabetes. At the end of the one-month period, the glucose levels of the rats treated with garlic extracts were within the normal range, and the rats were healthy and moving about with speed and agility.

However, glibenclamide, a conventional anti-diabetic drug used in the experiment as a reference standard, demonstrated higher activity than the two garlic extracts. However, the two garlic extracts are recommended as reliable medicinal plants for the treatment of diabetes mellitus of all types due to their availability and affordability with little or no side effects. Comparatively, the purple garlic (*A. ophioscorodon*), which is the local garlic, is cheaper, available, and has also been shown to contain more phytochemicals and exhibit high anti-hyperglycemic activity than the white garlic (*A. sativum),* as displayed by the results of the experiments in this research work. Therefore, we recommend that more research be carried out to explore more bioactive components of this purple garlic to improve pharmacognosy and ethnomedicines.

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REVIEW

ENVIRONMENTAL POLLUTION RESULTING FROM WARS: A NEED FOR NON-KINETIC RESOLUTION OF CONFLICTS

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ABSTRACT

Environmental pollution resulting from wars has become a critical issue in contemporary global discourse. Presently there are about 56 conflicts ongoing around the world. The United Nations, an organization founded 75 years ago, continues to play crucial role in managing conflicts in various ways including Preventive Diplomacy and Mediation, aimed at preventing conflicts in the first place; Peacekeeping, by assisting countries transition from conflict to peace (as it is currently the case in MONUSCO – Congo DR); and Peacebuilding, where it supports countries throughout all stages of conflict, including post-conflict recovery and socio-economic development. This paper explores the multifaceted dimensions of environmental degradation caused by armed conflicts and advocates for non-kinetic resolution methods as imperative solutions. Warfare is synonymous with destruction, human suffering and environmental pollution. Modern warfare utilizes a complex arsenal, leaving a trail of environmental destruction. Explosives and heavy weaponry contaminate soil and water with heavy metals, persistent organic pollutants (POPs), and unexploded ordinance. These pollutants enter the food chain through bioaccumulation, posing risks to wildlife and human health. Deforestation caused by military activities disrupts ecosystems and impacts biodiversity. Deliberate targeting of industrial sites and oil fields exacerbates pollution by releasing hazardous substances into air, water, and soil. Military activities contribute significantly to greenhouse gas emissions, thereby exacerbating climate change. The carbon footprint of military operations, including transportation, logistics, and energy consumption, underscores the urgent need for eco-friendly conflict resolution strategies. In response to these challenges, the concept of non-kinetic resolution of conflicts emerges as a compelling alternative. Non-kinetic approaches encompass diplomacy, mediation, and arbitration aimed at preventing armed conflicts and promoting peaceful negotiations. Such strategies prioritize dialogue, consensus-building, and conflict prevention over militaristic responses, thereby minimizing environmental destruction. Only through concerted efforts can we mitigate the devastating environmental consequences of wars and forge a path towards a more peaceful and environmentally resilient world.

Key word: environmental pollution, war, environmental sustainability, POPs, heavy metals

INTRODUCTION

Conflict has been an ever-present aspect of human civilization. Environmental pollution resulting from wars has become a critical issue in contemporary global discourse. Since World War II, the world has witnessed more than 200 armed conflicts, mostly in developing countries and these wars have killed more than 20 million people and displaced several millions more, while causing serious environmental and economic damages **(**Biswas, 2001). Presently there are 56 conflicts ongoing around the world. Biswas, (2001) observed that the environmental impacts of wars are often multi-dimensional and that they also often have repercussions in areas long distances away from those of concentrated battle and over prolonged periods of time, long after the wars have ended. In recent times, the Russia-Ukraine war heightened the concern over environmental pollution from wars and there are concerns that the invasion may cause specific environmental risks, like the release of radioactive substances from nuclear power plants and contaminated soils (Harada *et al*., 2022). Military conflict is associated with the testing, production, transportation, and deployment of weapons. At each of these stages, there exists the potential for environmental contamination (Lawrence *et al*., 2015).

Several papers in diverse areas of chemistry have been submitted for the AbiaChem Chemical Society of Nigeria Maiden Conference. This paper aims to bring to our attention an often-overlooked topic - the implications of wars and conflicts on the environment. Wars activities contribute to the pollution of the air, water and soil. This paper explores the multifaceted dimensions of environmental degradation caused by armed conflicts and advocates for non-kinetic resolution methods as imperative solutions.

METHODOLOGY/APPROACH

A critical evaluation of the global literature on the consequences of conflicts on environmental resources and state-of-the-art protection measures was conducted to address the research questions. This study adopted only desk study. Research into environmental impacts of conflicts and wars was carried out using the regular search engines such as Google Scholar and also by searching through ScienceDirect using selected key words including: conflict; pollution; war; chemical warfare; nuclear arsenals; war; bombs; nerve agents; toxic chemical; chemical warfare agents; chemical weapons; history; WWI; agent orange; Ukraine war etc.

Historic Overview of Wars and their Environmental Impacts

Warfare on Earth has evolved significantly over time, with warriors leaving their homes early to fight. Tools of combat changed, and the backdrop remains constant. Historically, forests were used for bows and arrows, causing minimal environmental damage. Fire weapons later became prevalent. Today, war is very different. It is obvious that warfare, which is historically synonymous with destruction and human suffering, extends its impacts beyond immediate casualties to include severe environmental consequences. With the advancement of weapons of mass destruction, modern wars generate devastating effects on the environment by using chemical, biological, radioactive weapons. Environment damages from these weapons have increased by massive proportions and the toxic effects persist for long time on war fields (Protosaltis, 2012; Tortorici and Fiorito, 2017).

The development and use of nuclear warheads, in both times of peace and conflict, has undoubtedly left a significant scar on the Earth's surface. Between 1945 and 2009, a lot of countries developed nuclear weapons (Protopsaltis, 2012). The Hiroshima and Nagasaki nuclear bombings are the most devastating events in human history, causing significant environmental damage. Radiation, fires, acid rain, and erosion impacted the Japanese ecosystem, and the environment has yet to fully recover from World War II. Documented reports show that as of the late 1990s, more than 2000 nuclear weapons tests have been conducted around the world (Lawrence *et al*., 2015; Protopsaltis, 2012).

It is obvious that in some previous conflicts, new weapons were developed to destroy the environment for military purposes. This has sometimes resulted in calls for improved environmental protection through international law revisions or UN recommendations. A typical example is the Vietnam War, during which the United States Air Force deployed Agent Orange, a chemical herbicide and defoliant, to destroy forest cover and crops from 1961 to 1971, leaving a legacy of environmental and medical devastation (Ba and Karp, 2024).

Modern Warfare and the use of Conventional and Unconventional Weapons

Explosives and heavy weaponry in conflicts contaminate soil and water with heavy metals, persistent organic pollutants (POPs), and unexploded ordinance (UXO), posing risks to wildlife and human health. Deforestation disrupts ecosystems, affecting biodiversity and weather patterns. Military leaders and personnel show little concern for these environmental impacts, with limited postwar restoration activities. Understanding the negative effects of combats on the environment is crucial for sustainable peace and prioritizing environmental care in developed countries (Meìaza *et al*., 2024). Aerial bombings have significant negative impacts on environmental conservation efforts and the ecology. War also exterminates wildlife and contributes to atmospheric and water pollution. Military leaders and personnel have shown little concern about these impacts, and limited postwar restoration activities are undertaken to reduce war-driven environmental impacts.

The use of conventional and unconventional weapons pollute the environment. Explosions and bombings devastate ecosystems, causing soil erosion, deforestation, and habitat destruction. The deliberate targeting of industrial sites, infrastructure, and oil fields exacerbates pollution by releasing hazardous substances into air, water, and soil, endangering human health and biodiversity. Moreover, the military activities contribute significantly to greenhouse gas emissions, thereby exacerbating climate change. The carbon footprint of military operations, including transportation, logistics, and energy consumption, underscores the urgent need for eco-friendly conflict resolution strategies.

Chemical warfare

Chemical warfare agents (CWAs) are deadly weapons that can cause severe toxicity and devastating effects on populations. Some CWAs used during World War I (WWI) are sulphur mustard, chlorine and other toxic agents. Almost all participants in World War I utilised chemical weapons. The substances employed were designed to irritate and disable, yet instead caused numerous injuries and fatalities. Between WWI and WWII, Germany synthesised nerve agents. Nerve agents, a category of CWAs, have been used in warfare since the 1930s. Organophosphorus compounds like soman, tabun, sarin, and cyclosarin are highly harmful chemicals that can cause severe health effects and even death. These agents, which are specific inhibitors of acetylcholinesterase in humans, insects, and other animals, pose a significant threat to humans and the ecosystem. Sarin, for example, is highly lethal, causing symptoms like headaches and stomach cramps (Saya *et al.*, 2024).

Post WWII, a boom in research and development of chemical compounds led to the misuse of CWAs. VX and its derivatives were horrifying and stockpiled in military stocks. VX, short for "venomous agent X", is one of the best known of the V nerve agents and originated from pesticide development work at Imperial Chemical Industries (ICI) (Wikipedia, 2024). VX is a human-made chemical warfare agent classified as a nerve agent and is one of the most toxic of nerve agents. VX is an extremely toxic synthetic chemical compound in the organophosphorus class (Formula: $C_{11}H_{26}NO_2PS$). VX fatalities occur with exposure to tens of milligram quantities via inhalation or absorption through skin; VX is more potent than sarin, another nerve agent with a similar mechanism of action. It is a clear odourless and tasteless liquid with an appearance similar to that of motor oil. VX is a rapid-acting, lethal nerve agent that affects the nervous system by interfering with the signals sent from the brain to the vital organs and other parts of the body. VX affects the body by blocking the action of the enzyme acetycholinesterase (ACh). When the enzyme is blocked, messages from the brain are short-circuited at the nerve endings. As a result, hyperactivity occurs in the organs stimulated by the nerves (US Army, 2024).

The use of chemical weapons continued throughout the minor wars and conflicts that occurred before to WW2, notwithstanding the Geneva Gas Protocol, which was signed in 1925 (Protopsaltis 2012). The Chemical Weapons Convention limited CW threat to non-member state parties and terrorist groups. Non-terrorist use was observed in a Moscow theatre in 2002 and as well as in the main chemical accidents connected with the release of toxic chemicals.

CWAs release volatile organic compounds (VOCs), which can cause serious health effects like mutagenesis and carcinogenesis. Degrading hazardous CWAs through catalytic reactions like hydrolysis, methanolysis, and oxidation is crucial.

Use of Chemical Specifically Designed for Environmental Destruction in Warfare

Not all chemical warfare agents are aimed directly at humans. Herbicides have also been employed in combat operations to change landscapes and remove foliage in order to improve vision. The Vietnam war (1961-1971) was a major conflict with significantly impact on the environment. It was the first war that saw the use of weapons specifically designed for environmental destruction. The Vietcong, a group that used the surrounding jungles for guerilla warfare and the United States used weapons designed to rob them of the cover and concealment provided by the jungle. Two main weapons used by the U.S. in their massive destruction of the Vietnamese Jungles were Agent Orange and napalm (Biswas, 2001; Lawrence *et al*., 2015). Agent Orange, was one of several dioxin-based herbicides sprayed by US soldiers to damage crops and block vegetation. During the conflict, the landscapes of Vietnam, Cambodia, and Laos were subjected to roughly 77 million L of herbicides, covering around 2600 million hectares of land (Lawrence *et al*., 2015). Agent Orange was used to kill grass, foliage, woody species, and leave soil infertile. It was responsible for the destruction of plant life, death, and birth defects in animals, including humans. Napalm was used to destroy vast areas of jungle, destroying 75-80% of the U Minh Forest (Vietnam). Today, many parts of Vietnam are described as looking like the surface of the moon (Swintek, 2006) and the chemicals used left a legacy of soil contamination and birth defects.

Case Study of Environmental Impacts of a War: The Russia-Ukraine War

The ongoing conflict between Russia and Ukraine is causing widespread destruction of military facilities, equipment, vehicles, and civilian buildings, leading to air, water, and land contamination. Chemical substances released from explosions, such as toxic gases and particulate matter, spread over residential areas, contaminating water and soil. Groundwater, agriculture, and animal products become primary sources of poisoning in humans. The Chornobyl nuclear power plant has reported 28 times higher gamma radiation levels than the annual limit (Harada *et al*., 2022).

The current conflict between Russia and Ukraine exemplifies modern warfare. The environmental damage caused by the war in Ukraine will persist for many years. Even if the war were to magically end today, it will take decades to recover from the negative impact on climate change, soil degradation and biodiversity loss (Ukraine accounts for 35% of the biodiversity of the entire European continent), and significant effort will be required to restore the ecosystem put under such severe strain (Tollefson, 2022; Harari and Annesi-Maesano, 2023). In addition, explosions and the heavy traffic of military vehicles result in the secondary emission of highly toxic substances into the air (including organic pollutants, polycyclic aromatic hydrocarbons, dioxin, carbon monoxide, polychlorinated biphenyls), some of which are persistent organic pollutants (Harari and Annesi-Maesano, 2023). Finally, it is expected that the long-term effects of air pollution will lead to increased incidence of inflammatory chronic diseases (Pereira *et al*., 2022; Tollefson, 2022). The attacks against fuel and gasoline storage depots in Ukraine will have caused high peaks in air pollution (Harari and Annesi-Maesano, 2023).

The Zaporizhzhia Nuclear Power Station in Ukraine, Europe's largest nuclear plant, was captured by Russian forces in March 2022. The facility, used as a military base and firebase for Russian army artillery, has been damaged by shelling, increasing fire risks and radioactive material leakage (Ba and Karp, 2024). The war has compromised Ukraine's agricultural production, which is vital for the country's economy and global food security (EPRS, 2023). The conflict may trigger the largest global food crisis since World War II (FAO, 2014), with food shortages in Nigeria and other countries being indirect impacts of the war in Ukraine. On June 6, 2022, Russian forces destroyed Ukraine's largest dam, Kakhovka, releasing 150 tonnes of toxic industrial lubricants, contaminants, and dislodged landmines, causing long-term environmental and health impacts (EPRS, 2023).

The Ukraine's Ministry of the Environment and Natural Resources launched *EcoZagroza* in July 2022 to record crimes committed by Russia. As of 18 July 2023, there have been 2450 reports of direct environmental damage caused by military actions by Russia. Estimates suggest that Russia's invasion has inflicted €52.4 billion in damage, including air, waste pollution, water, and soil damage. The UN Environment Programme (UNEP) warns of a toxic legacy in Ukraine and the region after the conflict ends (EPRS, 2023).

Environmental Impacts of Wars and Conflicts

The impact of war activity on the environment, particularly on-air pollution, starts with the development and testing of all aspects related to military weapons, hardware and armament, and the necessary training in its use (Protopsaltis, 2012). Wars have adverse environmental impacts, regardless of direct military actions, strategic counteractions, collateral damages, or military support activities. The total environmental damage is influenced by factors such as the war type, weapons, duration, terrain, strategies used, and prewar environmental conditions. These factors also affect the duration of specific environmental impacts. Therefore, the total environmental damage caused by a war is invariably adverse **(**Biswas, 2001).

The use of conventional weapons and the fires caused by the fighting is leading to high levels of air pollutants in the form of particulate matter (PM), toxic gases and heavy metals (Harari and Annesi-Maesano, 2023). Explosions and building collapses, as well as the digging of tunnels and trenches, cause an enormous spike in PM levels. The health impact of air pollution, especially in the case of acute exposure, is well known. In a war zone, air pollution is likely to result in more deaths than bombs (Solarin *et al*., 2018; Harari and Annesi-Maesano, 2023). Conflicts have been linked to environmental pollution, exposure to radioactive elements, heavy metals, and water-borne diseases (Harada *et al*., 2022). Also, hydrocarbons from destruction of refineries, crude oil exploration facilities and oil-waste spills entering surface water and groundwater contain a range of chemical pollutants, including heavy metals such as mercury, lead, and arsenic, and cause air pollution from polycyclic aromatic hydrocarbons (PAHs), volatile organic compounds, particulate matter, sulphur, and nitrogen oxide (PAX, 2021).

Water contamination due to warfare, including chemical, biological, or nuclear weapons, poses health hazards for humans and ecosystems. Remediation techniques are often technologically impossible, expensive, complex, and require high scientific expertise, which are not readily available in many developing countries where most wars have occurred in recent decades (Biswas, 2001).

It is obvious that warfare has a significant environmental impact beyond the battlefield, requiring significant resources and causing increased carbon emissions. It involves hazardous materials and energy-intensive processes in weapons and equipment production, causing damage to ecosystems and biodiversity. Military infrastructure also results in pollution, fuel spills, and deforestation. Indirect effects include disruption of sanitation and waste management, increased industrial activity, displacement of people, and changes in land use patterns. War production contributes to environmental degradation beyond the battlefield, with unsustainable extraction and disposal of resources having long-term ecological consequences.

The Iraq war (2003-2011) caused soil, water, and air damage, with radioactive substances like uranium-238, uranium-235, cesium-137, and cobalt-60 found in cities. These particles spread through dust storms and contaminated food, causing cancers and birth defects. Depleted uranium in Iraq increases the risk of breast cancer, with cancer patients having higher average uranium concentrations (Harada *et al*., 2022).

War significantly impacts health, especially in at-risk populations like pregnant women, children, elderly, sick, lower-class, migrants, and refugees (Harari and Annesi-Maesano, 2023)

leading to long-term health consequences for millions of people (Harada *et al*., 2022). The health impacts of pollution from wars include human health impacts of air, water, and soil pollution. International efforts are needed to address these issues, including global monitoring of pollution levels within conflict zones post-conflict to protect returnees (Harada *et al*., 2022).

The Need for Non-kinetic Approaches to Conflict Resolution

In response to the challenges of environmental degradations from wars and conflicts, the concept of non-kinetic resolution of conflicts emerges as a compelling alternative. Non-kinetic approaches encompass diplomacy, mediation, arbitration, and international cooperation aimed at preventing armed conflicts and promoting peaceful negotiations. Such strategies prioritize dialogue, consensus-building, and conflict prevention over militaristic responses, thereby minimizing environmental destruction. Implementing non-kinetic methods requires global cooperation and commitment to international treaties and agreements that protect the environment during conflicts.

The environmental cost of wars necessitates a paradigm shift towards non-kinetic conflict resolution. Diplomacy, mediation, and international cooperation offer alternative pathways to resolving disputes. These methods not only minimize human casualties but also protect the environment from the destructive consequences of armed conflict. Investing in Peaceful Solutions is key to non-kinetic conflict resolution. Shifting from kinetic to non-kinetic solutions requires significant investment in diplomacy, conflict resolution training, and international institutions. Additionally, promoting sustainable practices within the military can help minimize environmental damage during operations. To ensure a Sustainable Future, we need to find alternatives to kinetic approaches to conflicts.

The environmental burden of wars necessitates a collective commitment to non-violent conflict resolution. By prioritizing diplomacy and investing in peaceful solutions, we can safeguard our environment for future generations. This requires a global shift in mindset, recognizing the interconnectedness of peace, security, and environmental sustainability.

Moving forward, there is a need to protect the environment in conflicts, when non-kinetic options fail. There is a need to promote sustainable practices in the military, increased investments in clean technologies for military operations and urgent need to build international cooperation to prevent and address environmental damage from war. Efforts and Initiatives for Environmental Protection in conflict zones would require the cooperation of the parties to the conflict, other international stakeholders and the NGOs and Civil Society Organizations. Technological Solutions and Innovations are also required to contain and clean up polluted sites. This will require remediation techniques and the adoption of innovative approaches to mitigate environmental damage.

Despite efforts to protect the environment from human destruction, the only way to truly protect it is to end war itself. Military manoeuvres can cause environmental damage, as bombs, tanks, battleships, chemical and biological warfare can destroy life and ecosystems. Peace is the only way to truly protect the environment from human conflict, and despite the hope for harmony, the ultimate fear is that conflict will take a toll on Earth and its resources (Swintek, 2006). Despite the constraints imposed by international agreements to assure environmental protection and air quality, artillery shells and bombs of various sizes, as well as chemical weapons, are regularly produced and tested (Protopsaltis, 2012).

International Efforts to Protect the Environment

The United Nations and affiliated agencies play a crucial role in advocating for sustainable peacebuilding and environmental protection, facilitating conflict resolution through preventive diplomacy and mediation, peacekeeping, and peacebuilding, humanitarian assistance, and environmental remediation efforts in war-torn regions. Civil society organizations and grassroots movements contribute significantly by raising awareness, advocating for policy change, and holding governments and armed groups accountable for environmental damage.

A paradigm shift towards non-kinetic resolution of conflicts is necessary to mitigate the ecological footprint of wars and safeguard natural resources for future generations. Global solidarity, supported by robust international frameworks and grassroots mobilization, is essential to promote sustainable development, protect ecosystems, and ensure environmental justice in conflict-affected areas.

There is currently no global legal instrument on ecocide, but various international law rules address environmental preservation during warfare (EPRS, 2023). International accords have been formed to safeguard the environment, with nuclear tests banned, limits on the stockpiling of environmentally hazardous weapons and chemicals imposed, and sanctions governing solid waste disposal (Swintek, 2006). The UN General Assembly has been working to address environmental threats in conflict situations and the need for legal mechanisms to address environmental damage.

The United Nations Environment Program (UNEP) works closely with governments, civil society organizations, and other stakeholders to assess and mitigate the environmental impact of conflicts, promote environmental recovery and restoration, and strengthen environmental governance in post-conflict settings. The UN Security Council has recognized the linkages between environmental degradation, conflict, and peace and has called for the inclusion of environmental considerations in peacekeeping mandates (Ba and Karp, 2024). The General Assembly's First Committee, which focuses on arms control and disarmament, is also aware of the environmental impact of warfare and weapons. The General Assembly has passed the Legal Principles on the Protection of the Environment in Relation to Armed Conflicts (PERAC), which offer guidance but remain unclear on how to ensure real action. The 27 principles are not legally binding on states but are hoped to be implemented through national legislation, military training manuals, business guidance, and outreach with non-state armed groups (Ba and Karp, 2024).

The Roles of the Analytical/Environmental Chemists

The intensive use of explosive weapons (EW) in Ukraine has taken a heavy toll on people, livelihoods and ecosystems. The project *Protecting the environment in armed conflict in Ukraine* was initiated by NPA and has been implemented together with CEOBS. The project has used remote sensing, field surveys and sampling to develop two case studies of conflict pollution and environmental harm in areas affected by EW use. By gathering environmental data to support assessments, remedial measures and relief and assistance, the project has been informed by the *principles on the Protection of the environment in relation to armed conflicts* (PERAC principles) (NPA/CEOBS, 2024).

Presently the Norwegian People’s Aid (NPA) and the Conflict and Environment Observatory (CEOBS) with funding from the Norwegian Ministry of Foreign Affairs has assessed the presence and likely extent of soil pollution and wider environmental harm in Ukraine, and gathered data on the interconnected and reverberating effects of the use of explosive weapons (EW), including the destruction of critical infrastructure, as well as impacts on local livelihoods and land use (NPA/CEOBS, 2024).

RECOMMENDATIONS

There seems to be little evidence that military strategists consider environmental consequences of military activities when planning or executing military actions related to conflict, at least until recently. In the US, each branch of the U.S. military has within it an organization educated to creating a more environmentally friendly and educated military (Swintek, 2006). The UN and NGOs should prioritize military environmental education among armed forces, raising awareness about the importance of avoiding environmental harm during and after conflicts. Establishing a body to draft uniform standards and establish training programs for Member States could promote responsible behaviour and prevent militaries from creating new environmental weapons. This might promote responsible behaviour. But oversight might be required to make sure militaries do not sue their new environmental awareness to create new environmental weapons, turning infight into targets. Environmental harm in armed conflict mainly arises from incidental damage or pollution during military operations, necessitating states to consider the indirect effects of their operations to mitigate civilian harm (CIVIC, 2023). Harada *et al*. (2022) emphasize the importance of international collaboration in addressing environmental problems. They suggest establishing scientific bodies to identify concrete actions and provide immediate assistance. They also highlight the need for raising awareness, promoting public education, and fostering a culture of peace for a sustainable future. Developing countries lack sufficient laboratory infrastructure for monitoring pollution from wars, and the international community can enhance public health monitoring through competent laboratories, data management tools, and improved health professional education to address this shortage post-war (Harada *et al.*, 2022).

CONCLUSION

Warfare represents a significant threat to environmental health. Its long-term consequences for ecosystems, biodiversity, and human health cannot be ignored. Embracing non-kinetic conflict resolution is an imperative for safeguarding our planet and ensuring a secure future for all. By prioritizing sustainable practices and fostering peace, we can build a world where the environment thrives alongside humanity. Building a sustainable future requires a concerted effort from national and international institutions, the military sector, and the general public. Only by prioritizing diplomacy and investing in peaceful solutions can we break the cycle of violence and pollution, ensuring a world where environmental sustainability thrives alongside peace. This paper underscores the urgent imperative for policymakers, international organizations, and civil society to collaborate effectively in promoting peacebuilding strategies that prioritize environmental sustainability. Only through concerted efforts can we mitigate the devastating environmental consequences of wars and forge a path towards a more peaceful and environmentally resilient world. The environmental cost of war necessitates a paradigm shift towards non-kinetic conflict resolution. Diplomacy, mediation, and international cooperation offer alternative pathways to resolving disputes. These methods not only minimize human casualties but also protect the environment from the destructive consequences of armed conflict.

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USE OF CASHEW NUTS SHELL OIL IN PRODUCTION OF TERMITE ATTACK ON THREE SOFT WOODS: *Gmelina arborea*, *Irvingia gabonensis* and *Milicia excelsa*

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ABSTRACTS

This study investigates the use of cashew nut shell oil in the production of termite attacks on three soft woods, *Gmelina arborea, Irvingia gabonensis,* and *Milicia excelsa.* The physicochemical parameters of cashew nut shell oil, including the acid value, free fatty acid value, peroxide value, iodine value, and saponification value. The results demonstrate that the acid value of the cashew nut shell oil was 12.70 ± 0.33, the free fatty acid value was 6.50 ± 0.09, the peroxide value was 10.04 ± 0.144, the iodine value was 43.02 ± 0.9, and the saponification value was 138.0 ± 3.47. Termiticidal activity was evaluated by treating the wood samples with different concentrations of (CNSO)and assessing the number of termites, furrows, and furrow length. The results showed that, as the concentration of CNSO increased, there was a significant decrease in the number of termites, furrows, and furrow length across all wood species. *Gmelina arborea* treated with the highest concentration of CNSO (Gm T3) exhibited the most effective anti-termite activity, with the lowest counts of termites (34.00 ± 1.73), furrows (9.00 ± 1.73), and furrow length (4.50 ± 0.46 cm). Similarly, *Milicia excelsa* wood treated with the highest concentration of CNSO (Iro T3) demonstrated the highest anti-termite activity among the Iroko samples. The toxic effects of cashew nut shell liquid (CNSL) and its derivatives on termites have been well documented, and immature CNSL have been identified as possessing anti-termite properties. These findings highlight the potential of CNSO and its derivatives as natural and effective solutions for termite control in various wood species.

KEYWORDS: cashew Nut shell oil, anti- termite, *Gmelina arborea*, *Irvingia gabonensis* and *Milicia excelsa*

INTRODUCTION

Cashew nut shell oil (CNSO) is derived from the shells of cashew nuts and comprises phenolic compounds, anacardic acid, cardol, and cardanol. These compounds exhibit significant termite-repellent properties. Phenolic compounds are known for their pesticidal properties that make them effective in repelling termites. Anacardic acid, a major component of CNSO, exhibits strong insecticidal and repellent effects against a wide range of insects, including termites. Cashew nut oil possesses antimicrobial, antioxidant, and insecticidal properties. In this study, we aimed to explore the use of cashew nut shell oil in the production of termite-resistant treatments for three soft woods: *Gmelina arborea*, *Irvingia gabonensis*, and *Milicia excelsa.*

Softwood such as *Gmelina arborea, Irvingia gabonensis*, and *Milicia excelsa* are commonly used in construction and furniture making because of their availability and affordability. However, they are highly susceptible to termite attacks, which can result in severe damage and compromise the structural integrity of wood. (Keplinger *et al.,* 2015). When termites infest softwood, they feed on the cellulose present in the wood, which gradually weakens over time. This can lead to structural failures in buildings and the need for expensive repairs. Additionally, termite damage can negatively affect the aesthetic appeal and longevity of the furniture made from these softwoods. (Goodell & Nielsen, 2023).

Termites can cause substantial damage to buildings and wooden structures by feeding on cellulose, which is the primary component of wood, compromising the structural integrity of buildings. Therefore, it is crucial to protect wooden structures from termite damage (Govorushko 2019). Synthetic termiticides have been used for many years to control termite infestation (Mahapatro and Chatterjee, 2018). Commonly used synthetic termiticides, such as chlorpyrifos, permethrin, bifenthrin, imidacloprid, and fipronil, are effective in controlling termites. However, concerns have been raised regarding their high toxicity, persistence in the environment, and impact on non-target organisms. Consequently, the use of natural products as alternatives to synthetic termiticides has gained attention in recent years because of their eco-friendliness, low toxicity, and sustainability (Oi, 2022).

This study aimed to determine the chemical composition of cashew nut shell oil and evaluate its effectiveness as a natural wood preservative against termite attack in three softwood species.

2.1 Materials and Method

2.1.1 Sample Collection

The nut samples were sourced from a domestic cashew plantation situated within Abia State University, Uturu. The botanical identity of the samples was confirmed by Mr. N. Ibe work in the forestry department of the Michael Okpara University of Agriculture, Umudike. The samples were carefully packaged in clean and dried polythene bags to protect them from heat, moisture, and physical damage, and were transported to Ceslab Global Services, Analytical Laboratory Umuahia, in a controlled environment to preserve their quality and prevent contamination prior to analysis.

2.1.2 Sample Preparation: The samples were prepared by removing cashew nut shells from the nuts and extracting oil from the shells. The shells were manually extracted from the nuts. First, the cashew nuts were removed from the front and sorted to remove any that showed signs of infection or spoilage. The "good" seeds were washed with clean water to remove any dirt or residual fruit pulp. The nuts were carefully cut longitudinally using a sharp kitchen knife, and the cotyledons were removed, leaving the shells. The shells were then spread on a laboratory tray and dried in an oven at 105^{o}C overnight to remove any moisture content before being ground into a powdered form using a laboratory mill (silver crest grinder 6500 W) for oil extraction.

2.2 Extraction of Cashew Nut-Shell Oil

Ground cashew nutshells (100 g) were weighed and packed into a pre-weighed Soxhlet thimble to minimize material loss during extraction. The Soxhlet apparatus was assembled using a thimble, a condenser, and a receiving flask. n-Hexane (400 mL) was selected as the solvent and weighed in the round-bottom flask of the Soxhlet apparatus owing to its low boiling point. The apparatus was then attached to a heating mantle, and the solvent was refluxed for 6 h to effectively extract oil from the nutshells. After cooling, the thimble was removed and the solvent-oil mixture was collected in a pre-weighed beaker. The mixture was transferred to a rotary evaporator to remove the n-hexane solvent, yielding cashew nut-shell oil. The oil was further dried in an oven at 80 °C for 30 min to remove residual solvent before cooling and weighing. The oil extract value was calculated using the following formula:

$$\% \text{ oil yield} = \frac{(w2-w-1)}{w\times100/1}$$

Where,

W = weight of sample analyzed W_1 = weight of empty extraction flask

W_2 = weight of flask + oil extract

2.3 Physicochemical Analysis of Cashew Nut Shell Oil

The physicochemical parameters of Cashew Nut Shell Oil (CNSO) for refractive index, moisture content, acid value, saponification value, perioxide value, free fatty acid value and specific gravity are carried out according to the method of AOAC (1990)

2.4 Test for Termiticidal Activity

The activity of cashew nut shell oil against termites in wood protection (or termiticidal activity) was determined by the direct treatment of three different wood types with the same dimensions and varying concentrations of the oil extract and exposing them to the presence of termites. The following procedure was followed.

2.4.1 Wood Sample Selection and Treatment

Three wood types, *Gmelina arborea, Irvingia*, and *Milicia excelsa*, were selected and used. Nine (9) spot-free wood cuts measuring 2 × 2 × 24 in were made from each of the three types of wood and grouped into three groups of three woodcuts, designated A, B, and C, respectively.

2.4.2 Wood Sample treatment

Group A was treated with 200 ml of 10% (v/v) CNSO mixture in 50% ethanol in water, group B was treated with 20 % (v/v) of the same solution, and group C was treated with 30 % of the mixture. The same treatment was performed for each type of wood. A separate control group contained three cut lengths for each wood type with no CNSO treatment. In each case, the test woodcut was coated completely with the test CNSO solution, covering all the parts.

Both the control woodcuts and the test-treated woodcuts were labelled approximately with “Nail indicators” where the position and number of nails on the woodcuts indicated the wood type and treatment. Wood was buried (0 –10 cm) in an open field (farm) under an old rubber plantation and left for 28 days. Finally, the wood samples were carefully washed and examined. The number of termites on each woodcut and the time it was unearthed were also recorded. Later, the number of furrows created by termites attacked the wood and the length of the furrows was recorded after careful washing of the wood. The obtained data were subjected to statistical analysis to determine the levels of variation between wood susceptibility (or resistance) to termite attack with respect to the CNSO treatments.

Statistics

All analyses were performed in triplicates. The data obtained were subjected to analysis of variance (ANOVA) Using the Statistical Package for Social Sciences (SPSS) version 20.

RESULTS

The results of the study are as shown below.

Table 1: Physicochemical Parameters of Cashew nut shell Oil

S.G (g/cm^3)	R. I	M.C(%)	A. V	F.F. A	P. V	I. V	S. V
0.92± 0.003	1.46 ± 0.006	3.24±0.024	12.70± 0.33	6.50±0.09	10.04± 0.144	43.02 ± 0.9	138.0± 3.47

Values represent the means of triplicate analyses ± standard deviation. Figures with different

The results of physicochemical parameters of the CNSO showed in Table 1 shows the acid value (AV) of CNSO oil was 12.70 ± 0.33. The free fatty acid (FFA) value was 6.50 ± 0.09. The peroxide value (PV) was 10.04 ± 0.144. The iodine value (IV) was 43.02 ± 0.9. The saponification value (SV) was 138.0 ± 3.47. of the CNSO show that the acid value (AV) of CNSO oil was 12.70 ± 0.33. The free fatty acid (FFA) value was 6.50 ± 0.09. The peroxide value (PV) was 10.04 ± 0.144. The iodine value (IV) was 43.02 ± 0.9. The saponification value (SV) was 138.0 ± 3.47. These physiochemical parameters provide important insights into the composition and quality of cashew nut shell oil, which can have various applications, including anti-termite activity.

Table 2: Termiticidal activity of Cashew nut shell oil

SAMPLE	No. OF TERMITES	No OF FURROW	FURROW LENGTH (cm)
Gm C	170.00 ± 6.25^{a}	38.33 ± 2.52^{a}	8.9 ± 0.27^{a}
Gm T1	121.00 ± 4.58^{b}	21.33 ± 3.06^{c}	7.1 ± 1.66^{b}
Gm T2	58.67 ± 7.51^{fg}	12.67 ± 1.16^{d}	4.67 ± 0.40^{de}
Gm T3	34.00 ± 1.73^{i}	9.00 ± 1.73^{e}	4.50 ± 0.46^{de}
Irv C	112.00 ± 4.00^{c}	28.67 ± 2.52^{b}	6.97 ± 0.57^{b}
Ir T1	79.00 ± 3.00^{e}	18.33 ± 2.52^{c}	5.33 ± 0.61^{cd}
Ir T2	52.67 ± 3.51^{gh}	9.67 ± 1.16^{de}	4.23 ± 0.21^{def}
Ir T3	14.00 ± 1.73^{j}	5.33 ± 0.58^{f}	3.07 ± 0.25^{f}
Iro C	97.00 ± 3.61^{d}	29.33 ± 2.31^{b}	6.37 ± 0.75^{bc}
Iro T1	62.00 ± 4.00^{f}	19.67 ± 2.08^{c}	4.60 ± 0.36^{de}
Iro T2	49.33 ± 4.16^{h}	9.67 ± 0.58^{de}	3.63 ± 0.15^{ef}
Iro T3	16.33 ± 1.53^{j}	5.33 ± 1.16^{f}	3.17 ± 0.60^{f}

Values represent the means of triplicate analyses ± standard deviation. Figures with different superscripts in the column are significantly different ($P<0.05$).

The results of the CNSO termiticidal activities shown in Table 2 shows the number of termites, number of furrows, and furrow length for different samples. the *Gmelina arborea* group, the sample Gm C shows the highest number of termites, furrows, and furrow length compared to samples Gm T1, Gm T2, and Gm T3. This suggests that cashew nut shell oil has varying degrees of effectiveness in inhibiting termite activity across different samples. The results showed that *Gmelina arborea* wood treated with "Gm T_3" demonstrated the most significant anti-termite activity, with the lowest counts of termites, furrows, and furrow length compared to other treated *Gmelina arborea* wood samples. Similarly, among the treated samples of *Milicia excelsa* wood, "Iro T3" showed the highest anti-termite activity, with the lowest number of termites, furrows, and furrow length. *Gmelina arborea* control (Gm C), the number of termites was 170.00 ± 6.25a. The number of furrows was 38.33 ± 2.52 The furrow length was 8.9 ± 0.27 cm. In *Gmelina arborea* treatment 1 (Gm T1), the termite count was 121.00 ± 4.58. The number of furrows was 21.33 ± 3.06. The length of the furrow was 7.1 ± 1.66 cm. For *Gmelina arborea* treatment 2 (Gm T2), the average number of termites was 58.67 ± 7.51 per gram (fg). The number of furrows was 12.67 ± 1.16. The furrow length was 4.67 ± 0.40 cm. For Gmelina arborea treatment 3 (Gm T3), the average number of termites was 34.00 ± 1.73. The number of furrows was 9.00 ± 1.73. The furrow length was 4.50 ± 0.46 cm.

For the *Irvingia gabonensis* control (Irv C), the number of termites was 112.00 ± 4.00 (mean ± standard error). The number of furrows was 28.67 ± 2.52. The length of the furrow was 6.97 ± 0.57 cm. For *Irvingia gabonensis* treatment 1 (Ir T1), the number of termites was 79.00 ± 3.00. The number of furrows was 18.33 ± 2.52. The furrow length was 5.33 ± 0.61 cm. For *Irvingia gabonensis* treatment 2 (Ir T2), the number of termites was 52.67 ± 3.51 g/h. The number of furrows was 9.67 ± 1.16. The furrow length was 4.23 ± 0.21 cm. For *Irvingia gabonensis* treatment 3 (Ir T3), the number of termites was 14.00 ± 1.73. The number of furrows was 5.33 ± 0.58. The length of the furrow was 3.07 ± 0.25 cm.

For *Milicia excelsa* control (Iro C), the average number of termites was 97.00 ± 3.61. The number of furrows was 29.33 ± 2.31 (mean ± standard deviation). The length of the furrow was 6.37 ± 0.75 cm. For Iroko treatment 1 (Iro T1), the average number of termites was 62.00 ± 4.00. The number of furrows was 19.67 ± 2.08. The furrow length was 4.60 ± 0.36 cm. For Iroko treatment 2 (Iro T2), the average number of termites was 49.33 ± 4.16. The number of furrows was 9.67 ± 0.58. The length of the furrow was 3.63 ± 0.15 cm. For Iroko treatment 3 (Iro T3), the average number of termites was 16.33 ± 1.53. The number of furrows was 5.33 ± 1.16. The furrow length was 3.17 ± 0.60 cm. The results showed that as the concentration of cashew nut shell oil increased, there was a decrease in the number of termites, number of furrows, and furrow length, indicating higher anti-termite activity.

As the concentration of cashew nut shell oil increased, the number of termites notably decreased. samples Gm C, Gm T1, Gm T2, and Gm T3, the number of termites decreases from 170.00 to 34.00 as the concentration of the oil increases. Furrow length also decreased with higher concentrations of cashew nut shell oil. In the samples Gm C, Gm T1, Gm T2, and Gm T3, the furrow length decreases from 8.9 cm to

4.50 cm as the concentration of the oil increases. These results showed that increasing the concentration of cashew nut shell oil led to a reduction in the number of termites and furrow length, indicating higher anti-termite activity. The toxic effects of cashew nut shell liquid (CNSL) and its derivatives on termites have been well-documented in various studies. These substances have been shown to exhibit toxicity towards termites, preventing them from tunneling into the soil, even at relatively low concentrations. Figure 1 complements the data in Table 2 by visually representing the anti-termite activity of cashew nut shell oil *on Gmelina arborea*, *Irvingia*, and *Milicia excelsa*.

DISCUSSION

The physicochemical properties of cashew nutshell oil (CNSO) presented in Table 1 indicate that the oil has a mean specific gravity (density) of 0.92 g/cm^3, suggesting that it is light and suitable for industrial production of products, such as disinfectants, among others. The moisture content of the oil was 3.24%, indicating that it had limited hydrophobic properties and could absorb minimal moisture when exposed to air. Although the moisture level is low, it could be beneficial for the growth of spores of lipase-producing microorganisms, which may cause oil to spoil during storage (Onwuka, 2018). The average refractive index of the oil was 1.46. Moreover, a mean value of 12.70 was obtained for the acid value of the oil. The acid value of the oil was moderate, which indicates the presence of double bonds that can lead to reactivity and oxidative rancidity, potentially resulting in early spoilage. A high acid value suggested the presence of free acids. Rancidity is typically accompanied by an increase in free acids as lipase-producing microorganisms degrade oil (Onwuka, 2018). The low iodine value of 43.02 I2/100 g suggests that the oil is of good quality, as it indicates a low level of unsaturation in the oil. The mean value of 10.04 mg/kg also indicated that the oil was fresh at the time of the analysis. The peroxide value of oil is an important factor for assessing its quality and is considered critical (Pike, 2003).

The oil peroxide value was 20 mg/kg, which indicated that the oil was not rancid. The saponification value of CNSO was low, with a mean value of 138 mg KOH/g, suggesting that the oil may not be suitable for use in soap making. Table 2 shows the effects of CNSO on its efficiency in deterring termite damage to wood. The data indicated significant differences in the level of termite infestation among the different wood types, as well as between the CNSO oil-treated woods and untreated controls. In the control group, the average numbers of living termites at the time of analysis were 170, 112, and 97 for the *Gmelina, Irvingia, and Iroko* test woods, respectively. Sample Gm C had the highest number of termites, furrows, and furrow length compared to samples Gm T1, T2, and T3. The anti-termite activity decreased in the order of Gm C > Gm T1 > Gm T2 > Gm T3. Sample Ir C had a higher number of termites, number of furrows, and furrow length than samples Ir T1, Ir T2, and Ir T3. The anti-termite activity decreased in the order of Ir C > Ir T1 > Ir T2 > Ir T3. Sample Iro C exhibited a higher number of termites, number of furrows, and furrow length than samples Iro T1, Iro T2, and Iro T3. The anti-termite activity decreased in the order of Iro C > Iro T1 > Iro T2 > Iro T3. Furthermore, immature cashew nut shell liquid has been shown to possess anti-termite properties. This suggests that even in the early stages of development, cashew nut shell liquid contains compounds or components that are effective in repelling or controlling termites . The presence of toxic effects in CNSL and its derivatives, along with the anti-termite properties found in immature cashew nut shell liquid, highlights the potential of these substances as natural and effective solutions for termite control

Overall, the anti-termite activity of cashew nut shell oil varied among the different samples within each wood species, with the control groups generally showing higher termite activity compared to the treated samples. The results suggest that cashew nut shell oil has varying degrees of effectiveness in inhibiting termite activity across the different wood species and treatment groups tested in this study.

In CNSO-treated woods, there was a significant reduction in the number of living termites adhering to the wood, depending on the concentration of CNSO. The termite population decreased from 121 to 34 termites in *Gmelina,* from 79 to 14 termites in *Irvingia,* and from 62 to 16.33 termites in Iroko test wood at CNSO concentrations of 2.5% to 7.5%. The variation in the number of living termites in the test wood was statistically significant (P<0.05). Furthermore, the number of furrows created on the test wood by termite attacks differed significantly among wood types.

The greatest number of furrows was observed in the controls, with *Gmelina c*ontrol wood being the most attacked, at an average of 38.33 furrows, while *Milicia excelsa* control wood was the least attacked, at 5.33 furrows, similar to *Irvingia* wood. The results also showed that the level of termite attacks was demonstrated in furrows and varied in proportion to the level of CNSO treatment. In the Gmelina test wood, there were 21.33, 12.67, and 9.00 furrows in the wood treated with 2.50%, 5.0%, and 7.5% CNSO, respectively. The corresponding furrows for the *Irvingia* test wood were 18.33, 9.67, and 5.33, respectively, while those for the *Milicia excelsa* test wood were 19.67, 9.67, and 5.33 termites, respectively. Hence, it is inferred that the type of wood has a combined effect on the resistance of termites, in conjunction with the potency of the oil.

The extent of the devastation caused by termite attacks on the test wood was assessed by examining the furrow length. In the control test woods, the average length of furrows was 8.90 cm for *Gmelina,* 6.97 cm for *Irvingia,* and 6.37 cm for *Milicia excelsa*. Upon treatment with 2.5% CNSO, the furrow lengths decreased to 7.1 cm, 5.33 cm, and 4.60 cm for the three wood types, respectively. At the highest CNSO treatment concentration of 7.5%, the furrow length was recorded at 4.50 cm, 3.07 cm, and 3.17 cm, respectively. The results indicated that there was a reduction in the number of live termites, number of furrows, and mean furrow size in the woods treated with CNSO compared with the untreated control. Moreover, there were significant differences (P<0.05) in the number of termites, furrows, and furrow sizes in wood treated with varying concentrations of CNSO. The decrease in termite attacks and their effects on wood were dose dependent. *Gmelina* is softer than *Irvingia* and *Milicia excelsa,* which are hardwoods. The results of the termite attack and their effects on the control indicated significant variations, which were attributed to the natural resistance (due to hardness) of the woods, which differed according to wood type. However, the application of CNSO offers protection to wood against termite attack. This, in turn, demonstrates the potential of oil as an antipest agent for both wood and other materials. The potential of cashew nut shell oil as a natural and effective solution for termite control in wood products, with variations in efficacy depending on the specific sample and treatment applied.

CONCLUSION

This study investigated the anti-termite activity of cashew nut shell oil (CNSO) on three wood species: *Gmelina arborea, Irvingia gabonensis*, and *Milicia excelsa*. The physicochemical properties of CNSO were analyzed, revealing acid, free fatty acid, peroxide, iodine, and saponification values. The termiticidal activity of CNSO was evaluated by measuring the number of termites, number of furrows, and furrow length at different treatment concentrations. The results showed that, as the concentration of CNSO increased, there was a significant decrease in the number of termites, number of furrows, and furrow length, indicating higher anti-termite activity. Among the treated samples, *Gmelina arborea* treated with "Gm T3" and Iroko treated with "Iro T3" demonstrated the most significant anti-termite activity. This study highlights the potential of CNSO as a natural and effective anti-termite agent. Therefore, the concentration of cashew nut shell oil is a critical factor in determining its effectiveness as termiticide.

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OPTIMIZATION OF BIOETHANOL PRODUCTION FROM BANANA PEELS: AN ALTERNATIVE ENERGY SOURCE

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ABSTRACT

The environmental issues associated with fossil fuels have resulted to increase in search globally for alternative and renewable energy sources such as bioethanol that are sustainable and environmentally friendly. In Nigeria, the use of fruit wastes such as banana peels for bioethanol production is yet to be harnessed effectively despite their rich carbohydrate content. This study is aimed at optimization of bioethanol produced from banana peels. The milled sample was subjected to pretreatment, hydrolysis, fermentation and distillation processes to produce bioethanol. The hydrolysis and fermentation process were optimized using classical optimization technique of one factor at a time to determine the effect of their parameters on the yield of glucose and bioethanol respectively. The results obtained indicated that maximum glucose yield of 42.14 ± 0.92 % was obtained at optimum factor conditions of 2 % acid concentration,116 ºC temperature and 25 minutes hydrolysis time while the maximum bioethanol yield of 44.68 ± 0.82 % was obtained at optimum factor conditions of 6 % yeast concentration, 5.5 pH, 35 ºC temperature and 3 days fermentation time. The bioethanol produced was characterized for fuel properties such as boiling point, flash point, kinematic viscosity, refractive index, density using American Society for Testing and Materials (ASTM) methods and the results obtained revealed that they conform to the standard. These findings suggest that banana peel is a good and sustainable feedstock for bioethanol production in Nigeria. Due to its relative abundance and availability for large scale production it should not be discarded in our environment as this is also a means of generating waste from wealth.

KEYWORDS: Bioethanol, Optimization, Pretreatment, Hydrolysis, Fermentation

INTRODUCTION

The need for renewable, sustainable, and ecologically friendly alternative fuels has increased due to the rising cost of petroleum (fossil fuels) and the environmental problems related to its use. One of the most affordable liquid fuel substitutes for non-renewable fossil fuels is bioethanol, which is produced from biomass resources (Tekaligne & Dinku, 2019). Known by the broad term "alcohol," bioethanol is an organic substance that has been used by humans since prehistoric times, when it was mostly consumed as a beverage (Chukwuemeka *et al*., 2020). It is currently used as an alternative source of fuel because it is biodegradable, made from renewable sources, has high octane number and is less toxic when compared to conventional petroleum-based fuels (Akhabue *et al*., 2018). Bioethanol is mainly produced by fermentation of sugar containing crops although it can be manufactured by chemical process of reacting ethylene with steam (Isah *et al*., 2019). as can be seen from the equation (1) and (2) below:

$C_6 H_{12} O_{6(s)} \rightarrow 2C_2 H_5OH (aq) + 2CO_2(g)$ (1)

$C_2H_4(g) + H_2O(g) \rightarrow C_2H_5OH(g)$ (2)

About 80% of the bioethanol produced worldwide is through the fermentation of sugar and starch containing crops which is known as first generation bioethanol or by product from industries based on such crops (Aristodou & Pentila, 2008). Although bioethanol has received a lot of recognition as the ideal replacement for petroleum, it is still not widely available, particularly in underdeveloped nations like Nigeria. This can be linked to the use of edible feedstock such as sugar and starch containing cops in the production of bioethanol which has now raised the price of these feedstock and increased competition between food and fuel, ultimately increasing the price of bioethanol in the international market (Aristodou. & Pentila, 2008; Egbosiuba, *et al*., 2014).

These issues can be resolved by using non-edible feedstock, such as lignocellulose substrates, agricultural wastes, forest wastes, and municipal wastes for bioethanol production Nwakaire *et al*., 2013). Bioethanol can be produced from mainly biomass materials, but the potential of using these materials as feedstock for large scale production, especially in developing countries like Nigeria, depends on their cost, abundance, carbohydrate content, and ease of conversion to ethanol (Khali *et al*., 2015). Large amounts of agro-industrial residues are generated worldwide from the processing of raw agricultural materials for food. Additionally, food processing industries produce large amounts of waste materials, and their disposal has become an environmental concern, especially when they are not been properly disposed (Sangeeta *et al*., 2013). Banana peels are not considered very useful and are therefore dried, ground, pelletized and sold to feed manufacturers at a low price. Although it is a fruit residue, it accounts for 30 – 40% of the total fruit waste and contains carbohydrates, proteins and fiber in significant amounts. Banana peel also contain low amount of lignin which implies that it could serve as a good substrate for the production of value-added products like bioethanol (Taherzade & Niklason, 2004; Chechet, 2016). The use of banana peel in bioethanol production contributes greatly to the conversion of biomass waste into wealth thereby enhancing waste management, cost efficiency and environmental sanitation.

Bioethanol is produced from banana peels using four fundamental processes which are; hydrolysis, fermentation, distillation, and pretreatment. Pretreatment is the first step which is used to increase the digestibility of the material by breaking the rigid structure of the lignocellulose to remove lignin for easy access to the cellulose, and hemicellulose molecules (Taherzade & Niklason, 2004). Hydrolysis of the pretreated sample is the next step used to convert the cellulose and hemicellulose to glucose which is followed by fermentation with yeast such as *saccharomyces cerevisiae* to produce bioethanol. The final stage is the distillation process carried out to obtain pure bioethanol.

Research has been done on the manufacture of bioethanol from a variety of sources, including apple, Kiwi fruit, peach, and maize wastes (Akpan *et al*., 2008), discarded newspapers, sugar cane waste, and maize waste (Braide *et al*., 2016), among others. The concentration of yeast, pH, temperature, time, and acid concentration are some of the primary process variables that affect the yield of bioethanol. Therefore, the purpose of this research is to maximize the concentration of bioethanol produced from banana peels by optimizing the fermentation and hydrolysis processes.

MATERIALS AND METHODS

Sample Collection

Fresh banana peels were obtained from banana purchased from Eke Market Afikpo. Plastic bag was used to collect the sample and transported to the Chemistry Laboratory, Akanu Ibiam Federal Polytechnic, Unwana for further analysis.

Sample Preparation

The banana peels were cut into smaller sizes (between 3 to 4cm) using a knife after it was rinsed with distilled water. The peels were dried in an oven to produce easily crushable materials for 72 hours at 60°C and ground into fine powder using an electric grinding machine. The powdered sample was sieved to a particle size of 1mm, stored in sealed plastic containers and kept at room temperature until the next stage of analysis (Isah *et al*., 2019).

Sample Pretreatment

Steam was used as a pretreatment for the sample to reduce the crystalinity of the cellulose and increase the material's porosity for hydrolysis. The steam pretreatment procedure was carried out in accordance with the method described by Wondale (2012). Batch analysis using 50g of the powdered sample was carried out by dissolving the sample in distilled water at a ratio of 10:1 (v/w). The mixture was transferred into a 1000ml conical flask, covered with aluminum foil and autoclaved. The autoclave's temperature was adjusted to a temperature of 121°C and the pretreatment carried out for 15 minutes. The sample was allowed to cool after the pretreatment and the soluble component separated from the non soluble component and stored for further analysis. The non-soluble component was used for acid hydrolysis step.

Hydrolysis

Dilute acid hydrolysis using H_2S0_4 was carried out on the non soluble fraction of the sample to break down the cellulose and hemicellulose polymers into fermentable sugars that will be used to produce bioethanol (Mekonnen *et al*., 2015). The pretreated sample was used for the hydrolysis in batches at different factor conditions of Acid concentration (1.0-3.0%), Temperature (100 – 132°C) and Time (10 – 30 minutes) to determine the optimal factor conditions that will give maximum yield of glucose and their effect on the yield. After hydrolysis, 1M NaOH was used to adjust the pH of the solution (Sudhagar *et al*., 2018). In order to eliminate the non fermentable lignin, the solid particles were separated from the sugar rich liquid by filtration and added to the previously filtered solution from pretreatment process. The solution was stored at room temperature for further analysis.

Fermentation Process

Fermentation was carried out under anaerobic condition according to the method described by Wondale (2012). The fermentation media was first prepared before the fermentation process to enable a conducive environment for yeast growth and to supply the required amount of nutrients [18]. The fermentation media was prepared using dextrose sugar (10g), urea (1.0g), yeast extract (0.2g), $MgSO_4.7H_2O$ (1.0g) and distilled water to make up 100ml.The samples were then mixed with the fermentation media in the ratio of 1:10 and added into the reactor using separating funnel. The conical flask was properly covered to maintain anaerobic condition with an outlet provided for the release of CO_2 as it turns lime water milky. Triplicate fermentation broths of the same composition were prepared and incubated under the same condition. The fermentation process was carried out initially at varying yeast concentration of (2 – 10%), temperature of 30°C for 72 hours at pH 5.5. The pH of the fermentation was adjusted below 5.5 to accommodate yeast growth by adding the required amount of 4M NaOH and 2.5M HCl (Tekaligne & Dinku, 2019). Subsequent fermentation process was carried out at various conditions of pH (4.0 – 6.0), temperature (20 - 40°C), time (1 – 5) days to determine the optimum factor conditions and their effect on the yield of bioethanol. After fermentation, the sample were taken out and distilled.

Filtration and Distillation of Bioethanol Produced

The samples were filtered using muslin cloth to separate the solid substrate from the liquid. The resulting mixture of bioethanol, water and other impurities was then transferred into the distillation flask and placed on a heating mantle fixed to a distillation column enclosed in a tap running water in order to obtain pure bioethanol. The distillate was collected at 78.5°C (boiling point of ethanol) for 3 hours with another flask fixed at the other end of the column (Isah *et al*., 2019). Distillation is the method used to separate two liquids based on their difference in boiling points.

Quantitative Estimation of Bioethanol Produced

The amount of bioethanol produced was estimated quantitatively using specific gravity method as described by Geirwyr (1995) and Aleme *et al* (2009). A 25ml Pycnometer (specific gravity bottle) was cleaned and dried first and weighed and the weight noted as Wo at 20°C. The bottle was filled with bioethanol and reweighed at 20°C to give W_1. The bioethanol sample was substituted with water after washing and drying the bottle and weighed at 20°C to give W_2. Using these observations, specific gravity was calculated and the percentage of bioethanol in the distillate was estimated from the relationship between the specific gravity and the proportion of the ethanol in alcohol solution using AOAC Table. The specific gravity of the sample was obtained using the following equation:

$$\text{Specific gravity} = \frac{W_1 - W_0}{W_2 - W_0}$$

Where W_0 = Weight(g) of the empty bottle

W_1 = Weight(g) of bottle + Sample (Bioethanol)

W_2 = Weight(g) of bottle + water

Statistical Analysis

The results were obtained in triplicates and expressed as Mean ± Standard deviation. Data obtained from the study were subjected to one –way analysis of variance (ANOVA) at 5 % level of significance ($P<0.05$) using SPSS version 23.0 software.

Optimization of Hydrolysis Process

The effect of the variables on the yield of glucose produced from banana peels was studied to determine the optimal factor conditions that gave the maximum yield. The hydrolysis process parameters studied include acid concentration, temperature and time. The acid concentration was varied from 1.0 to 3.0 % at a step increase of 0.5 % while the other parameters were kept constant. The effect of hydrolysis temperature on the yield of reducing sugar from potato peels was determined by varying the temperature from 100 – 132 ^{o}C at step increment of 8 ^{o}C while keeping other parameters constant. The hydrolysis time was varied from 10 to 30 minutes with step increase of 5 minutes and other parameter kept constant.

Optimization of Fermentation Process

The effect of fermentation process variable on the yield of bioethanol production from banana peel hydrolysate was investigated in order to determine the optimum factor conditions that gave the maximum bioethanol yield. The fermentation process variables studied were: yeast concentration, pH, temperature and time. The concentration of yeast was varied from 2 to 10 % at a step increment of 2% while keeping the other parameters constant. To determine the effect of pH on the yield of bioethanol the pH was varied from 4.0 to 6.0 at a step increment of 0.5 while keeping other parameters constant. The effect of fermentation temperature on the yield of bioethanol was studied by varying the temperature from 20 – 40 ^{o}C at a step increment of 5 ^{o}C while keeping other parameter constant. The fermentation time was varied from 1 to 5 days with step increase of 1 day while keeping the other parameters constant.

RESULTS AND DISCUSSION

Optimization of Acid Concentration

The result of the effect of acid concentration on the glucose yield is shown in Table1. From the result obtained, increase in acid concentration increased the glucose yield till it reached the maximum value of 29.03±1.21% at optimum acid concentration of 2% then it started decreasing with further increase in the concentration of acid. The decreased glucose yield with high acid concentration results from the fact that low acid concentration is conducive for glucose production during hydrolysis. However, the use of high acid concentration for hydrolysis results to browning and charring of the hydrolysates as a result of the degradation of monomeric sugars (xylose, glucose) to fufural and 5 HMF which leads to decrease in glucose yield (Nutawan *et al*., 2010; Isah *et al*., 2019; Umeuzuegbu, 2022).

Optimization of Temperature

The result of the effect of temperature on the yield of glucose is presented in Table 2 and it was observed that the yield increased initially with increase in hydrolysis temperature till it attained a maximum value of 28.22±0.89 % at optimum hydrolysis temperature of 116 ^{o}C. Further increase in temperature decreased the yield of glucose. The results obtained indicated that extreme temperature has unfavorable effect on the conversion of sugar from the substrates due to the degradation of the simple sugar which result in the formation of fufural and 5 HMF that are toxic for *Saccharomyces cerevisiae* in fermentation (Nutawan *et al*., 2010)

Optimization of Hydrolysis Time

The result of the effect of time on the glucose yield presented in Table 3 reveals that increase in hydrolysis time increased the yield till it reached the maximum value of 42.14 ±0.91 %

at optimum time of 25 minutes. On exceeding the optimum time, the glucose yield reduced with further increase in time. The decrease in yield on exceeding the optimum time is attributed to the decomposition of glucose to degradation product (Fufural and 5HMF). Therefore, maximum yield of glucose was obtained at optimum 2 % acid concentration, 116 °C temperature and 25 minutes hydrolysis time.

Table 1: Glucose Yield from Hydrolysis of Banana Peels at Different Concentration of Acid

Acid Concentration (%)	Glucose yield (%)
1.0	25.41± 0.55
1.5	27.27 ±1.28
2.0	29.03 ± 1.2
2.5	26.32 ± 0.79
3.0	24.28 ± 0.79

Table 2: Glucose Yield from Hydrolysis of Banana Peels at Different Temperature

Temperature (°C)	Glucose Yield %
100	2.1.16 ±0.96
108	24.72± 0.73
116	28.22± 0.89
124	25.29 ±0.86
132	23.08 ±1.04

Table 3: Glucose yield from hydrolysis of Banana peels at Different Time

Time (Minutes)	Glucose yield (%)
10	30.50± 0.74
15	35.20± 0.90
20	37.26 ±0.94
25	42.14± 0.91
30	34.18 0.93

Optimization of Fermentation Yeast

The result obtained for effect of yeast concentration on the bioethanol yield is presented in Table 4 which shows that the yield of bioethanol increased initially with increase in yeast concentration till it reached a maximum value of 26.20 ± 1.05 % at an optimum yeast concentration of 6 %. On exceeding 6 % optimum concentration of yeast, the bioethanol yield decreased and this may be due to the fact that at very high yeast concentration, the cells grow rapidly resulting in rapid consumption of the glucose and a reduced yield of bioethanol (Umeuzuegbu, 2022).

Optimization of pH

The result of the effect of pH on bioethanol yield is shown in Table 5 below which revealed that bioethanol yield increased with increase in pH till it attained the maximum value of 30.50 ± .0.77 % at an optimum pH of 5.5 when it started to decrease as the pH increased further. The optimum pH for bioethanol production using *saccharomyces cerevisiae* has been reported to be 4.0 to 5.5. On exceeding pH of 5.5, the yeast is denatured and the catalytic activities reduced which results to the decrease in the bioethanol production (Umeuzuegbu, 2022).

Optimization of Fermentation Temperature

The result of the effect of temperature on the yield of bioethanol is as shown in Table 6 which revealed that bioethanol yield increased with increase in fermentation temperature until it attained the maximum value of 37.15 ±1.08 % at optimum temperature of 35 ^{o}C. On exceeding the optimum temperature, the bioethanol yield decreased. One of the characteristics of microorganism is that temperature has a stimulating effect on them over narrow range (Umeuzuegbu, 2022). According to Egbosiuba *et al*., (2014) high fermentation temperature above 40 ^{o}C could lead to the death yeast of cells which enhances reduction in their activity thereby decreasing the yield of bioethanol produced while lower temperature slows them down. The results are similar to that obtained by Duhan *et al* (2013) who studied the effect of temperature on bioethanol yield and obtained maximum yield at 35 ^{o}C.

Optimization of Fermentation Time

The result obtained is presented in Table 7 which showed that bioethanol yield increased with increase in fermentation time until it attained the highest value of 44.67±0.82 % at an optimum time of 3 days. On exceeding the optimum fermentation time, the bioethanol yield started decreasing. The optimum time of 3 days is similar to the result obtained by Phisalaphong *et al* (2006).

Table 4: Bioethanol Yield Banana Peel Hydrolysate at Different Concentration of Yeast

Yeast extract %	Bioethanol yield %
2	23.64 ±0.77
4	24.70 ±0.72
6	26.20 ±1.05
8	24.60 ±0.74
10	22.46 ±0.75

Table 5: Bioethanol Yield from Banana Peel Hydrolysate at Different pH

pH	Bioethanol yield
4.0	27.09±0.77
4.5	28.14 ±0.91
5.0	29.30 ±1.01
5.5	30.50 ±0.77
6.0	26.73 ±0.75

Table 6: Bioethanol Yield from Banana Peel Hydrolysate at Different Fermentation Temperature

Temperature (°C)	Bioethanol yield %
20	34.23 ± 0.92
25	34.28 ± 0.94
30	35.06 ± 1.04
35	37.15 ± 1.08
40	35.27 ± 0.95

Table 7: Bioethanol Yield from Banana Peel Hydrolysate at Different Fermentation Time

Time (days)	Bioethanol Yield
1	39.14±0.93
2	40.19±0.88
3	44.67±0.82
4	42.21±0.83
5	40.23±1.06

Physicochemical Properties of Banana Peel Bioethanol

The physicochemical properties o the bioethanol produced were compared with American Society for Testing and Materials and the result presented in Table 8. From the result, the density of bioethanol produced is 0.79±0.04 which is within the ASTM standard limit for bioethanol. Density is the ratio of mass to volume of the fuel which greatly affects the ignition quality of the fuel. It has significant impact on the fuel consumption as the fuel introduced into the combustion chamber is determined numerically (Umeuzuegbu, 2022).

Viscosity is another very important property of fuel. The biofuel should neither be too viscous nor too thin. The kinematic viscosity of the bioethanol produced was determines as 1.41± 0.57 mm^2/s and is therefore within ASTM limit. High kinematic viscosity of biofuels results in poor atomization and incomplete combustion which gives rise to cocking of injector tops (Umeuzuegbu, 2022) on the other hand, very low viscosity fuel produces very subtle spray which cannot be properly transferred into the combustion chamber thereby forming a fuel rich zone that give rise to sooth formation (Ezekwe & Ajiwe, 2014).

Flash point measures the degree of flammability of the fuel and the flash point value of 13.7± 1.51 °C obtained from the bioethanol produced is within the ASTM limit. The pH value of 7.33± 0.05 obtained is within the ASTM limit of bioethanol. The neutral pH implies that the bioethanol produced is of good quality. According to Okoh (2021), bioethanol with pH below 6.5 may contribute to failure in fuel pump and fuel injector as a result of corrosion while pH above 9.0 may negatively impact the plastic parts in the system. The water content of the produced bioethanol is 1.2 ± 1.26 % which is within the ASTM Standard limit for bioethanol. High water content predisposes the oxidation of the fuel as well as being the major cause of corrosion in storage tanks when stored for a very long period. The water content obtained therefore has little or no effect on the degradation of the fuel or on the corrosion in the tanks during storage. The boiling point of bioethanol was evaluated as 78.65± 0.47 °C when is within ASTM Standard for bioethanol. Refractive index indicates the state of purity of a substance. The refractive index of bioethanol produced is 1.36± 0.01 °C and is within the ASTM Standard.

Table 8: Physicochemical Properties of Bioethanol Produced from Banana Peels Compared to ASTM Standard

Parameter	Unit	Banana Peel	ASTM Standard
pH		7.33±0.05	6.5-9.0
Density	glcm^3	0.79±0.04	0.794
Refractive index	(°C)	1.362±0.01	1.357 – 1.44
Boiling point	(°C)	78.65±0.47	78.5
Kinematic viscosity	(mm^2/s)	1.41±0.57	1.2 – 1.5
Flash Point	(°C)	13.7±1.51	<14
Water content	(°C)	1.21±1.26	0-3

CONCLUSION

This study focused on the pretreatment and hydrolysis of banana peels to produced glucose and subsequent fermentation of the sugar to bioethanol. The result obtained for hydrolysis and fermentation process indicated that acid concentration, temperature, and time of hydrolysis affects the optimum yield of glucose significantly as the yield of 42.13± 0.92 % was obtained at optimum factor condition of 2.0 % acid concentration temperature of 116 °C an time of 25 minutes while the maximum bioethanol yield of 44.68± 0.08 % was obtained at optimal factor condition of 6 % yeast concentration, pH of 5.5, 35 °C temperature and 3 days fermentation time. Also, the physicochemical properties of bioethanol produced when compared to ASTM standard specification for bioethanol were all within limits. This demonstrates that banana peel wastes can be converted into value added and eco-friendly product such as bioethanol through hydrolysis and fermentation process. This will offer better waste management process options thereby solving the problem of waste disposal and mitigating of environmental pollution challenge.

RECOMMENDATION

Biomass wastes such as banana peels are rich in fermentable sugars and are in abundance in Nigeria. They are renewable sources hence bioethanol production from them holds tremendous potential in terms of meeting the energy needs and promoting environmental benefits. It is recommended that the use of these wastes as alternative sources of producing bioethanol should be encouraged to help alleviate the problem of waste disposal and environmental pollution thereby boosting the economy of Nigeria.

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Full Length Research Paper

ANTICORROSION AND DISPERSIVE ADSORPTION STUDIES OF *Berchemia discolor* ON MILD STEEL IN ACIDIC MEDIA

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ABSTRACT

Corrosion is the deterioration or destruction of metals and alloys in the presence of an environment by chemical or electrochemical means. This study investigates the corrosion inhibition of mild steel in 1.0 M H_2SO_4 media using extract of *Berchemia discolor* and this was studied using gravimetric and gasometric methods. The weight loss of the metal was observed to increase with increase in immersion time and decrease with increase in the concentration of the inhibitors in acid system. The percentage inhibition efficiency decreased with time but increased with increasing inhibitor concentration for inhibitor-acid system with the highest inhibition efficiency obtained for gravimetric study being 71.43%. This conforms to earlier findings that corrosion occurs with time and further connote the inhibitive ability of the plant extract in the acidic media. A linear plot of Log (W_o/W_f) against time showed that the corrosion inhibition process was of the first order kinetics. From the result gotten from the gasometric analysis, the volume of hydrogen evolution was seen to reduce as the extract concentration increased but increased with increase in temperature, this proves the plant to be a good corrosion inhibitor. The plant extract was seen to have a maximum inhibition efficiency of 90.76 %, the mechanism of adsorption obeyed the Langmuir, Freundlich and Temkin isotherm which is evident in its straight-line plot, at lower temperature Langmuir isotherm was best fit while at higher temperature it fitted more to the Temkin isotherm. From the thermodynamic study, the higher values of activation energy (E_a) in the presence of the inhibitor compared to the blank (80.52 KJ/mol) proves the mechanism to be a physical adsorption mechanism, negative values of heat of adsorption (Q_{ads}) is evident that the reaction was exothermic, negative values of Gibbs free energy less than -20 KJ/mol further confirm the adsorption mechanism to be physisorption. The methanolic leaf extract of *Berchemia discolor* was seen to be a good corrosion inhibitor.

Keywords: Corrosion Inhibition-Adsorption- *Berchemia discolor* -Gasometric-Gravimetric

INTRODUCTION

Corrosion processes are responsible for numerous losses mainly in the industrial scope. It is clear that the best way to combat it is prevention. Among the various methods to avoid or prevent destruction or degradation of metal surface, the corrosion inhibitor is one of the best know methods of corrosion protection and one of the most useful on the industry. This method is following stand up due to low cost and practice method. Important researches have been conducted with government investment mainly in large areas such as development construction of new pipelines for shale gas and growth in construction (Al-Otaibi *et al*., 2012). The focus of these researches has been the inhibitors applications in water and concrete for the protection of metals (Al-Otaibi *et al*., 2012b).

Corrosion is a costly and life-threatening problem in any industry. Wherever there is a metal, the potential for a corrosive reaction exists. It is a natural part of nature and there is no escaping it. Corrosion of metals can be slowed down, managed or even stopped by the use of proper technique (Satya *et al.,* 2012; Fetouh *et al.,* 2014; Zhang *et al.*, 2012).

Corrosion is caused through chemical interactions between metal and goes in the surrounding environment. Metals deterioration can be reduced by removing the metal or by changing the type of environment. Methods to reduce the Sulphur, chloride or oxygen content in the surrounding environment can limit the speed of metal corrosion (Ofoma *et al.,* 2018; Singh *et al.,* 2016).

Cathodic protection involves converting unwanted anodic (active) sites on a metal's surface to cathodic (passive) sites through the application of an opposing current. The opposing current supplies free electrons and force local anodes to be polarized to the potential of the local cathodes. The introduction of galvanic anodes also known as sacrificial system is a form of cathodic protection which uses metal anodes, introduced to the electrolytic environment to sacrifice themselves (corrode) in order to protect the cathode. The second method is the impressed current protection. It requires an alternative source of direct electrical current to be supplied to the electrolyte and is often used to protect buried pipeline and ship hulls (Ofoma *et al.,* 2018).

Monitoring of surface is important in the protection of metals against deterioration against corrosion. The elimination of vulnerable surface condition, proper monitoring and ensuring that a corrosive agent is not used in the maintenance and cleaning of metal parts are necessary for effective corrosion reduction. Also, change to the type of metal being used can lead to effective reduction to corrosion (Ofoma *et al.,* 2018; Umeron *et al.*, 2016).

A corrosion inhibitor is a substance that when added in a small concentration to an environment reduces the corrosion rate of a metal exposed to that environment. Inhibitors often play an important role in the oil extraction and processing industries where they have always been considered to be the first line of defense against corrosion (Obi-Egbedi *et al.,* 2012).

Berchemia discolor is a shrub or a tree 3-20 m high; with a straight bowl; rough, dark grey bark that flakes longitudinally; dense, rounded crown; slash yellow; young branches conspicuously lenticellate; branchlets glabrous to densely pubescent with short, spreading, whitish hairs. Leaves alternate or sub-opposite, entirely or obscurely crenate, shiny above, dull and glaucous below, broadly elliptic or ovate, obtuse or acute at the apex, rounded or cuneate at the base; leaf stalks glabrous or pubescent, 1-1.8 cm long. The local names include:

Amharic (jejeba); English (mountain date, bird plum, brown ivory, dog plum, wild almond); Lozi (mukumba,muzinzila); Nyanja (mziyi,mtacha); Somali (deen); Swahili (mnago); Tigrigna (aba).

Plate 1: Leaves of *Berchemia discolor*

Taxonomical Classification

Kingdom	*Plantae*
Order	*Rhamnales*
Family	*Rhamnaceae*
Phylum	*Magnoliophyta*
Class	*Magnoliopsida*
Genus	*Berchemia*
Species	*Berchemia discolor*

METHODS

Materials and Equipment

The materials and equipment that were used to carry out the analysis were; Methanol, Acetone, Sulphuric acid (H_2SO_4), Mild steel coupons, Distilled water, Water, Ice block, *Berchemia discolor* Leaves, Volumetric flask (1000 ml and 100 ml), Beakers (100 ml and 250 ml), Funnel, Wash bottle, Sieve, Emery paper (sand paper320, 800 cm), Water bath, Bristle brush, Weighing balance, Measuring cylinder, Thread, Foil.

Materials Collection, Preparation and Identification

The leaves of *Berchemia discolor* were collected within the environment of ABSU in Isuikwuato L.G.A of Abia state, Nigeria. The leaves were identified by Dr. Mrs. Mary Iwuagwu of the department of Plant Science and Biotechnology, Abia State University, Uturu. The leaves were air dried in the Laboratory under room temperature away from direct sunlight. The leaves were pulverized using a mechanical grinder to fine powder. The pulverized leaves materials were stored in an air tight container. The resins were extracted using modified Harborne Method. 100 g of the pulverized leave were soaked with 750 ml of methanol, it was allowed to stay for 48 hours, with intermediate shaking every 3 hours, the solution was filtered. The filtrate was distilled in a water bath at 60 °C and allowed to stay for 48 hours. Stock acid solution of 1 M H_2SO_4 was prepared using conc 1 M H_2SO_4 (analytical grade). The distilled methanol plant extract (1.0 g) was dissolved in 1000 ml of 1 M H_2SO_4 and left to stand for 24 hours while shaken at intervals. The resultant solution was filtered and stored in a 1.0 L volumetric flask each. Similarly, 2.0 g, 3.0 g, 4.0 g and 5.0g of the leaf extracts were dissolved in 1000 ml of the 1 M H_2SO_4. These solutions were then used to test the inhibitive power of the plant.

Preparation of Mild Steel Coupons

The mild steel coupons used in this work were obtained from Urata market, Aba in Abia State, Nigeria. They were mechanically cut into 5.0 x 1.5 x 0.07 cm^2. The surfaces of the mild steel coupons were polished with fine grade emery paper (Grit size 320 and 800). The polished coupons were then washed thoroughly with distilled water, degreased with methanol, dried with acetone. The dried coupons were weighed using a digital Atom 2.0 weighing balance. The weights were recorded as the initial weights. The weighed coupons were used for the gravimetric (Weight loss) and gasometric analysis.

Phytochemical Screening

The plant extracts were assessed for presence of the phytochemical composition by using the following standard methods.

Test for Alkaloids

A 100 mg of an extract was dissolved in dilute hydrochloric acid and filtered. The filtrate was tested with Dragendroff's reagents. Formation of reddish-brown precipitation indicated the presence of alkaloids (Njoku *et al.*, 2014; Papoola *et al.*, 2013).

Test for Saponins

0.5 g of methanol extract was mixed with 5 ml of distilled water in a water bath for 10 minutes. The mixture was filtered while hot and allowed to cool. 1 ml of the filtrate was diluted to 5 ml with 4 ml distilled water and shaken vigorously for 2 minutes. Appearance of frothing indicated the presence of saponin in the filtrate (Njoku *et al.*, 2014).

Test for Terpenoids

2 milliliters chloroform was added to the extract and mixed well. 3 milliliters Conc H_2SO_4 was carefully added to the mixture to form two layers. A red-brown colour at the interface of the layers was an indication of the presence of terpenoids.

Test for Phenols

1 ml of 70% acetone was added to 1 ml of extracts to a final concentration of 50 mg/ml. A few drops of 10% ethanolic ferric chloride solution were added to 1 ml of this mixture. A colour change to blue green/dark blue was indicative of the presence of phenolic compound

Test for Flavonoids

1.0 g of the extract was treated with dilute NaOH, followed by addition of dilute HCl. A yellow solution with NaOH which turns colourless with dilute HCl indicated the presence of flavonoid (Njoku *et al.*, 2014).

Test for Tannin

10% alcoholic ferric chloride was added to 2-3 ml of methanolic extract (1:1). Dark blue or greenish grey coloration of the solution indicated the presence of tannin (Obi-Egbedi *et al.*, 2012; Njoku *et al.*, 2014).

EXPERIMENTAL

The weighed mild steel coupons were suspended in beakers containing 100 ml of the test solution at ambient temperature. The mild steel coupons were dipped completely into the test solutions and retrieved every 1 hours for 1-5 hours. The retrieved coupons were washed, scrubbed with bristle brush under fast flowing water, degreased in methanol, dried using acetone, re-weighed and re-immersed in the corrodent. The weight loss of the mild steel was evaluated in grams as the difference in the initial and final weight of the coupons and also the average of the weight loss was taken due to the triplicate immersion. The experiment was carried out for the *Berchemia discolor* leaves extract using concentrations of 1.0 g/L, 2.0 g/L, 3.0 g/L, 4.0 g/L, and 5.0 g/L at ambient temperature. As corrosion occurred on the coupons coupons, there was a reduction in the weight of the coupon and this reduction is directly related to the corrosion rate.

From the weight loss data, the corrosion rates (CR) were calculated using equation 1 (Okafor *et al.,* 2012).

$$\mathrm{CR} = \frac{\mathrm{W.L}}{\mathrm{At}} \qquad (1)$$

Where W.L. is weight loss in mg, A is the metal surface area and t, the time of immersion in hours. From corrosion rate, the surface coverage (ϴ) as a result of adsorption of inhibitor molecules and inhibition efficiencies of the plant extracts (I%) were determined using equation 2 and 3 (Obike *et al*., 2016).

$$\Theta = \left[\frac{\mathrm{CR_{blank}} - \mathrm{CR_{Inh}}}{\mathrm{CR_{blank}}}\right] \qquad (2)$$

$$\%\,\mathrm{I} = \left[\frac{\mathrm{CR_{blank}} - \mathrm{CR_{Inh}}}{\mathrm{CR_{blank}}}\right] \times 100 \qquad (3)$$

Where $\mathrm{CR_{blank}}$ and $\mathrm{CR_{inh}}$ are the corrosion rates in the absence and presence of the plant extracts respectively.

In the present study of mild steel in 1 M H_2SO_4 solution, a plot of the logarithm of the initial weight of the mild steel coupon divided by the weight after post treatment against immersion time was used to know the order of reaction (Obike *et al*., 2016; Roy e*t al*., 2014).

$$Log\left(\frac{wo}{wf}\right) = \mathrm{kt} \qquad (4)$$

Where W_o and W_f are weight in grams before and after post treatment of the mild steel coupons respectively, k is the rate constant obtained from the slope of the graph and t is the time in hours.

From the rate constant values, the half-life values $t_{1/2}$ of the metal in the test solutions were calculated using the equation: (Obike *et al*., 2016).

$$T_{1/2} = \frac{0.693}{K} \qquad (5)$$

Gasometric Method (Hydrogen Evolution Technique)

The gasometric technique was conducted using a gasometric assembly consisting of a reaction chamber, connected to burette that contained paraffin oil through a reservoir. In determining the rate of hydrogen evolution per surface area, the contribution of other gases, including water vapour at higher temperature is assumed to be insignificant. In the gasometric measurements the volume of hydrogen evolved was determined following procedures previously described (Okafor *et al.,* 2012; Obike *et al.,* 2016). 100 ml of the corrodent (acidic test solution) was introduced into the reaction chamber, connected to a burette through a delivery tube. A mild steel coupon was dropped into the acidic test solution in the chamber and the reaction vessel was quickly closed to avoid any escape of hydrogen gas. The volume of the hydrogen gas evolved from the reaction was monitored by the depression (in ml) in the level of paraffin oil. This depression in the paraffin oil level was recorded every minute for 15 minutes at 303 ^{o}K. The same experiment was repeated in the presence of the inhibitor, *Berchemia discolor* (BD) leaves extract, with concentrations 1.0 g/L, 2.0 g/L, 3.0 g/L, 4.0 g/L and 5.0 g/L. the same procedure was repeated at elevated temperature of 333 ^{o}K. The rate of evolution of hydrogen gas (R_H) was determined from the slope of the graph of volume of the hydrogen gas evolved (VHE) against time (t) and the inhibitors efficiencies (IE%) determined using equation

$$IE = \frac{Rb - Ri}{Rb} \times 100 \qquad 6$$

Where R_b and R_i are corrosion rates of mild steel without and with inhibitors respectively.

RESULTS AND DISCUSSION

Phytochemical Screening

Researches have shown that the inhibitory action of some natural plant products is due to the presence of organic compounds or phytochemicals such as flavonoids and alkaloids. Some of these compounds are present in the leaves extract of *Berchemia discolor* which was revealed by the phytochemical screening of the plant. However, the number of phytochemical constituents adsorbed onto the metal surface from the plant extract increased as the inhibitor concentration was increased, this shows that inhibitor efficiency increased at higher concentration. The phytochemical screening of the plant extract shows the presence of alkaloids, tannins, flavonoids, saponins, terpenoids and phenols as shown in Table 1.

Weight Loss Result

Figures 1 and 2 shows the plot of weight loss against time and plot of Inhibition efficiency against concentration respectively.

The weight loss was observed to increase with increase in immersion time and decrease with increase in the concentration of the inhibitors in acid system. The inhibition efficiency increased with increasing inhibitor concentration for inhibitor-acid system with maximum inhibition efficiency of 71.43%. The results show that the leaf extract effectively restrained the acid corrosion of mild steel in the acid environments and that increased adsorption and consequently an increasing surface coverage of the inhibitor molecules on the metal surface may occur with increasing inhibitor concentration.

Table 1: Qualitative analysis of *Berchemia discolor* leaves extract

Phytoconstituents	Results
Alkaloids	+ve+
Flavonoids	+ve++
Tannins	+ve++
Terpenoids	+ve+
Saponins	+ve++
Phenols	+ve+

Key: (+) indicate presence: (-) indicate absence: (++) indicates moderately present.

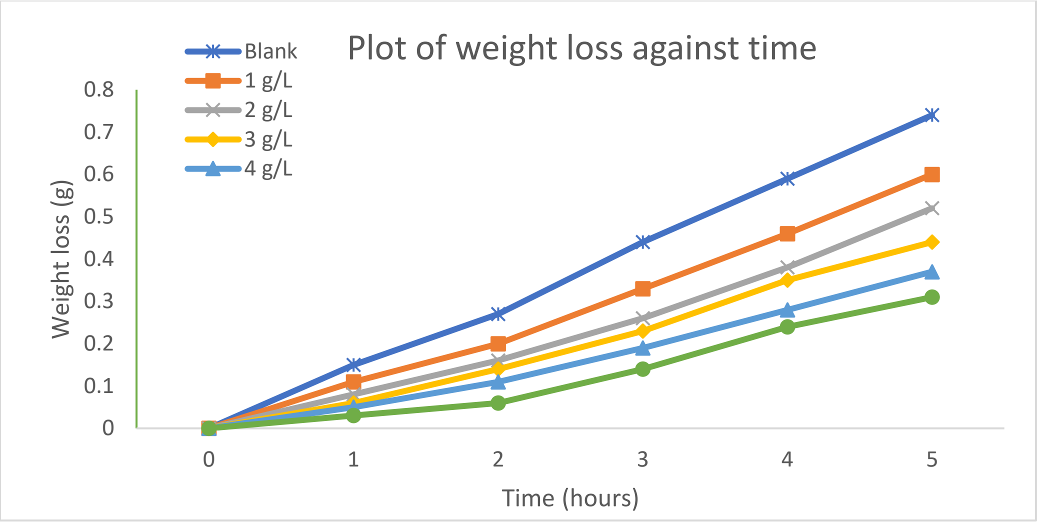

Fig 1 Weight loss against time of *Berchemia discolor* in 1.0 M H_2SO_4

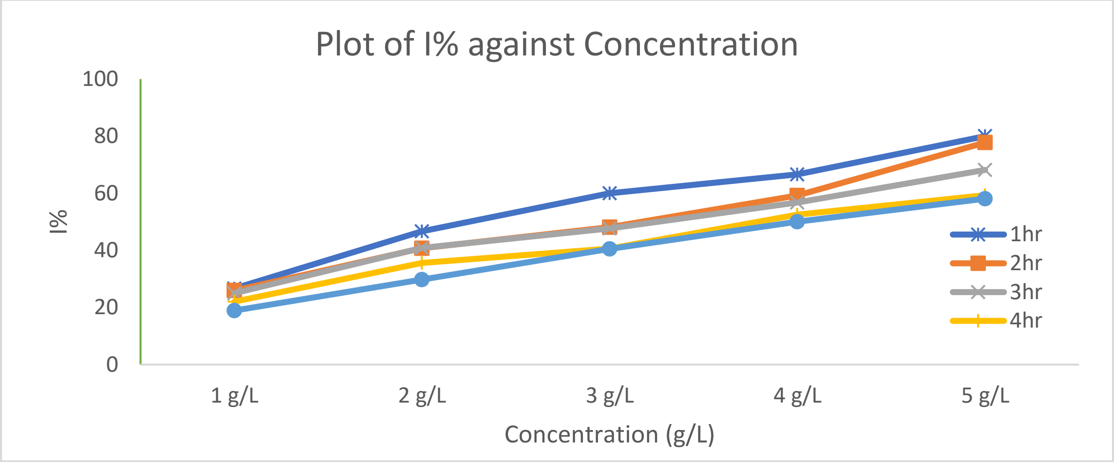

Fig 2: I% against extract concentration of *Berchemia discolor* in 1.0 M H_2SO_4

This similar trend was recorded by Hammouti *et al.*, 2014 and Obike *et al.*, 2012 in their studies. From the plots in Fig 1 and 2 respectively, it was observed that the weight loss decreased with increase in the concentration of the extract and increased with increase in time, the inhibition efficiency was also seen to increase with increase in concentration and decreased with time of immersion, this proved the inhibitive ability of the plant extract in 1 M H_2SO_4 acid solution.

Effect of Corrosion Rate on Time and Extract Concentration

The rate of corrosion was deduced from the result of the weight loss and displayed in fig 3. The plot in fig 3 showed that the corrosion rate relatively decreased with increase in extract concentration and increased with time. This could be attributed to the fact that as the time passes on, the stability of adsorbed film decreases and results in desorption to attain the equilibrium (Sethuraman and Raja, 2008) and that the increase in the concentration of the extract improves the corrosion inhibition potentials.

Kinetics Consideration

The plot of log (W_o/W_f) against Time (hours) for the leaf extract is shown in Figure 4. This plot ascertains that the inhibition efficiency is of the first order reaction. The K, $t_{1/2}$ and R_2 are shown respectively in Table 2.

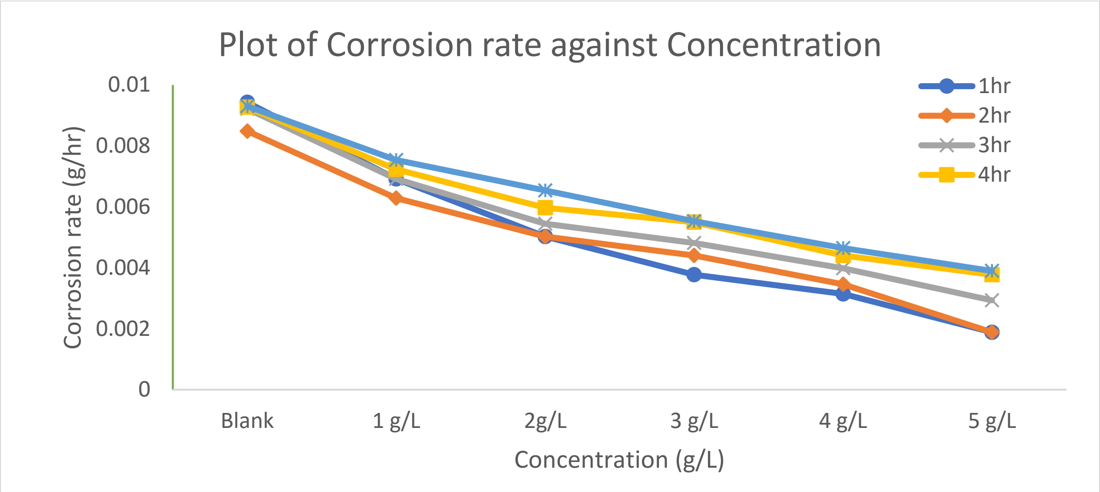

Fig 3: Corrosion rate against extract concentration of *Berchemia discolor* in 1.0 M H_2SO_4

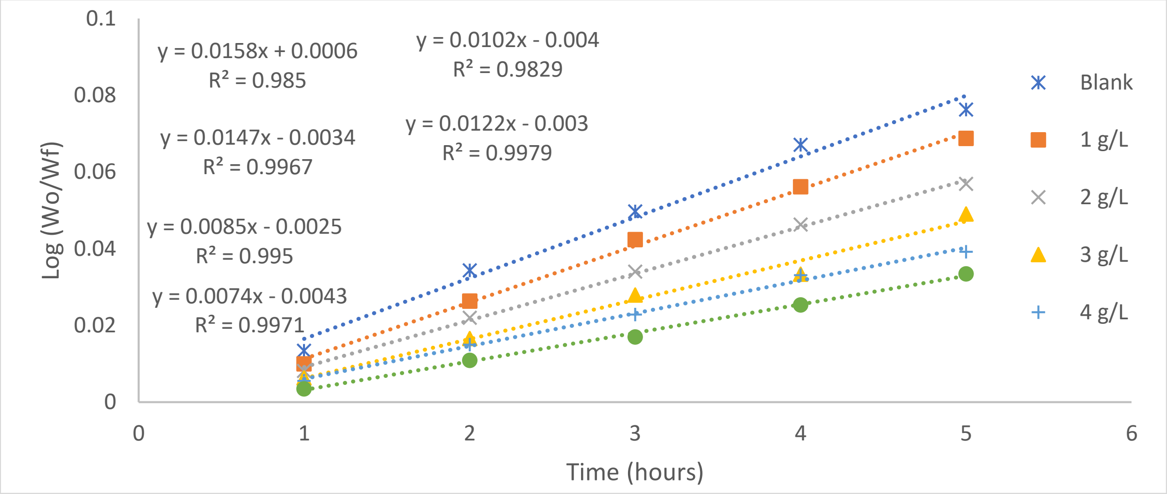

Fig 4: First order kinetics plot for extract of *Berchemia discolor* in 1.0 M H_2SO_4

Table 2: Values of rate constant, half-life and the coefficient of correlation of extract of *Berchemia discolor* in 1 M H_2SO_4

	K	$t^1/_2$	R^2
Blank	0.0158	43.86076	0.9850
1.0 g/L	0.0147	47.14286	0.9967
2.0 g/L	0.0122	56.80328	0.9979
3.0 g/L	0.0102	67.94118	0.9829
4.0 g/L	0.0085	81.52941	0.9950
5.0 g/L	0.0074	93.64865	0.9971

This linear plot represents the first order kinetics. The rate constants (k) gotten from the slope of the plots were used to calculate the half-life $(t_{1/2})$ and the half-life was seen to increase with increase in extract concentration, this showed that with increase in the concentration of the extract, it will take a longer time for the metal to corrode, further proving the inhibitive ability of the plant extract. The R^2 values obtained from the plots were very close to unity and this shows that the data fitted to the first order kinetics.

Gasometric Result

The hydrogen evolution technique was employed to access the inhibition efficiency of the plant extracts at elevated temperatures and to obtain some thermodynamic data. The acid corrosion of mild steel is characterized by evolution of hydrogen and the rate of corrosion is proportional to the amount of hydrogen gas evolved (Okafor *et al.*, 2012; Obike *et al.*, 2017). The volume of hydrogen gas evolved from cathodic sites during corrosion of mild steel immersed in 1.0 M H_2SO_4 solution in the absence and presence of *Berchemia discolor* extracts was assessed and measured with time at different temperatures of 303 °K and 333 °K, The plot of hydrogen volume per time for mild steel corrosion in 1.0 M H_2SO_4 solution without and with different concentrations of *Berchemia discolor* extracts are shown in figure 5 and 6 for test carried out at 30 °C and 60 °C respectively. The results reveal an increase in the volume of hydrogen gas evolved with time and a reduction in the volume of hydrogen gas as the plant extracts concentration increased in the solutions at both temperatures studied, the rate of evolution of the hydrogen gas was determined from slope of the linear plot of the graph of volume of hydrogen gas evolved against time.

From the slope of the volume of hydrogen evolved with time we were able to calculate the rate of hydrogen evolution with time, surface coverage and inhibition efficiency (I%) and these values are tabulated in Table 3 below;

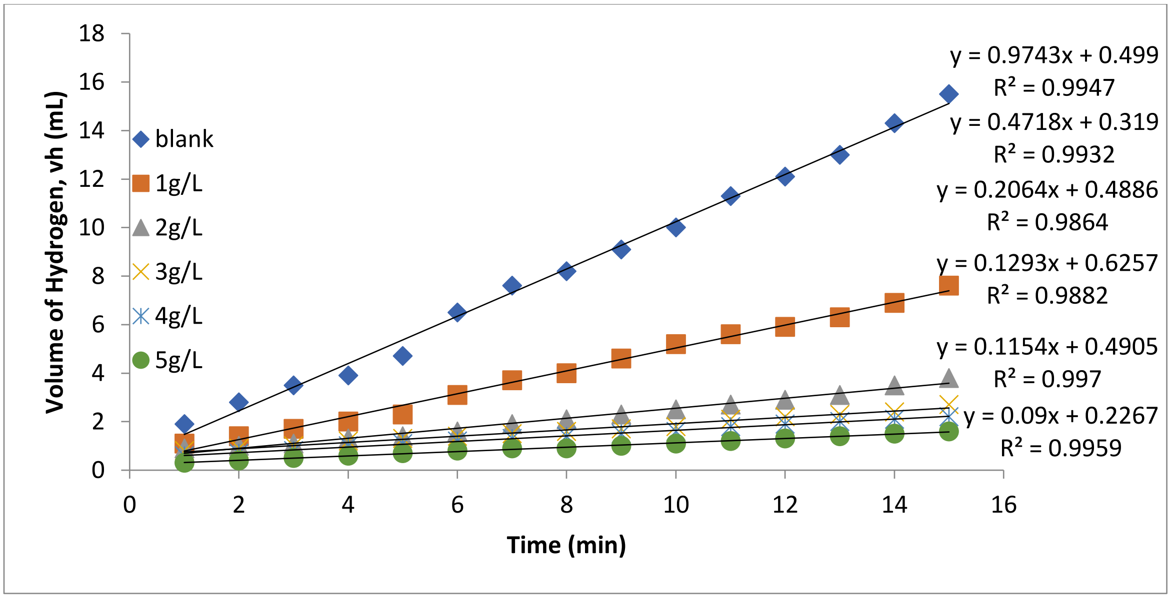

Fig 5: Variation of hydrogen evolved with time for corrosion of mild steel in 1.0 M H_2SO_4 solution of different concentration of *Berchemia discolor* extract at 303 °K

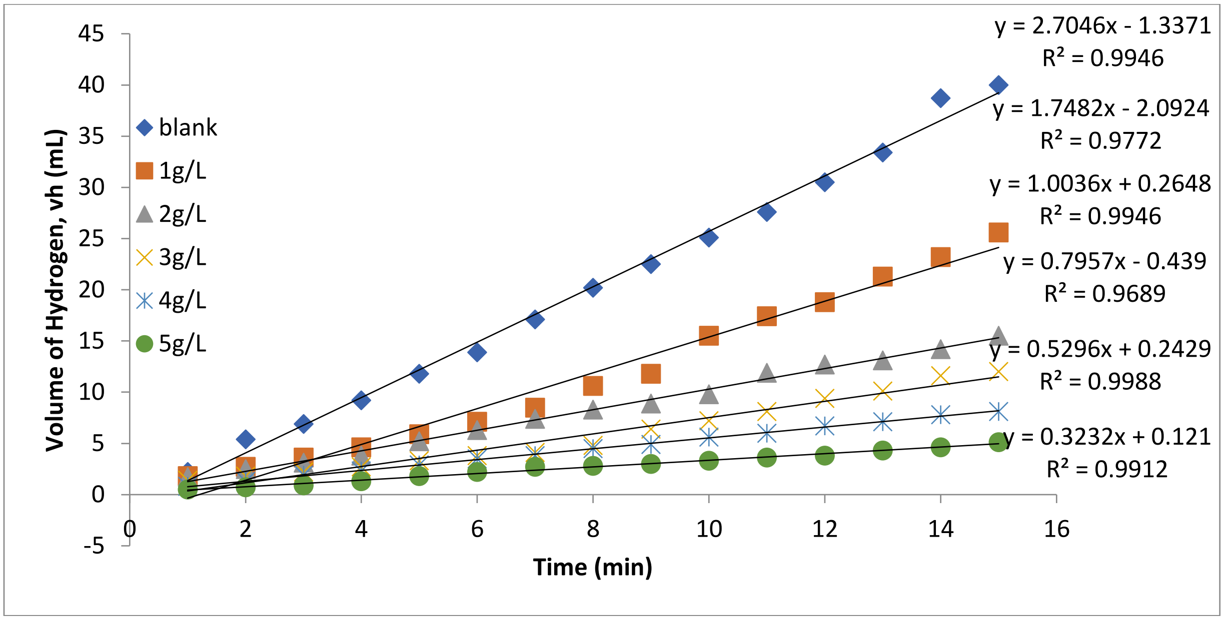

Fig 6: Variation of hydrogen evolved with time for corrosion of mild steel in 1.0 M H_2SO_4 solution of different concentration of *Berchemia discolor* extract at 333 °K.

Table 3: Gasometric data of rate of hydrogen evolution (cm^3/min), surface coverage and inhibition efficiency (I%) for mild steel coupon in 1.0 M H_2SO_4 solution containing different concentration of extracts of B.D at 303 °K and 333 °K.

Acid Media	**Concentration**	**CR (cm^3/min)**	**Θ**	**I.E (I%)**
H_2SO_4 (303 °K)	Blank	0.974	0	0
	1g/L	0.472	0.516	51.575
	2g/L	0.206	0.788	78.816
	3g/L	0.129	0.867	86.729
	4g/L	0.115	0.882	88.156
	5g/L	0.090	0.908	90.763
H_2SO_4 (333 °K)	Blank	2.705	0	0
	1g/L	1.748	0.354	35.362
	2g/L	1.004	0.629	62.893
	3g/L	0.796	0.706	70.580
	4g/L	0.530	0.804	80.419
	5g/L	0.323	0.881	88.050

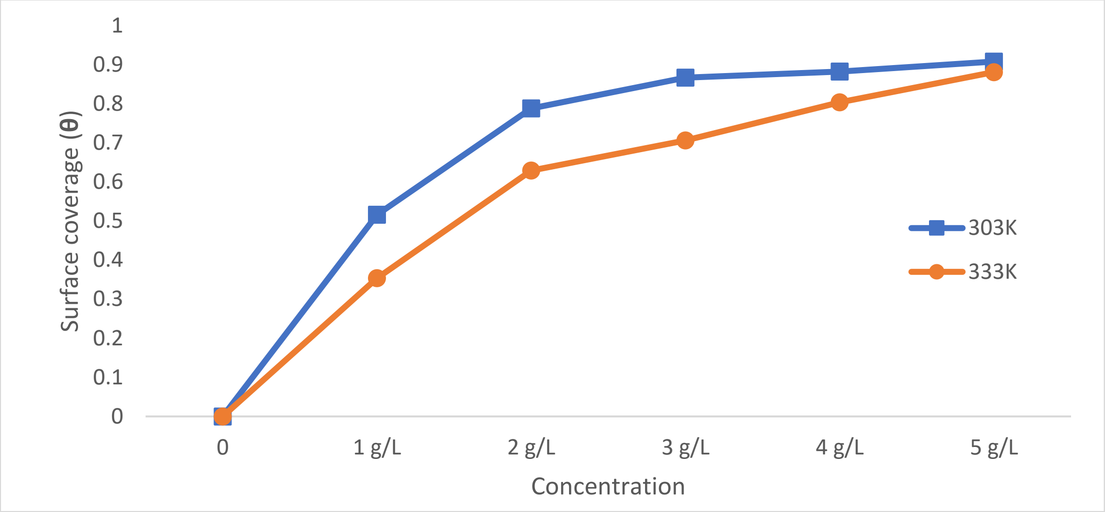

Fig 7: Variation of surface coverage with extract concentration for mild steel in 1.0 M H_2SO_4 solutions containing *Berchemia discolor* at 303 ºK and 333 ºK.

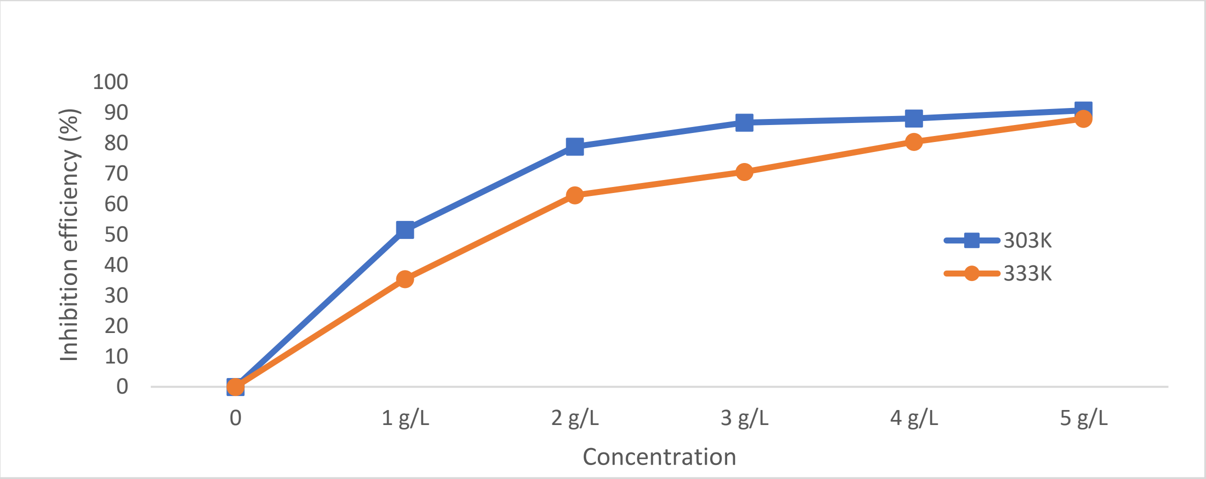

Fig 8: Variation of Inhibition efficiency with extract concentration for mild steel in 1.0 M H_2SO_4 solutions containing *Berchemia discolor* at 303 ºK and 333 ºK.

From the values of the rate of hydrogen evolution against time which was obtained from gradient of linear portion of the graph of volume of hydrogen gas evolved versus time and displayed in Fig 5 and 6 for the acidic solution at 30 ^{o}C and 60 ^{o}C respectively, it was observed that the rate of hydrogen evolution reduced with increase in the concentration of *Berchemia discolor* plant extract and increased with temperature for 1.0 M H_2SO_4 acidic medium studied, this collaborates the results gotten from previous researches (Obike *et al.*, 2017; Samuel *et al.*, 2015; Pavithra *et al.*, 2013) and further proves the plant extract to be a good corrosion inhibitor. Also, from the plots of Surface coverage against concentration and inhibition efficiency against concentration shown in fig 7 and 8 respectively, the surface coverage was seen to increase with increase in concentration of the inhibitor. This implies that the corrosion of the metal has been inhibited and large fraction of the surface is covered against acid with an increase in plant extracts concentration. Similar trend was observed for inhibition efficiency where the inhibition efficiency of *Berchemia discolor* plant extract in H_2SO_4 solution increased with increase in extract concentration at both temperatures. There was a reduction in inhibition efficiency as the temperature rise to 333 ^oK for *Berchemia discolor* extract in the acid solutions suggesting physical adsorption (Okafor *et al.*, 2012; Obike *et al.*, 2012; Hammouti *et al.*, 2014).

Adsorption Isotherms

The inhibitive action of organic compounds in plant extracts is generally related to adsorption of inhibitor on the surface of the metal and subsequent formation of layer of insoluble complex on the metal surface. The adsorbed layer acts as a barrier for mass and charge transfer leading to a reduction in the rate of corrosion of the metal (Okafor *et al.*, 2012). Adsorption isotherms provides information on the relationship between the amount of inhibitor adsorbed per unit area of the metal surface and the concentration of the inhibitor molecule in the solution at a given temperature. To describe the adsorption characteristics of the plant extracts, the most frequently used adsorption isotherms which were used in the present study are Langmuir, Freundlich and Temkin adsorption isotherms.

Langmuir Adsorption Isotherm: Langmuir model assumes that adsorption occur on specific homogenous sites on the metal surface with formation of a monolayer. It relates the concentration of the bulk of the electrolyte to the degree of surface coverage. If a plot of C/θ versus C gives a straight line, then Langmuir assumption is obeyed.

Temkin Adsorption Isotherm: Temkin shows the relationship between concentrations of the inhibitor to the degree of surface coverage. The plots for Temkin isotherm shown in Fig 10 show a linear graph and describe the adsorption characteristics of the extract of *Berchemia discolor* in 1.0 M H_2SO_4 acid solution (Samuel *et al.*, 2015).

Freundlich Adsorption Isotherm: Freundlich is an adsorption isotherm that shows the empirical relation between the concentrations of a solute on the surface of an adsorbent to the concentration of the solute in the liquid with which it is in contact (Okafor *et al.*, 2012).

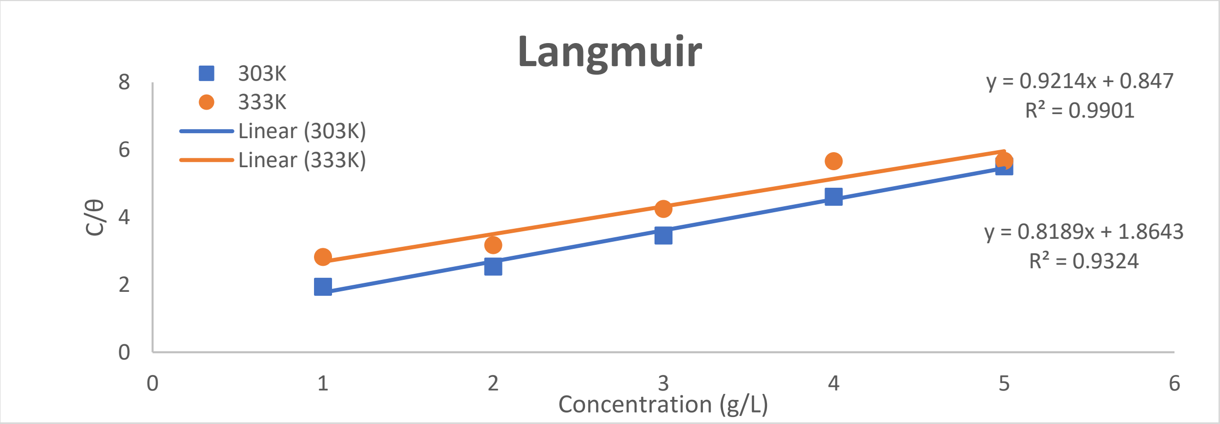

Fig 9: Langmuir Adsorption Isotherm plot for *Berchemia discolor* extracts in 1.0 M H_2SO_4

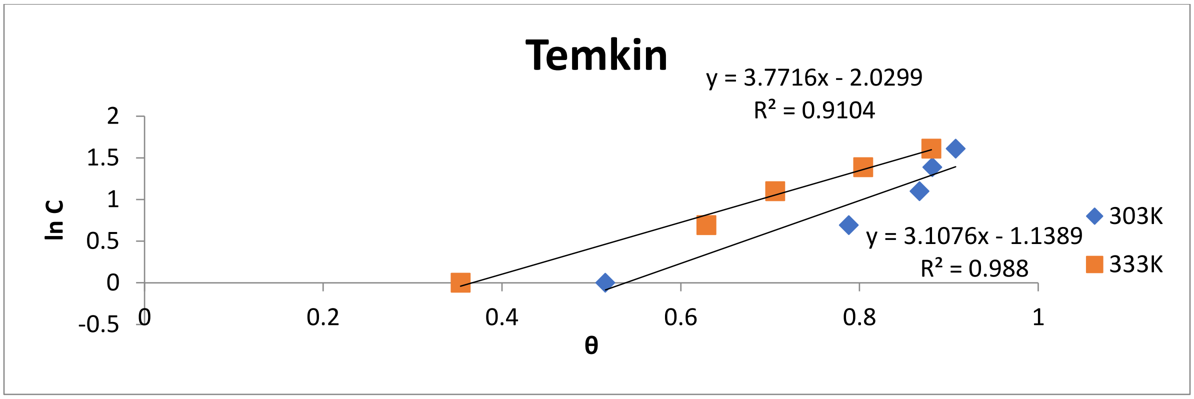

Fig 10: Temkin adsorption isotherm plot for *Berchemia discolor* extracts in 1.0 M H_2SO_4

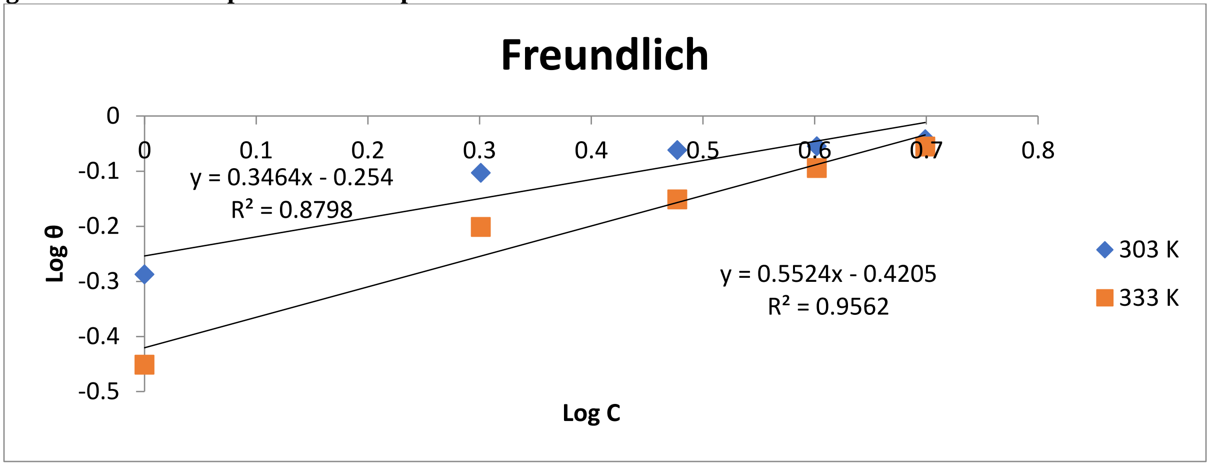

Fig 11: Freundlich adsorption isotherm plot for *Berchemia discolor* extracts in 1.0 M H_2SO_4

Table 4: Adsorption Parameters of *Berchemia discolor* on mild steel in 1.0 M H_2SO_4 solution

				30 °C					
Inhibitor solution	**Langmuir**			**Freundlich**			**Temkin**		
	Constant (K_{ads})	**ΔG^o_{ads} (KJ/mol)**	**R^2**	**Constant (K_{ads})**	**ΔG^o_{ads} (KJ/mol)**	**R^2**	**Constant (K_{ads})**	**ΔG^o_{ads} (KJ/mol)**	**R^2**
BD-H_2SO_4	1.181	-10.536	0.990	0.557	-8.645	0.880	0.584	-8.762	0.910
				60 °C					
BD-H_2SO_4	0.536	-8.549	0.932	0.379	-7.676	0.956	0.693	-9.195	0.988

From the Langmuir, Freundlich and Temkin isotherms, linear plots were obtained and the correlation coefficients close to unity suggests that the adsorption followed Langmuir, Freundlich and Temkin isotherms. However, a comparison of correlation coefficients of the three studied adsorption isotherms showed that the data fitted more to Langmuir at lower temperature and temkin at higher temperature. The values of K_{ads} from Langmuir and Freundlich were seen to decrease as the temperature rises from 303 °K to 333 °K. The temkin isotherm assumes that heat of adsorption decreases linearly with increasing surface coverage and that adsorption is characterized by a uniform distribution of binding energy. The increase in the value of K_{ads} in temkin with increasing temperature points to the fact that the inhibitors were physically adsorbed on the surface of the mild steel.

Thermodynamic Studies

The activation energies (E_a) for the corrosion process in the absence and presence of sample extracts were calculated from condense Arrhenius equation and the heat of adsorption (Q_{ads}) for BD in H_2SO_4 solution and presented in Table 5.

Table 5: Calculated values of the activation energy and heat of adsorption for mild steel coupons in 1.0 M H_2SO_4 containing *Berchemia discolor* extracts.

Inhibitor Concentration	Activation Energy, E_a(KJ/mol)	Average E_a(KJ/mol)	Heat of Adsorption, Q_{ads}(KJ/mol)
Blank	80.52		----
1g/L BD+H_2SO_4	103.29	118.46	-18.63
2g/L BD+H_2SO_4	124.73		-21.99
3g/L BD+H_2SO_4	143.30		-28.03
4g/L BD+H_2SO_4	120.17		-16.63
5g/L BD+H_2SO_4	100.82		-8.05

The average activation energy was above 80 KJ/mol in H_2SO_4 acidic medium which is suggestive of chemical adsorption, however, the data obtained showed that the values of the average activation energies (E_a) in the presence of the plant extract in the acidic solutions (118.46 KJ/mol) was higher than the blank (80.52 KJ/mol), the values of activation energy obtained in the presence of the inhibitor being more than the blank is suggestive of a physical adsorption mechanism or physisorption, contrasting the earlier suggested chemical adsorption.

The values of heat of adsorption (Q_{ads}) of extracts of BD on mild steel was calculated and presented in Table 4.7. It can be deduced from the table that the values of heat of adsorption (Q_{ads}) were negative in the acidic medium signifying that the adsorption of the plant extract inhibitor was an exothermic process (Obike *et al.,* 2017). The exothermic process implies either physical or chemical adsorption and is distinguished by considering the absolute value of heat of adsorption. Energy values more than 40 KJ/mol is suggestive of Chemical adsorption (Obike *et al.,* 2017). The absolute values of the heat of adsorption are below 40 KJ/mol which further suggests physical adsorption of the plant extracts on mild steel surface in the acidic media (Ofoma *et al.,* 2018).

It is the view of well-known authors (Ofoma *et al.,* 2018; Samuel *et al.,* 2015; Obike *et al.,* 2017) that the adsorption of organic inhibitor molecules is often a displacement reaction involving the removal of adsorbed water molecules from the metal surface. The equilibrium constant of adsorption K_{ads}, obtained from the intercept of the Langmuir and Freundlich graph was seen to reduce as the temperature increased which further proved the reaction to be exothermic, and this rate constant was used in calculating Gibbs free energy of adsorption (ΔG^o_{ads}) which was tabulated in Table 4.6. The results showed a negative value, indicating that the inhibitor adsorption of *Berchemia discolor* on the mild steel surface is a spontaneous exothermic adsorption process (Ofoma *et al.,* 2018). Though the values obtained for ΔG^o_{ads} were all negative in all cases and less than -20 KJ/mol which are consistent with physisorption reflecting physical adsorption for the *Berchemia discolor* inhibitor, this further correlates the finding of the activation energies (E_a) being higher than the blank, and further proves the reaction to be a physical adsorption mechanism (Ofoma *et al.*, 2018; Okafor *et al.*, 2010).

RESEARCH FINDINGS

Based on the results of gravimetric and gasometric measurements at different temperatures, the following have been drawn from this study:

- The leaves extract of *Berchemia discolor* was found to be an effective inhibitor for corrosion of mild steel in acidic solution.
- The data obtained shows that its inhibitive activity is dependent on the concentration of the extract inhibitor.
- The inhibition potential of the extracts was attributed to the adsorption of phytochemical constituents on the mild steel surface by blockage of its active sites.
- Inhibition efficiency of the extracts increased with increase in inhibitor concentration in the acidic system and decreased with increase in time of immersion. Inhibition efficiency decreased with rise in temperature, this showed that temperature affects inhibition efficiency.
- A closer observation of the close values of rate constant (k) confirmed first order reaction kinetics.
- Thermodynamic study carried out reveals the inhibition process to be Physical adsorption.
- The result of the heat of adsorption of the extract on mild steel proves the reaction to be an exothermic process showing that heat was released.
- The value of heat of adsorption Q_{ads}, obtained for 303 ^oK and 333 ^oK are all negative indicating that the inhibitor is strongly adsorbed on the mild steel surface and that the adsorption process is spontaneous.
- In general, the acidic corrosion of mild steel was reduced upon the addition of an appropriate concentration of *Berchemia discolor* extracts.

CONCLUSION

Berchemia discolor (BD) extract, proved to inhibit the corrosion of mild steel in 1 M H_2SO_4 acid solution. BD maximum efficiency was observed to be 71.43% at a time interval of 1 hour in the corrosive media with concentration 5.0g/L for weight loss investigation. The trend of the inhibition efficiency increased with increase in the concentration of the extracts and decreased with the increase in time. A linear plot of Log (W_o/W_f) against time was obtained. The linear plot showed that the corrosion inhibition process was of the first order kinetics. The rate constants (k) were gotten from the slope of the plots and they were used to calculate the half-life ($t_{1/2}$). The $t_{1/2}$ were seen to increase with increase in the concentration of the extract. From the result gotten from the gasometric analysis, the volume of hydrogen evolution was seen to reduce as the extract concentration increased but increased with increase in temperature, this proves the plant to be a good corrosion inhibitor, the mechanism of adsorption obeyed the Langmuir, freundlich and temkin isotherm which is evident in its straight line plot, at lower temperature Langmuir isotherm was best fit while at higher temperature it fitted more to the temkin isotherm. From the thermodynamic study, the higher values of activation energy (E_a) in the presence of the inhibitor compared to the blank (80.52 KJ/mol) proves the mechanism to be a physical adsorption mechanism, negative values of heat of adsorption (Q_{ads}) is evident that the reaction was exothermic, negative values of gibbs free energy less than -20 KJ/mol further confirm the adsorption mechanism to be physisorption. The findings generally proves that plant extract of *Berchemia discolor* functioned as a good and efficient corrosion inhibitor.

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Conference Proceedings

Full Length Research Paper

REMEDIATION OF Pb^{2+}, Cd^{2+} AND Zn^{2+} POLLUTED WATER BY ADSORPTION ONTO CARBONISED *Chrysophyllum albidum* SEED SHELL

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ABSTRACT

Heavy metal contaminations of water bodies by human activities have been confirmed to exert significant role in the environment because of expanding risk factor such contamination can cause. In this study, batch adsorption method is adopted to removed Pb^{2+}, Cd^{2+} and Zn^{2+} from aqueous solution using *Chrysophyllum albidum* seed shell. The adsorption data reflected strong dependency of the adsorption on pH, temperature, and initial metal ion concentration. The adsorption of the three metal ions proceeded through physical adsorption mechanism and the trend was supported by maximum adsorption capacity values of Pb(II), Cd(II) and Zn(II) ions was 0.0613, 0.0678 and 0.0720 mg/g) respectively and free energy change data parameters. The adsorption was spontaneous and best fitted was in this decreasing order: Temkin> Langmuir > Dubinin-radushkevich > Freundlich adsorption models. Results of the present investigation revealed that *Chrysophyllum albidum* seed shell is an excellent adsorbent for lead, cadmium and zinc ions.

Key Words: Remediation, waste water, heavy metals, sorption, *Chrysophyllum albidum*

INTRODUCTION

The presence of heavy metals ions in the environment has significant impact because of their toxicity and subsequent consequences (Eddy *et* al., 2004). Unfortunately, heavy metal generation and discharge to the environment is growing proportionally with increasing urbanization, industrialization, agricultural practices and other anthropogenic activities (Guyo *et al*., 2015). Heavy metals are those metals whose density is greater than 5 g/cm^3 and they include the cadmium, mercury, lead, nickel, iron, zinc, selenium and others. Unique property of these metals is that they are toxic above certain concentration Okoyeagu *et al*., 2020).

Cadmium, lead and zinc exist as divalent heavy metals whose toxicity regime has been widely reported. For example, cadmium ion accounted for the popular itai ita diseases that recorded global toxicity signal. Cadmium ion can replace calcium ion in bone, teeth and other organs and can lead to softening of bones and kidney failure (Fu and Wang, 2011). Lead ion exert its toxic effect on the blood and can manifest its taxological signs and symptoms in the central nervous system and the gastrointestinal tract disorder (Amadi *et al*., 2020). Chronic exposure to lead ion above 1 mg/L has been confirm to be precursor for mental retardation, birth defects, psychosis, autism, allergies, dyslexia, weight loss, hyperactivity, paralysis, muscular weakness, brain damage, kidney damage and eventual death (Martin & Griswold, 2009).

In view of the known and established toxicity of most heavy metals in the environment, some conventional methods such as ion exchange, filtration, chemical precipitation, complexation, adsorption, electrodeposition and reverse osmosis, etc has been designed and implemented as technologies for the removal of heavy metal ions from the environment (Anwar, *et al*., 2010; Panida *et al*., 2014). Both natural and synthetic adsorbents have been studied by various researchers for the removal of heavy metal ions from dilute solutions (Panida *et al*., 2014).

However, the use of plant materials has been linked to ecofriendliness and optimum efficiency. The use of plant waste has given hope toward effective waste management. For example, Essien and Eddy (2015) reported the effectiveness of Sorghum waste (from Champion brewery industry) for the adsortion of some heavy metals. Similar findings have been reported by Amadi *et al*., (2019) for the removal of nickel, cadmium and lead ions from aqueous solution using *Calopogonus mucunoides* seed pod. The seeds of *Chrysophyllum albidum* are normally wasted and may attract disposal problem in some cases. Therefore, adoption of effective remediation plan towards the control of these heavy metal ions in industrial and other effluent is essential. However, the potential of the seed as adsorbent for the removal of heavy metals from aqueous solution has not been widely investigated. Therefore, the present study is aimed at using *Chrysophyllum albidum* seed shell as an adsorbent for the removal of heavy metal from aqueous solution.

MATERIALS AND METHODS

All the reagents used were of analytical grades from Sigma-Aldrich and were used without further purification. Double de-ionized water was used in the preparation of all sample solutions. 1000 mg/L solutions of lead, cadmium and nickel were prepared as stock solutions from their salts $Pb(NO_3)_2$, $CdSO_4.8H_2O$ and $Zn(NO_3)_2$ respectively.

Preparation of the adsorbent

Samples of *C. albidum* seed shell were obtained from Michael Okpara University of Agriculture Umudike, Abia state Nigeria. The shells were carefully removed, washed with de-ionized water, dried, carbonised in furnace at 550 ^{0}C and crushed to powder form using a blender. The carbonised adsorbent was then stored in a tight plastic container ready for use.

Batch Adsorption Experiments

Batch adsorption experiments were carried out by agitating the 250 mL volumetric flasks containing 0.08 g adsorbent and 20.0 cm^3 solution of the metal ions on a rotary shaker at 150 rpm for 60 min. The effect of solution pH on the adsorption of the metal ions was studied at a fixed temperature of 30 ºC and at an initial metal ion concentration of 50 mg/L. The adsorption was carried out using varying pH of the solution ranging from pH 2 to pH 8. This was done by introducing 20 cm^3 of each metal ion solution into different 250 cm^3 Erlenmeyer flasks and the pH of the solutions adjusted to pHs of 2, 4, 6, 7 and 8 and thereafter 0.08 g of the adsorbent was added. The mixtures were agitated intermittently for 1 h in a rotary shaker and then filtered. Influence of temperature was investigated by keeping other factors constant except temperature (303 K (30°C), 313 K (40°C), 323 K (50°C), 333 K (60°C) and 343 K (70°C)). Batch adsorption experiment carried out by varying the initial concentration of the respective heavy metal ions at constant temperature, pH, contact time and adsorbent dosage was used to study the effect of initial heavy metal ion concentration. In each case, the percentage of heavy metal ion removed from the solution through adsorption was calculated using equation 1 while the equilibrium amount of metal ions adsorbed was calculated using equation 2

$$\%R = \frac{C_0 - C_e}{C_0} \times \frac{100}{1} \qquad (1)$$

$$q_e = \frac{C_0 - C_e}{C_0} \times \frac{v}{m} \qquad (2)$$

where C_0 is the initial concentration of the metal ion, C_e is the equilibrium concentration, V is the volume of solution and m is the mass of the adsorbent. Concentration of metal ions in solution was analysed using UNICAM (Solar AAS 500) atomic absorption spectrophotometer. Calibration curves were prepared separately for zinc, cadmium and lead respectively. Each solution containing the respective metal ion was aspirated into the spectrophotometer. Concentration of the respective metal ion was determined through extrapolation after the absorbance has been read from the spectrophotometer.

RESULTS AND DISCUSSION

Figure 1 shows the influence of pH on biosorption capacity of Pb(II), Cd(II) and Zn(II) ions on aqueous solution. It is indicated that % removal of Pb(II), Cd(II) and Zn(II) ions reached a maximum in a slight acidic medium and decreased in slight basic medium. The % removal of Pb(II), Cd(II) and Zn(II) ions increased from 94.0%, 96.78% and 94.26% respectively at pH 3 to maximum, 95.35%, 99.48% and 98.32% at pH 6. While decreased slightly with increasing the pH values to 8. Therefore, further adsorption experiments were performed at pH 6 as an optimum pH value. It was found from our study that the predominant species of Pb(II), Cd(II) and Zn(II) ions occurred at pH 6 in agreement with Heidari's report (Heidari *et al.*, 2013). However, in presence of high concentration of H^+ ions at pH 3, hydroxonium ions H_3O^+ ions would compete with Pb(II), Cd(II) and Zn(II) ions for the binding sites, leading to lower the % removal of these metal ions. While decreasing the concentration of H_3O^+ ions at pH 6 leads to decrease the positive charge on the surface of adsorbent which lower the electrostatic repulsion between the surface of adsorbent and metal ions hence increased %removal to 95.35%, 99.48% and 98.32%. A similar trend was previously reported by the adsorption of Pb(II), Cd(II) and Zn(II) ions reached maximum biosorption at pH 5.5 using chemically modified orange peel (Feng *et al.*, 2011) On the other hand, increasing the pH to 8 would increase the concentration of OH^- ions leading to the formation of the predominant species of $Pb(OH)_2$, $Cd(OH)_2$ and $Zn(OH)_2$ (Giraldol, *et al.*, 2008).

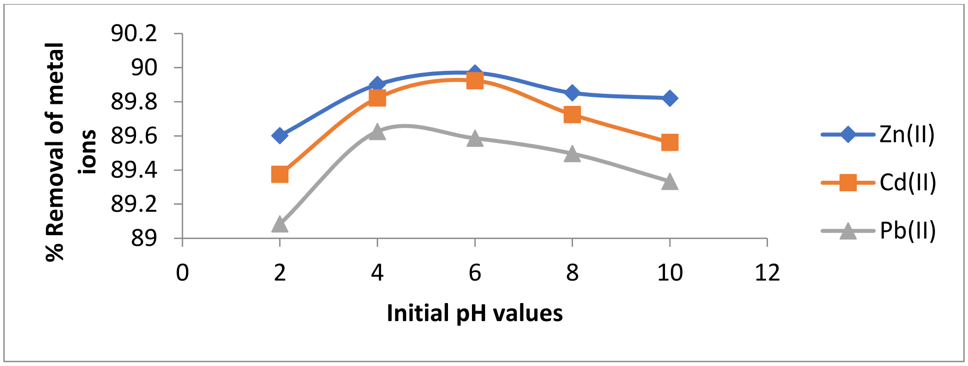

Figure 1: Effect of pH on sorption of the metal ions onto the adsorbent.

Effect of *initial metal ion concentration* on the adsorption of the metal ion

The removal percentage of Zn (II) ions decreased from 98.58 % at 10 mg/L to 95.67% at 50 mg/L as seen from Figure 2. For Cd (II) the removal percentage decreased from 98.06 % at 10 mg/L to 95.03% at 50 mg/L metal ion concentration. Moreover, for Pb(II) ions, the removal percentage decreased from 97.48 to 94.58 %. Occurrence of more unoccupied surface binding sites on the adsorbent at low concentration of metal ions could possibly be responsible for higher removal efficiency at low concentration. But as the concentration increased, the number of ions competing for available binding sites on the adsorbent increased and hence the adsorption of metal ions decreased (Shoaib *et al*., 2013).

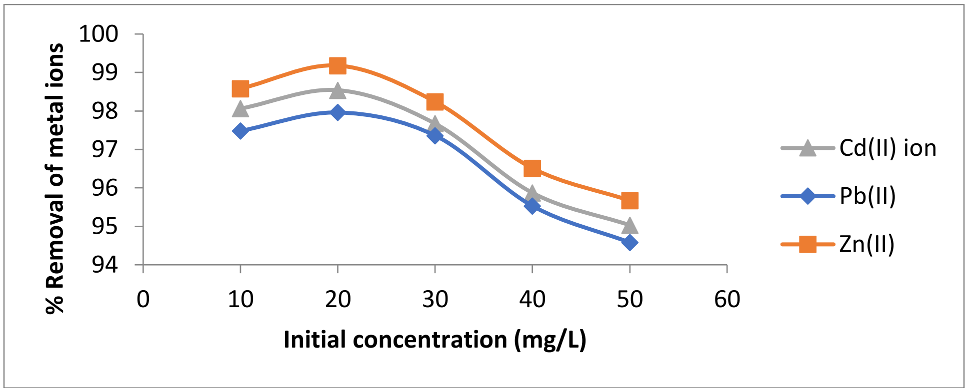

Figure 2: Effect of initial metal ion on the adsorption of metal ions onto the adsorbent

Equilibrium Isotherm Modelling.

Adsorption properties and equilibrium parameters, commonly known as adsorption Isotherms, describe how the adsorbate interact with adsorbents and comprehensive understanding of the nature of interaction. Isotherm helps to provide information about the optimum use of adsorbents. **Langmuir Isotherm model**

Langmuir I. (1918) proposed a theory to describe the adsorption of gas molecules onto metal surface. The Isotherm equation assumes that adsorption takes place at specific homogenous sites within the adsorbent. It further assumes that once a metal ion occupies a site, no further adsorption can take place at the site. Moreover, the Langmuir equation is based on the assumption of a structurally homogenous adsorbent where all sorption sites are identical and energetically equivalent. Therefore, a saturation value reached beyond which no further sorption can take place. The saturated or monolayer capacity can be represented by the expression:

$$\frac{Ce}{qe} = \frac{1}{Qob} + \frac{Ce}{Qo} \qquad (1)$$

Where Q_o is a constant which signifies the adsorption of the monolayer capacity of the adsorbent (mg g^{-1}). b is the Langmuir constant related to the adsorption energy (dm^3 mg^{-1}).The plot of Ce/qe vs Ce gives a straight line and from the intercept and slope of such plot, constants Q_o and b were evaluated. A dimensionless equilibrium parameter, R_L can express the essential characteristics of Langmuir Isotherm.

$$R_L = \frac{1}{1+bCo} \qquad (2)$$

The value of R_L indicate the type of Isotherm to be either irreversible ($R_L = 0$) favorable ($0< R_L <1$); linear ($R_L =1$); or unfavorable ($R_L >1$). The correlation coefficients of the model were all greater than 0.9, showing good fitting trends. The Langmuir isothermic model showed that the saturated monolayer adsorption of Zn(II) was higher than that of Cd(II) and Pb(II), demonstrating that Zn(II) ions were better adsorbed onto the adsorbent surface. For the initial of the metal ions concentration of 50 mgL^{-1}, the RL values negative, indicating that the metal ions adsorption onto the adsorbent are not favorable under the studied conditions.

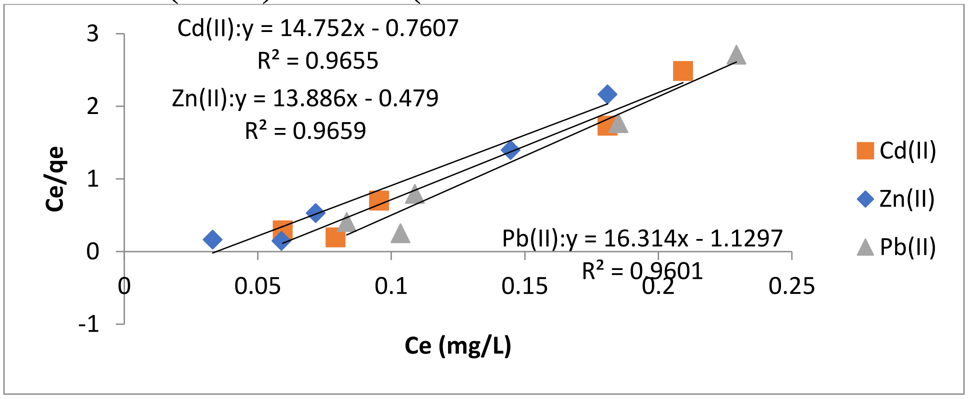

Figure 3. Langmuir isotherm plot of Ce/qe vs Ce for the adsorption of the metal ions.

Table 1: Langmuir Isotherm constants and correlation coefficients (R^2 values) for sorption of Cd (II), Pb (II) and Zn (II) ions by carbonized *Chrysophyllum Albidum* seed shell.

	Metal ions		
Constants	Pb (II)	Cd (II)	Zn (II)
b (L/mg)	-14.440	-19.389	-28.996
Q_o (mg/g)	0.0613	0.0678	0.072
R_L	-0.00139	-0.00103	-0.00069
R^2	0.9601	0.9655	0.9659

Freundlich Isotherm model

The Freundlich sorption isotherm, one of the most widely used mathematical descriptions, usually fits the experimental data over a wide range of concentrations. This isotherm gave an expression encompassing the surface heterogeneity and the exponential distribution of active sites and their energies. The well-known logarithmic form of the Freundlich isotherm is given by the following equation (Mohan and Singh, 2002):

: $\log q_e = \log K_F + 1/n \log C_e$ (3)

where Kf is a constant related to adsorption capacity (mgg^{-1}) and 1/*n* is an empirical parameter related to adsorption intensity. Kf and 1/n are determined by the adsorbent properties. The value of 1/*n* varies with the sorbent heterogeneity and provides a criterion for determining the favourability of the adsorption process. There are four possible values for 1/*n* (Mckay *et al.*, 1982): (i) for favorable adsorption, 0 < 1/*n* < 1 (ii) for unfavorable adsorption, 1/*n* > 1 (iii) for linear adsorption 1/*n* = 1 (iv) for irreversible adsorption 1/*n* = 0. The 1/*n* values, calculated using the Freundlich isothermic model, were > 1.5, which suggested the unfavourability of the adsorption process.

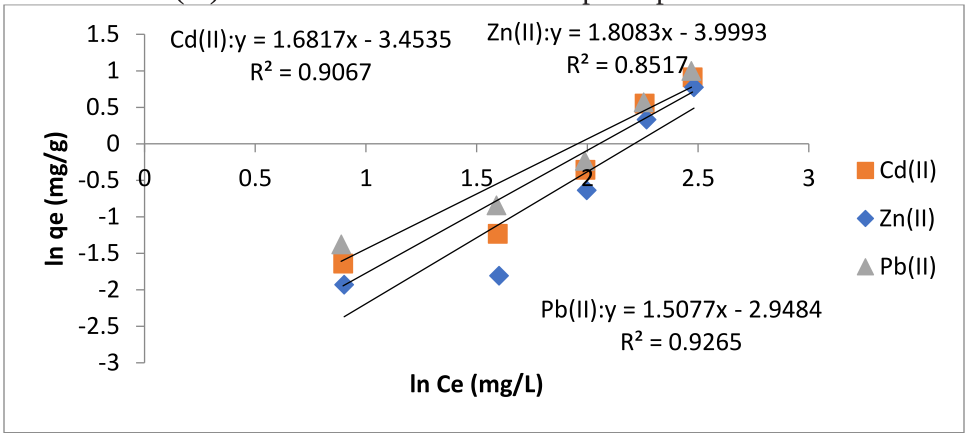

Figure 4.: Freundlich isotherm plot of Ln qe vs Ln Ce for the adsorption of the metal ions.

Table 2: Freundlich Isotherm constants for adsorption of Cd (II), Pb (II) and Zn (II) ions by the adsorbent.

	Metal ions		
Constants	Pb (II)	Cd (II)	Zn (II)
K_f (Lg $^{-1}$)	0.0524	0.0316	0.0183
1/n	1.5077	1.6817	1.8083
N	0.6633	0.5946	0.5530
R^2	0.9265	0.9067	0.8517

Dubinin-Radushkevich Isotherm model

The Dubinin-Radushkevich (D-R) isotherm model describes the adsorption on a single uniform pore. The D-R model was applied the equilibrium data to assess the nature of the adsorption process, i.e; whether it is physical or chemical adsorption. The Dubinin-Radushkevich isotherm is generally expressed as follows (Subha R *et al.*, 2009):

$qe = q_D \, e^{-} \; B_D \varepsilon 2$ (5)

The linear form of D-R Isotherm equation is represented as:

$Lnqe = In\ q_D - B\varepsilon^2$ (6)

$\varepsilon = RT\ In\ (1+ \frac{10}{Ce})$ (7)

Where q_D is the theoretical saturation capacity (mol/g), B is is a constant related to the mean free energy of adsorption per mole of the adsorbate (mol^2/J^2), E is the Polanyi, R = 8.314(J/mol/K) is the gas constant and T (K) is the absolute temperature. The D-R constants q_o and B were calculated from the linear plot of Inqe versus ε ^{2} Figure 4 and the results are given in Table 1. The constant B gives an idea about the mean free energy E (KJ/mol) of adsorption per molecule of the absorbate when it is transferred to the surface of the solid from infinity in the solution and can be calculated from the following relationship.

$E = \frac{1}{\sqrt{2B}}$ (8)

The adsorption process is physisorption when the energy of activation is 5 to 40 kJ/mol and chemisorptions when the energy of activation is 40 to 800 kJ/mol (Arh-Hwang Chen *et al.*, 2009) From Table 1, it was suggested that the adsorption of the metal ions by the adsorbent is physisorption in nature. D-R isotherm describes the experimental data properly because of the good correlation coefficient.

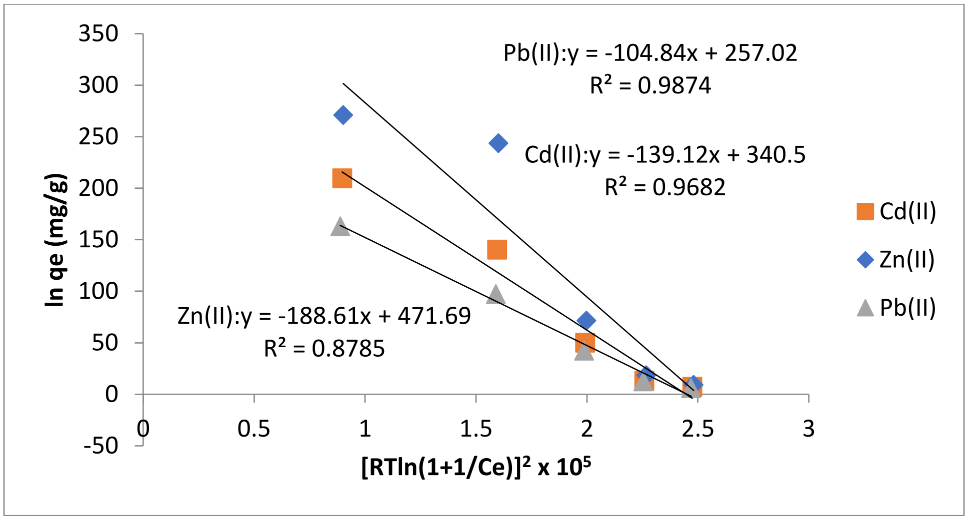

Figure 6: DRK plots of metal ions

Table 3: Dubinin-Radushkevich Isotherm constants for adsorption of Pb (II), Zn (II) and Cd (II) ions

	Metal ions		
Constants	Pb(II) (II)	Cd (II)	Zn (II)
Lnq (mgg^{-1})	257.02	340.50	471.69
B_n (mol^{2}KJ^{-2})	104.84	139.12	188.61
E_n (kJ mol^{-1})	0.0691	0.05995	0.0515
R^2	0.9874	0.9682	0.8783

It is known that magnitude of apparent adsorption energy E is useful for estimating the type of adsorption and if this value is below 8 kJ/mol the adsorption type can be explained by physical adsorption, between 8 and 16 kJ/mol the adsorption type can be explained by ion exchange, and over 16 kJ/mol the adsorption type can be explained by a stronger chemical adsorption than ion exchange (Wang et al., 2004). As shown in Table 1, the E value are 0.0515 for Zn(II), , 0.0600 for Cd(II), and 0.0691 kJ/mol for Pb(II) ions on the adsorbent.

Temkin isotherm model

The derivation of the Temkin isotherm assumes that the fall in heat of sorption is linear rather than loganthmic, as implied in the Freundlich equation. The Temkin isotherm has commonly been applied in the following form (Wang *et al.*, 2005).

$q_e = RT/b\ln(AC_e)$ 8

The Temkin isotherm equation (8) can be simplified to the following equation

$q_e = \beta \ln \propto + \beta \text{ In } C_e$ 9

A plot of q_e /s In C_e gives a straight line (Figure 5) with a slope of β and intercept of $\beta \ln \propto$. The parameters $\propto$ and β were given in Table 1 Where $\beta = (RT)/b$, T is the absolute temperature in Kelvin and R is the universal gas constant 8.314J (molK)$^{-1}$. The constant b is related to the heat of adsorption. Examination of the data shows that the Temkin isotherm fitted well with Pb(II), Zn(II) and Cd(II) ions adsorption for the carbonized *Chrysophyllum albidum* seed shell. The correlation coefficient R^2 obtained from Temkin model were comparable to that obtained for Langmuir and Freundlich equations, which explains the applicability of Tempkin model to the adsorption of Pb(II), Zn(II) and Cd(II) ions onto carbonized *Chrysophyllum Albidum* seed shell.

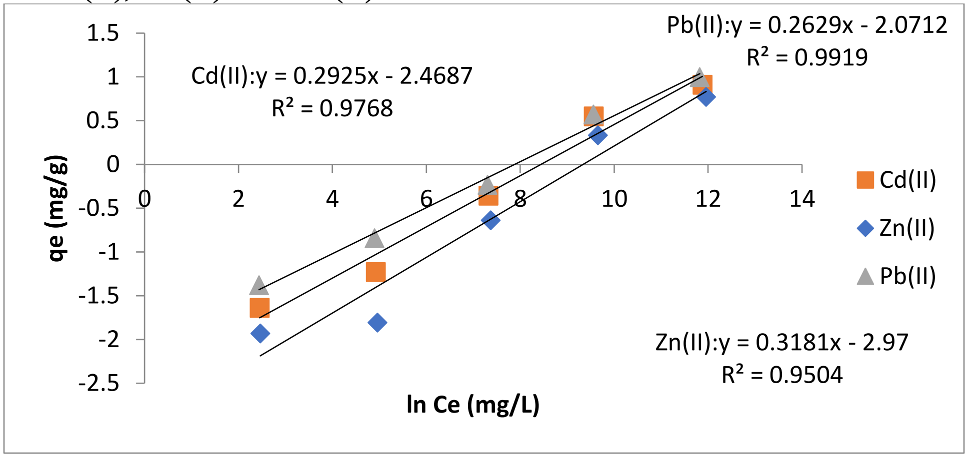

Figure.5: Temkin isotherm plot of qe vs Ln Ce for the adsorption of the metal ions.

Table 5: Temkin Isotherm constants for adsorption of Pb (II), Zn (II) and Cd II)

	Metal ions		
Constants	Pb (II)	Cd (II)	Zn (II)
∝ **(Lg^{-1})**	37.89 x 10^{-5}	21.61 x 10^{-5}	8.81 x 10^{-5}
β **(mg L^{-1})**	0.2629	0.2925	0.3189
B	9582.13	8612.45	7919.34
R^2	0.9919	0.9768	0.9504

CONCLUSION

The study investigates the potential of carbonized *Chrysophyllum Albidum* seed shell in removing four heavy metal ions: Pb(II), Cd(II), (II), Zn(II) ions from aqueous solutions. The influences of metal ions concentration, temperature and pH were examined. The equilibrium experimental data were tested with four different isotherm models; the Langmuir, Freundlich, Dubinin-Raduskevich, Temkin isotherms. The coefficients of determination of the four models were high with Temkin providing best data description for adsorption of the metal ions onto carbonized. Assessment of the maximum amount of metal ion adsorbent onto the adsorbent showed that Zn(II) ion were better adsorbed onto the adsorbent compared Pb (II) and Cd(II) ions. The affinity of the adsorbent for the metal ions also follows the trend Zn (II) > Cd (II) > Pb (II).

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CHEMICAL SOCIETY OF NIGERIA (CSN) ABIA CHAPTER

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Conference Proceedings

Full Length Research Paper

FORMS OF SULPHUR AND SOME PHYSICO-CHEMICAL PROPERTIES OF TWO NIGERIAN SOILS

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ABSTRACT

The Sulphur status of two benchmark soils from Amakama and Bende pits in Abia State were evaluated by determining their various Sulphur forms and correlating same with horizon depths and some physico-chemical properties of the sample soils. The organic matter levels in both locations are irregular, but in greater percentages on the two topsoils. Apart from organic matter that had a positive significant ($P<0.05$) correlation with inorganic form of Sulphur at Amakama location other forms of Sulphur analyzed showed no dependence on the physico-chemical properties of the two soils studied. There was no relationship between particle size and depth in the samples analyzed. Total Sulphur distribution on the horizons for Amakama and Bende locations followed no regular pattern. Amakama had total Sulphur range of 250.00-476.00mg/Kg with a mean of 373.94± 32.69 while the range and mean for Bende location are 226.42-442.99mg/Kg and 393.20±34.14 respectively. The mean pH at Amakama location was 5.28±0.08 while that of Bende was 4.19±015**.**

Key words: Sulphur, Environment, Top soil, Physical properties,

INTRODUCTION

Soil and agricultural practices are strongly tied to the environment (Batia, 2002). Sulphur (S) is essential for many growth functions in plants and is also capable of causing environmental pollution when sulfur dioxide combines with water and air, it forms sulfuric acid, which is the main component of acid rain. **The physico-chemical properties of soil influences the availability of S in the soil. Therefore, an understanding of the relationship of the relationship of the various forms of S in soils with their physical and chemical properties is essential for efficient management.**

MATERIALS AND METHOD Two benchmark soils, utisol of coastal plain sands from Amakama in Umuahia South Local Government Area of Abia State and alfisol of shake parent material from Bende (Ajata Ibeku, in Umuahia North Local Government Area of Abia State) were used for this study. Samples were collected from 7 horizons (0-21cm depth) from the Amakama profile pit and eight horizons (0-190cm depth) from the Bende profile pit.

Samples of each soil were analyzed for particle size distribution by the hydrometer method as described by the hydrometer method prescribed by Bouyoucos (1951). The soil pH was determined in 1:2.5 soil-water suspensions as described by Ano (1994). The organic matter of the different soil samples was measured as percentage carbon (%) content in the soils as prescribed by Walkley-Black, wet oxidation method (Walkley and Black, 1934).

Total Sulphur in the samples was determined by fusion in sodium trioxocarbonate(iv) ($NaNO_3$) as prescribed by Udo and Ogunwale (1978). The available Sulphur for all the samples were determined using the Morgan reagent as prescribed by Udo and Ogunwale (1978).

Briefly, 5ml aliquot of extract from each fractionation stage was used in developing the colour for spectrophotometric determination of the concentrations of the different forms of sulphur. 5 ml aliquot of each of the sample filtrates was used to determine organic sulphur concentration by the method by Udo and Ogunwale (1978).

RESULTS AND DISCUSSION

Physical and chemical properties of the soil samples are as shown in Table 1.

pH

The soils from both locations were generally acidic with pH range of 4.90-5.60 and mean value of 5.28±0.08 for Amakama and 4.10-5.50 and mean value of 4.19±015 for Bende. The increased concentration of total Sulphur obtained in this research may be as result of improved farming practices over the years and perhaps Sulphur introduction through plant residue and animal manures, fertilizer and Sulphur-bearing minerals. For both locations, variation in pH levels had no definite relationship with dept.

ORGANIC MATTER

The organic matter levels in both locations are irregular, but in greater percentages on the two top soils (0-13cm depth in Amakama and 0-9cm depth in Bende). This is because organic matter from de composed plant leaves and roots tend to accumulate in the uppermost horizons of a soil profile, giving the horizons a darker color than the lower horizons (Brady and Weil, 1999). The range for Amakama location was 0.27%-2.21% with 0.27% at the last horizon (157-210cm) and a mean value of 0.91± 0.30 while the range at Bende pit was 0.60%-2.61% with a mean value of 1.09± 0.24.

Enwezor *et al*., (1988) classified soil organic matter less than 2.00% as low (values below critical limits), 2.10 to 3.00 as medium (values above critical level) and greater than 3.10 as high. The mean percentage of organic matter for the two profile pits show organic matter below critical limit. Mokwunye and Batino (2002) reported similar values (0.60%) for Alfisol from Benin. This is also in agreement with mean organic matter result reported by Osodeke *et al*., (1993) for Akwuete soils. The low organic matter result may be attributed to constant use these sites are put into for cropping.

SOIL TEXTURE

In Amakama, percentage sand > percentage clay >percentage slit. From table 1, it is evidence that highest percentage sand occurred at 13-27cm horizon with the value of 68.60%. Highest percentage slit occurred at 0 to 13cm horizon (6.70%) while that of clay occurred between 27 and 210cm depth with 37.1% each for the five horizons that make up the depths. Bende soil had highest percentage of clay for all horizon except for the 0-9cm horizon (topsoil) where the percentage sand was high with the value of 42.60%.

Highest percentage of silt occurred on the surface horizon that is 0-9cmwith value of 19.70% at this location. The distribution of the various soil particle sizes indicates that they are formed from natural processes of weathering of the underlying parent material. The clay fraction was high in Bende soil and ranged from 37.7% to 77.70% than in the Amakama soil which ranged from 26.70% to 37.10%. this is an indication that adsorption will be more on Bende soil than on Amakama since clay (colloidal fraction of soil mineral) is the soils active solid (Isirimah *et al.*, 2003). The mean values of clay content for Amakama and Bende are 34.00±1.90% and 66.20±5.19% respectively.

TOTAL SULPHUR

Total sulphur distribution on the horizons for Amakama and Bende locations followed no regular pattern. Amakama had total Sulphur range of 250.00-476.00mg/Kg with a mean of 373.94± 32.69 while the range and mean for Bende location are 226.42-442.99mg/Kg and 393.20±34.14 respectively. Trivedi *et al* (1998) had similar total Sulphur range (116.0-446.0mg/Kg) for Northern Madgya Pradesh (India) Alfisol.

On the other hand, the results were in sharp contrast with those obtained by Enwezor (1976) (range= 50.0 –170.0mg/Kg) for sixteen Southeastern Nigerian top soils. The increased concentration of total Sulphur obtained in this research may be as result of improved farming practices over the years and perhaps Sulphur introduction through plant residue and animal manures, fertilizer and Sulphur-bearing minerals.

ORGANIC SULPHUR

For the Amakama location, the organic Sulphur concentration ranged between 226.42 and 442.19mg/Kg, with mean value of 346.34±34.73. The concentration ranged from 193.80 to 440.52mg/Kg and mean value of 361.07 ± 33.36 for Bende location. On the average, organic Sulphur accounted for 92.63% and 91.82% of the total sulphur for Amakama and Bende locations respectively. This is in line with what is reported by Bettany *et al*., (1973); Freney and Williams, (1983) that organic sulphur accounts for 90% of total sulphur in conceptual sulphur cycle.

INORGANIC SULPHUR

The difference between total and organic forms of Sulphur gave the values for inorganic sulphur in all the horizons at the two profile pits studied. When the mean values for the two locations are considered, inorganic Sulphur accounted for about 7.37% and 8.17% for the Amakama and Bende profile pits respectively. This in agreement with the view of Stewart and Sharpley (1987); Bettany Stewart (1983); Freney and Williams (1983) that the inorganic pool of soluble and adsorbed sulphates (in well-drained soils) and sulphides (in poorly drained soils) account for <10% of the total S.

AVAILABLE SULPHUR

For both Amakama and Bende soils, available Sulphur was not significantly correlated (P> 0.005) with percentage organic matter (Table 3). The reports of Couto *et al*., (1979), Haque and Walmsly (1974) on the contrary showed that soil organic matter levels in A horizon of soils (surface soil) could account for sulphate movement and accumulation in B horizon (sub soil). This implies that increase in organic matter levels decreases available Sulphur concentration.

The relationship of available Sulphur with percentage organic matter in these soils may have been masked by other soil factors because availability of Sulphur is influenced by various soil factors and hence the status of different forms of Sulphur in soil varies widely with nature of soil (Balpriagoudar and Satyanarayana, 1990). Also, according to Trivedi, *et al*., (1998), distribution of Sulphur forms and their interrelationship with some important soil characteristics, decide the Sulphur supplying power of soil by influencing its release and dynamics in soil.

CORRELATION OF THE PHYSICO-CHEMICAL PROPERTIES OF THE SOIL WITH FORMS OF SULPHUR

Correlation analysis was used to examine the association of the forms of Sulphur upon the physico-chemical properties of the two soils. The correlation coefficient (r values) for this analysis are as ahown on table 3. Apart from organic matter that had a significant and positive correlation with inorganic form of Sulphur at the Amakama location, all other forms of Sulphur analysed showed no dependency on the physico-chemical properties of the soil. From Table 1, sand was the predominant particle size in Amakama soil profile and decreased down the profile. This was an indication that the finer particles are leached down the profile. The distribution of the various particle sizes along Bende soil profile was irregular. However, after the surface soil, clay predominated the sub soil.

Table 1: PHYSICAL AND CHEMICAL PROPERTIES OF TWO BENCH MARK SOILS

	DEPTH	**pH IN H_2O**	**ORGANIC CARBONATE**	**ORGANIC MATTER**	**PARTICLE SIZE ANALYSIS**			
					CLAY %	**SILT %**	**SAND %**	**TEXTURE**
Profile Pit 1 Location (Amakama)	0-13	4.90	1.28	2.21	26.70	6.70	66.60	Sandy, Clay loam
	13-27	5.30	0.93	1.61	27.70	3.70	68.60	Sandy, Clay loam
	27-63	5.40	0.51	0.87	37.10	3.00	59.90	Sandy, Clay
	63-99	5.30	0.62	1.07	37.10	3.00	59.90	Sandy, Clay
	99-127	5.60	0.08	0.13	37.10	3.40	59.50	Sandy, Clay
	127-159	5.20	1.12	0.20	37.10	5.00	57.90	Sandy, Clay
	159-210	5.25	0.16	0.27	37.10	5.00	57.90	Sandy, Clay
Profile Pit 1 Location Bende (Ajata Ibeku)	0-9	5.25	1.51	2.61	37.70	19.70	42.60	Clay, Loam
	9-28	5.50	0.47	0.80	48.70	18.70	32.60	Clay
	28-60	5.10	0.43	0.74	77.70	9.70	12.60	Clay
	60-80	4.85	0.47	0.80	72.70	9.70	17.60	Clay
	80-101	4.95	0.85	1.47	74.70	9.70	18.60	Clay
	101-128	4.86	0.35	0.60	73.70	4.70	21.60	Clay
	128-154	4.70	0.58	1.00	74.70	10.70	14.60	Clay
	154-190	4.10	0.39	0.67	69.70	11.70	18.66	Clay

FORMS OF SULPHUR

The distribution of the various forms of sulphur are shown below.

Table 2: DISTRIBUTION OF THE VARIOUS FORMS OF SULPHUR IN Mg/kg OF SOIL.

		Forms of sulphur			
Profile	Depth	Total Sulphur	Organic sulphur	Inorganic sulphur	Available sulphur
Amakama	0-13	338.00	271.98	66.02	117.89
	13-27	375.60	252.02	23.58	117.89
	27-63	250.00	226.42	23.58	141.47
	63-99	426.00	397.94	28.06	423.40
	99-127	426.00	415.26	10.74	273.50
	127-159	426.00	417.75	8.25	287.65
	159-210	476.00	442.99	3.01	339.52
	MEAN	373.94	346.39	23.32	243.05
Bende	0-9	478.00	440.52	37.48	384.31
	9-28	442.00	409.46	32.54	357.29
	28-60	302.00	273.71	28.29	218.79
	60-80	447.10	423.52	23.58	216.79
	80-101	441.90	397.10	44.80	443.26
	101-128	410.70	337.69	33.01	438.54
	128-164	431.50	402.73	28.57	403.18
	164-190	192.40	193.80	28.57	408.68
	MEAN	393.20	361.07	32.13	358.87

Table 3: Correlations between forms of sulphur and physico-chemical properties of the two soils

	Forms of sulphur			
Physico-chemical properties of soil	Total sulphur	Organic sulphur	Inorganic sulphur	Available sulphur
		Amakama		
OM	0.60^{ns}	-0.73^{ns}	0.91*	-0.59^{ns}
% Clay	0.53^{ns}	0.64^{ns}	-0.74^{ns}	0.70^{ns}
% Slit	0.18^{ns}	0.03^{ns}	0.48^{ns}	-0.23^{ns}
% Sand	-0.65^{ns}	-0.73^{ns}	-0.68^{ns}	-0.71^{ns}
pH	-0.07^{ns}	0.23^{ns}	-0.69^{ns}	0.26^{ns}
		Bende		
OM	0.50^{ns}	0.46^{ns}	0.58^{ns}	0.23^{ns}
% Clay	0.38^{ns}	-0.37^{ns}	-0.28^{ns}	-0.15^{ns}
% Slit	0.19^{ns}	0.20^{ns}	0.02^{ns}	-0.08^{ns}
% Sand	-0.45^{ns}	-0.44^{ns}	-0.39^{ns}	0.25^{ns}
pH	-0.36^{ns}	0.66^{ns}	0.65^{ns}	0.29^{ns}

**Correlation is significant at 0.01 level; *Correlation is significant at 0.05 level; ns Correlation is not significant at 0.05 level; OM Organic matter

RECOMMENDATION

For the soils studied it is recommended that lower concentrations of sulphate be used in adsorption studies or other models used for the test of fit.

CONCLUSION

The results of this study show that the relationship of available sulphur with percentage organic matter in these soils have been masked by other soil factors because availability of sulphur is influenced by various soil factors and hence the status of different forms of sulphur in soil varies widely with nature of soil. Also, the distribution of sulphur forms and their interrelationship with some important soil characteristics, decide the sulphur supplying power of soil by influencing its release and dynamics in soil.

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CHEMICAL SOCIETY OF NIGERIA (CSN) ABIA CHAPTER
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Conference Proceedings

Full Length Research Paper

ASSESSMENT OF POLLUTION AND HEALTH RISK OF HEAVY METALS IN AIR AROUND IBOM POWER PLANT IN IKOT ABASI LOCAL GOVERNMENT AREA OF AKWA IBOM STATE, NIGERIA

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ABSTRACT

The study assessed the pollution and health risk of heavy metals in air around Ibom Power Plant in Ikot Abasi L.G.A during a period of one year. Analysis was carried out using standard analytical methods. The heavy metals pollutant studied were: Pb, Cd, Ni, As and Hg. The concentration of Pb ranges 0.001-0.23 ppm. The average monthly concentration of Pb (0.023ppm) in the Sept 2020 differs significantly than other months (Nov, Dec, 2019, Jan, Feb, Mar, April, May, June, July, Aug, and Oct, 2020 respectively at $p<0.05$). The concentration of cadmium ranges from (0.001 – 0.059ppm). There was no significant difference in the concentration of Cd at ($p<0.05$) and it was within the 0.05 permissible standard limit of with FEPA / WHO standards. The concentration of nickel (Ni) ranges from 0.00 – 0.01 ppm. There was a significant difference in the concentration of Ni in Sept 2020 compared to all other months at $p < 0.05$, when compared to WHO / FEPA (0.05ppm) were within the permissible limit. The concentration of as ranges from 0.00 – 0.01 ppm. The concentration of as shows a significant difference in the month of Nov 2019, Dec, 2019, Jan, Feb, 2020 and Oct, 2020 at $p<0.05$ but when compared to WHO / FEPA standard was within the 0.01 ppm permissible limit. The concentration of Hg ranges from (0.00 – 0.02) ppm which is within the FEPA and WHO permissible limit of 0.01 ppm but the concentration of Hg was significantly different in April, May, June, July, August, Sept, and Oct than other months (Nov, Dec, 2019, Jan, Feb and March 2020). The heavy metal concentration of Pb, Hg and Ni were significantly different in wet season than in dry seasons ($p<0.05$). Result also indicates that concentration of Cd and as were significantly different in dry season compared to wet season ($p<0.05$). Correlation analysis for the trace metal concentration of Pb, Hg and Ni differs significantly in wet than in dry seasons ($p<0.05$). Result also indicates that concentration of Cd and as was significantly different in dry season compared to wet season ($p<0.05$). The significant negative association shows that any anthropogenic factor responsible for the increase in the concentration of Hg will cause the decrease in Ni in the atmosphere. The THQ for the heavy elements varied to various degrees from month to month with the following ranges: (0.0005 – 0.3923) for all the heavy metal pollutants, this showed that all the heavy metals was below the exposure limit (THQ<1), suggested that these heavy metals pose no hazard. The result of geographical information system mapping for the average concentration of heavy metals showed that the concentration of Pb, Ni and as were very low; Cd and Hg were at critical concentration. From the results of this research, these significant variations in air quality is an indication of presence of possible heavy metals pollutants in the study area which on accumulation may result in many health problems.

Keywords: Pollution, heavy metal, and health risk

INTRODUCTION

Heavy metal pollution refers to the presence of harmful substances in our environment including air, water and soil. These metals emanate from various sources, such as; industrial processes/discharge, vehicular emissions, industrial waste, waste disposal/incinerations, mining activities, domestic heating and gas flaring. The level of these pollutants in an area is generally influenced by various factors such as concentration, circulation of the local emission sources, environmental as well as prevailing meteorological factors. Heavy metal pollution in many areas worldwide has been significantly increased due to an increase in pollutants generated by anthropogenic activities under the context of rapid urbanization and industrialization. Many heavy metals are of outstanding technological significance e.g. iron, zinc, tin, lead, copper, tungsten, etc., in many cases act as the central atom of artificially designed "bio-organic" catalysts for special chemical transformations. Amongst them we find precious noble elements like gold, silver, iridium and rhodium, and others like lead, mercury, cadmium, arsenic, chromium, thallium which classically represent the "dark side of chemistry, having toxic effects at low concentration (Khan *et al*., 2004). Trace metals are usually non-degradable and their homeostasis mechanism is not well understood. Though, they may accumulate in the fatty tissues of human body and affect the central nervous system, disrupt the normal functioning of the body's internal organs and sometimes act as cofactors in other disease and thus, at its elevated levels are potential threats to life. Trace metal pollutants in urban street dust are also a good indicators of contamination as they appear in gasoline, car components, oil lubricants, industrial and incinerator emission and their accumulation in these dust is one major way through which they find their way into soil and subsequently living tissues of plants, animals and human beings which thus impair important biochemical processes, posing a threat to human health, plant growth and animal life, hence, has become a growing / global concern in recent years (Ward *et al*., 1977; Michalke, 2003, Silva *et al*., 2005 and Mashi, *et al*., 2005) (Li and Liu, 2001, Shinggu *et al.*, 2007). Pollutants can attack specific sites or organs of the body and disease can develop as a consequence of such exposure (Archer and Barette, 1976; Ayodele and Gaya, 1998). Although they have been considerable number of studies on the concentration of heavy metals in street dust, the vast majority have been carried out in developed countries with long histories of industrialization (Jaradat and Momani, 1999; Bris *et al*., 1999; Christoforidis and Stamatis, 2009).

Respirable dust which reaches the lower bronchioles and alveolar regions of lungs carries with it a high load of contaminated traces of metals which serves as an indicator to the level and distribution of metals contamination. This affect air quality with environmental consequences such as; formation of acid rain, visibility impairment, ambient thermal conditions, effect on vegetation and animal life, corrosion effect on materials / artefacts, as well as coastal erosion and flooding. Heavy metals along with other respiratory/total suspended particulates matter ((RSPM /TSP) enters the tiny air sacs in the lungs causing breathing difficulties, bronchitis, and aggravation of asthma, cardio-respiratory disorders, pulmonary oedema, eye disorders and skin disorders. Therefore, the quality of air we breathe is very important, hence there is need to know the state of ambient air possible sources of pollutants and the effect of such pollutants on human health in the environment.

MATERIALS AND METHODS

Study area

Ikot Abasi Local Government Area occupies the South Central territorial part of Akwa Ibom State (Figure 1) with general coordinates between 4^{o}32’02”N, 4^{o}36’02”N.36 and 7.48”E, 8^{o}17’42”E, and based on data from 2006 Nigeria’s national census, it is home for 74,840 people (NPC, 2006). Ikot Abasi is host for oil producing, several oil servicing companies and electricity power plant which are dynamic in their own ways and attracts complimentary economic activities. Sampling station: Ibom Power Plant (IK_{IPP}) was selected based on the activity areas and human presence.

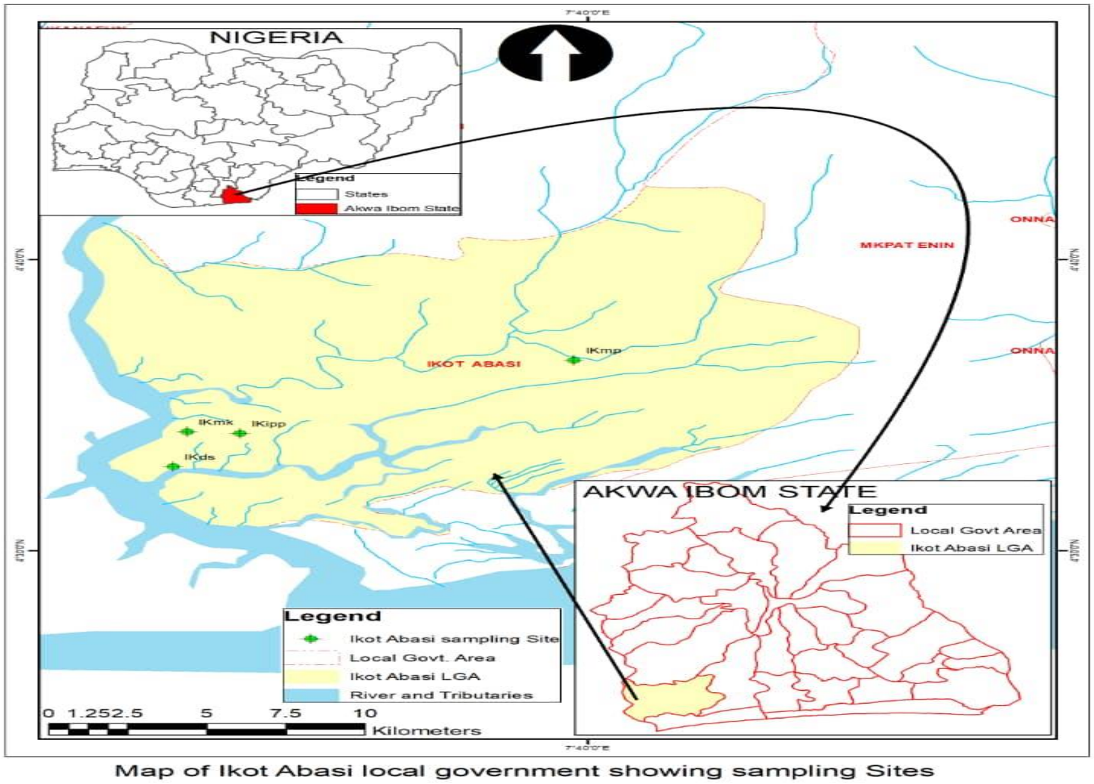


Figure 1: Map of Ikot Abasi local government showing sampling Site (IK_{ipp})

Digestion procedure for Filters

The exposed Whatman glass fiber filter papers was cut into pieces by means of clean stainless-steel scissors and transferred into a 250 ml beaker. To the beaker 6 ml of concentrated nitric acid, 4 ml of hydrogen peroxide (30 %) and 50 ml of distilled water was added, and then covered with a watch glass. This was heated on a hot plate until most of the acid evaporated. Same procedure was repeated at least twice. This was repeated until the residue was barely dry and a white ash appeared. The residue was dissolved in 5 ml of concentrated nitric acid. The digest was filtered, with repeated small washings of nitric acid into a 25 ml volumetric flask and made up to mark with dilute nitric acid. A blank unexposed filter paper was similarly digested for blank correction.

Determination of trace metal concentration

The concentration of trace metals was determined using atomic absorption spectrophotometer (AAS; SOLAAR 939, ATI UNICAM) equipped with flame furnace. All analyses were carried out in duplicate and for each run. Two blanks and a reference sample was analysed using the same procedure in order to ensure precision and accuracy of the analytical methods.

Calculations of trace metals

The mass concentration of trace metal ($\mathrm{X = Pb, Cd, Ni, As, and\ Hg}$) expressed in micrograms per cubic meter in air sample.

$$\mathrm{X_{Conc.}(mg/m^3)} = \frac{\mathrm{A \times DF}}{\mathrm{Slope \times V_S}}$$

Where, $\mathrm{X_{(Conc)}}$= mass concentration of mg/m^3

A= absorbance

DF = dilution factor

$\mathrm{V_S}$ = sample volume

Slope = $\frac{\text{change in absorbance}}{\text{change in concentration}}$.

Determination of Target Hazard Quotient (THQ)

The target hazard quotient was calculated as per USEPA Region III Risk-Based Concentration Table (USEPA, 2011). The THQ is an estimate of the non-carcinogenic risk level due to pollutant exposure by respective element and was calculated by the following equation:

$$\mathrm{THQ} = \frac{\{\mathrm{M_C \times (IR \times 10^{-3}) \times EF \times ED}\}}{\{\mathrm{R_fD\ \times BW \times AT_n}\}}$$

Where THQ is non-carcinogenic risk and it's dimensionless. $\mathrm{M_C}$ Was the metal concentration (in mg / kg.dw), IR was the ingestion rate (g/day, and 19.5 g/day was used), EF was the exposure frequency (days/year) and 5 days per week or 240 days per year was used. ED is the exposure duration in years over lifetime, and 30 years was used which is 10950 days for non-carcinogens as per USEPA, 2011. $\mathrm{R_f}$Dis the oral reference dose of individual metal (mg/kg/day) as per. BW is an average adult body weight (70 kg was used) $\mathrm{AT_n}$ is the average time for non-carcinogens and 60 years was used, that is, 21900 days (USEPA, 2011). Simply put, $\mathrm{THQ\ (M)} = \frac{(19.5 \times 10^{-3} \times 240 \times 10950\ \mathrm{M_C})}{(70 \times 21900 \times \mathrm{R_fD})} = \frac{51246\ \mathrm{M_C}}{1533000\ \mathrm{R_fD}} = \frac{0.3342\ \mathrm{M_C}}{\mathrm{R_fD}}$

Statistical analysis

Statistical and cluster analyses was carried out using statistical package for social sciences (SPSS version 13). Statistical parameters determined through this method include: the average, standard deviation (SD), Pearson's correlation analysis, principal component analysis. The mean and standard deviations calculated elicit how chemical parameters deviate from stipulated guidelines. Correlation analysis measures the closeness of the relationship between chosen variables. If the correlation coefficient is nearer to +1 or -1, it shows a perfect linear relationship between the two variables and attempts to establish the nature of the relationship between them (Abdul Raheem *et al.*, 2008).

Geographical Information System Mapping

The GIS mapping was done using ARCMAP 10, software which allows one to view spatial data, create layered maps, and perform basis spatial analysis.

RESULTS AND DISCUSSION

The results are as follows.

Heavy metals in Suspended Particulate Matter

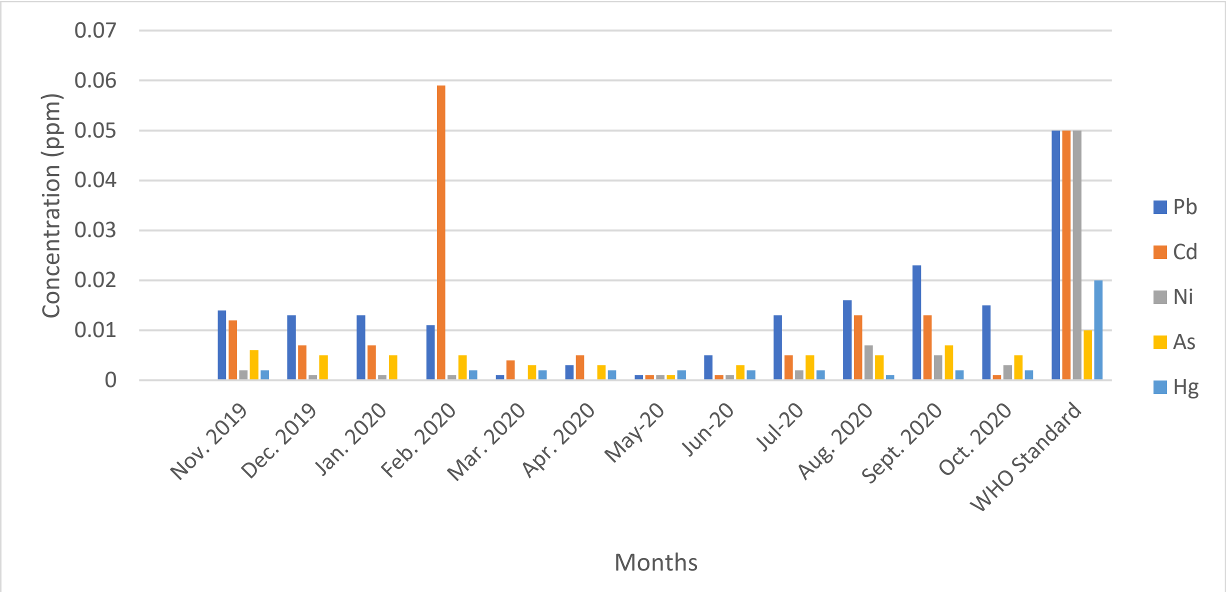


Figure 2: Average monthly concentration of trace metals in suspended particulate matter in Ibom Power plant in Ikot Abasi.

Average monthly concentration of heavy metals in suspended matter (Figure 2) shows the concentration of Pb ranges 0.001-0.23 ppm. The concentration of Pb (0.023ppm) obtained in the month of Sept 2020 was significantly higher than other months (Nov, Dec, 2019, Jan, Feb, Mar, April, May, June, July, Aug, and Oct, 2020 respectively at $p<0.05$). The concentration of Cadmium ranges from (0.001 – 0.059). There was no significant difference in the concentration of Cd at ($p<0.05$) but when compared with FEPA / WHO standards, it was within the 0.05 permissible standard limit. The concentration of nickel (Ni) ranges from 0.00 – 0.01 ppm. There was a significant difference in the concentration of Ni in Sept 2020 compared to all other months at $p < 0.05$. The concentration of Ni when compared to WHO / FEPA (0.05 ppm) was within the permissible limit. The concentration of As ranges from 0.00 – 0.01 ppm. This shows that there was a significant difference in the concentration of As in the month of Nov 2019, Dec, 2019, Jan, Feb, 2020 and Oct, 2020 at $p<0.05$ but when compared to WHO / FEPA standard shown that the concentration of As was within the 0.01 ppm permissible limit. The concentration of Hg ranges from 0.00 – 0.02 ppm which is within the FEPA and WHO permissible limit of 0.01 ppm but the concentration of Hg was significantly different in April, May, June, July, August, Sept, and Oct than other months (Nov, Dec, 2019, Jan, Feb and March 2020).

Table 1: Average trace metals concentration at wet and dry season for Ibom Power Plant

		Heavy metals				
Site	Season	Pb (ppm)	Cd (ppm)	Ni (ppm)	As (ppm)	Hg (ppm)
Ikot Abasi	Wet	0.019 ± 0.014^{a}	0.006 ± 0.007^{a}	0.004 ± 0.004^{b}	0.003 ± 0.002^{a}	0.002 ± 0.001^{b}
	Dry	0.015 ± 0.008^{b}	0.009 ± 0.007^{b}	0.002 ± 0.003^{a}	0.004 ± 0.003^{b}	0.001 ± 0.001^{a}

Similar superscript letters means not significantly different ($p>0.05$) while different superscript letter means significantly different ($p<0.05$)

Results in Table 2 revealed that concentration of Pb was significantly different in wet season than in dry seasons ($p<0.05$). While the concentration of Hg obtained in wet season was significantly different compared to the dry season ($p<0.05$). Result also indicates that concentration of Ni was significantly different in wet season compared to the dry season ($p<0.05$) while Cd was significantly different in dry season compared to wet season. The concentration of As differs significantly in dry season than in wet season ($p<0.05$).

Correlation Analysis

Pearson's correlation is used to examine the associations between air pollutants as well as identify pollutants with similar source of pollution. To evaluate correlation coefficients, the significance value was calculated and significance values of 0.05 ($p<0.05$)) was marked with a single asterisk sign (*), while the significance level of 0.01 (that is 97%) was marked with double asterisk (**) sign.

Table 3: Correlation between trace metals during wet season in Ibom Power Plant

Metals	Pb	Cd	Ni	As	Hg
Pb	1				
Cd	$.337^{**}$	1			
Ni	$.480^{**}$	$.613^{**}$	1		
As	$.265^{**}$	$.368^{**}$	.138	1	
Hg	.192	-.160	-.156	-.134	1

**Correlation is significant at 1 % ($p<0.01$), *correlation is significant at 5 % ($p<0.05$)

As shown in Table 3, there is positive and significant association between Cd and Pb ($r = 0.337$, $p<0.01$), Ni and Pb ($r = 0.480$, $p<0.01$), Ni and Cd ($r = 0.613$, $p < 0.01$), As and Pb ($r = 0.265$, $p<0.01$) and between As and Cd ($r = 0.368$, $p < 0.01$). The positive association implies that an increase in one pollutant will bring about a corresponding increase in the other pollutant and vice versa. It also suggests that they pollutants are influenced by similar anthropogenic factors. This was similar to the report of Ewa *et al*. (2013).

Table 4: Correlation between trace metals during dry season in Ikot Abasi

Heavy metals	Pb	Cd	Ni	As	Hg
Pb	1				
Cd	.069	1			
Ni	$.240^{*}$	-.059	1		
As	$.335^{**}$	.170	$.204^{*}$	1	
Hg	-.038	.055	$-.221^{*}$	$-.205^{*}$	1

**Correlation is significant at 1% ($p<0.01$), *Correlation is significant at 5% ($p<0.05$)

The result in Table 4, revealed that there is positive and significant association between Ni and Pb ($r = 0.240$, $p < 0.05$), As and Pb ($r = 0.335$, $p < 0.01$), and between As and Ni ($r = 0.204$, $p < 0.05$). It also showed that negative and significant association existed between Hg and Ni ($r = -0.221$, $p < 0.05$), and between Hg and As ($r = 0.205$, $p < 0.05$). The significant negative association implies that an increase in the concentration of Hg result in a corresponding decrease in the concentration of Ni. The positive association implies that an increase in one pollutant will bring about a corresponding increase in the other pollutant and vice versa. It also suggests that they pollutants are influenced by similar anthropogenic factors. These were similar to the result by Bilos *et al.* (2001) and Ewa *et al.*

(2013).

Health Risk Assessment

The calculated target hazard quotient for the heavy element in the suspended particulate matter samples on monthly is shown in Figure 2.

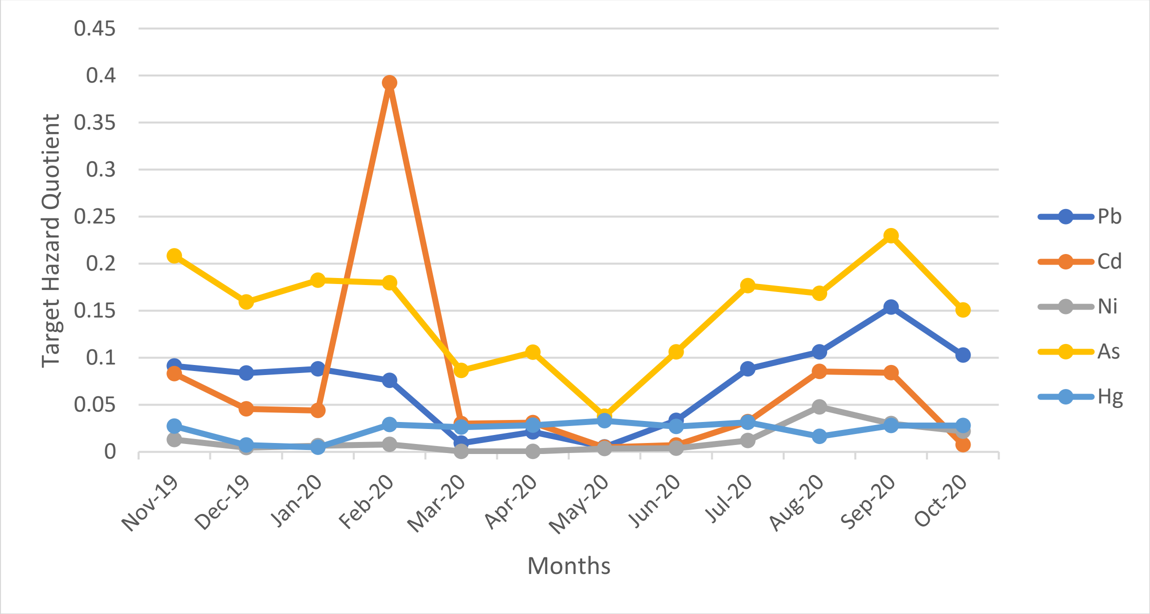
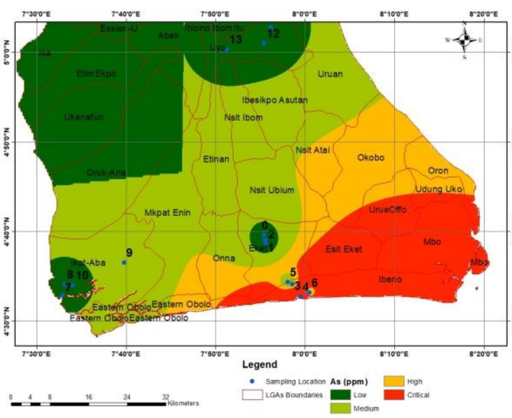


Figure 3: Monthly variation of Target Hazard Quotient (THQ) for trace metals in Ibom Power Plant in Ikot Abasi.

The THQ for the heavy elements varied to various degrees from month to month (Figure 3) with the following ranges: 0.0051 – 0.1539 for Pb in the months of Nov 2019 to Oct 2020; 0.0048 to 0.3923 for Cd in the months of Nov 2019 to Oct 2020 respectively; 0.0005 – 0.0478 for Ni in the months of Nov 2019 to Oct 2020; 0.0379 – 0.2295 for As in the months of Nov 2019 to Oct 2020 respectively and finally, 0.0048 to 0.0312 for Hg in the months of Nov 2019 to Oct 2020 respectively. The highest THQ was that for Cd (0.3923 – Feb 2020) while the lowest was for Ni (0.0005 – March and Apr 2020). This showed that all the heavy metals was below the exposure limit (THQ < 1) suggested that these heavy elements pose little hazard. The THQ ranges differed with the result of Moses and Orok (2005); Liu *et al.* (2015), but comparable with the results of Abbasi and Tufail (2003).

Geographical Information System Mapping

The result of geographical information system mapping for the average concentration of heavy metals in Ibom Power plant, Ikot Abasi is presented in Figures 4-6 respectively.



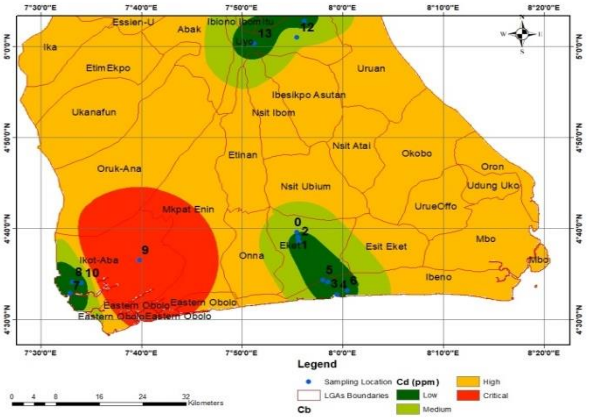
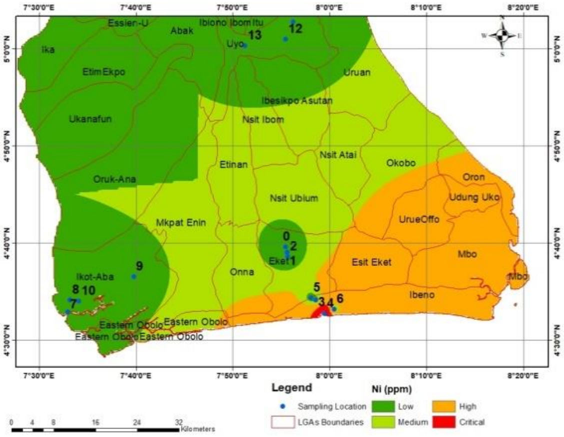


Fig. 4a: Spatial interpolation of As **4b:** Spatial interpolation of Cd (average monthly)

10 = IK_{IPP} (Ikot Abasi, Ibom Power Plant)

The spatial mapping for average monthly concentration of As (Figure **4a**) revealed a very low concentration (pigmented green) and this may have been due to increased wind speed and changes in wind direction.

While Cadium (Figure **4b**) (pigmented red) revealed that the concentration was at a critical stage probably because of very high commercial and high traffic activities within this location or wider dispersion from the point source and mobile vehicular. Different concentration levels and distribution was shown in the work of Narayanan, (2009).



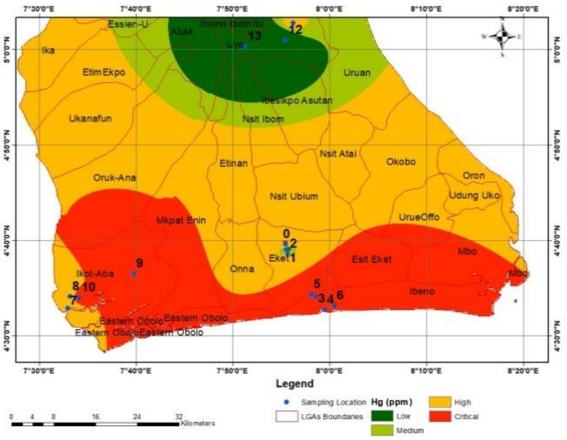


Fig. 5a: Spatial interpolation of Hg **5b:** Spatial interpolation of Ni

Where: 10 = IK_{IPP} (Ikot Abasi Ibom Power Plant)

Figure 5**a** showed that the spatial distribution for average monthly concentration of mercury (Hg) in the study area was critical (pigmented red). Probably because of very high industrial, commercial and high traffic activities within these locations or wider dispersion from the point source and mobile vehicular, while the concentration of Ni (pigmented green revealed very low concentration and this suggested inversion by wind or temperature. Higher concentration and different distribution pattern were shown in the results of Zheng *et al.* (2015) and Weng and Yang (2006).

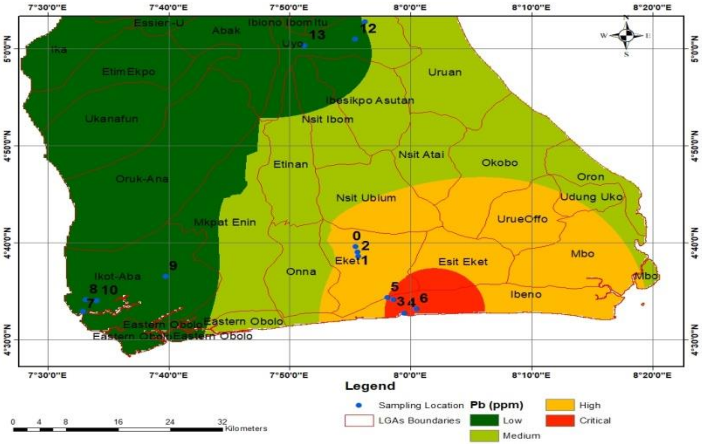


Figure 6: Spatial interpolation of Pb (**Where: 10 = IK$_{IPP}$ (Ikot Abasi Ibom Power**)

The spatial distribution for average monthly concentration of lead (Pb) in the study area of revealed a medium concentration (pigmented light green) probably due to low commercial and low traffic activities within this location. Similar distribution pattern were shown in Weng and Yang (2006).

CONCLUSION

The study area covers a substantial portion of Ibom power plant in Ikot Abasi LGA, the site-specific analysis of heavy metal pollutants obtained revealed that Ibom Power Plant is the most polluted area with maximum concentration of pollutants at variable levels. The presence of these metal pollutants Pb, Cd, Ni, As and Hg may be attributed to predominantly emission of gas from gas plant, smoke emanating from vehicles and possibly decomposition of organic waste as the major sources of air contaminant in the area under study. Consequently, on accumulation, the air pollutants may pose some health challenges if not properly monitored.

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CHEMICAL SOCIETY OF NIGERIA (CSN) ABIA CHAPTER

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Conference Proceedings

Full Length Research Paper

URBAN MINING: RECOVERING CRITICAL RAW MATERIALS AND FOREIGN EXCHANGE FROM WASTE RECHARGEABLE BATTERIES IN NIGERIA

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ABSTRACT

Urban mining involves extracting raw materials from waste as a sustainable approach to resource recovery. In Nigeria, waste rechargeable batteries (WRB) represent a major prospect for urban mining, particularly within the framework of recovering critical raw materials (CRM) and foreign exchange value. Improper disposal of WRB not only poses environmental risks but also results in the loss of valuable resources that could be recycled and reused. Urban mining provides a feasible solution by converting waste into wealth, thus contributing to a circular economy. The process of urban mining involves collection, disassembly, and chemical processing of WRB to extract metals. In Nigeria, this practice could reduce the dependency on raw material imports or virgin material mining and provide a new revenue flow through the sale of recovered metals on the international market. This study mined data from the UN Comtrade database for battery importation into Nigeria from 1999 – 2022 and used the mean metal levels determined in WRB (Co, 28.9 g/t; Li, 66 g/t; Mn, 18.3 g/t; and Ni, 24.3 g/t) to estimate recoverable CRM. Data from UN Comtrade showed importation of 2.63 Mt of WRB into Nigeria. If the WRBs are collected and recycled, 76 t of Co, 174 t of Li and 48.3 t of Mn and 64.1 t of Ni can be recovered can be recovered from the batteries considering results of this study. Considering the CRM unit prices in the mineral market (Co, US$28550/t; Li, US$15343/t; Mn, US$1690/t and US$16863 for Ni) the recoverable metals are worth US$6 Million. This shows that much forex can be obtained from WRB if collected and recycled, stimulating economic growth. However, if disposed with municipal waste, they will contaminate the environment; endangering the lives of plants, animals and humans.

Key words: Urban mining, resource recovery, circular economy, recycle, forex

INTRODUCTION

Electronic Waste or e-Waste, has become a pressing issue as a result of the speedy advancement of technology and the widespread use of electronic devices (Choudhary, 2016; Meshiram *et al.*, 2020). E-waste is generated when electronic device is discarded and it can include everything from cell phones and computers, to refrigerators and washing machines (Mrozik *et al.*, 2021). According to the United Nations, the world generates approximately 53 million tons of e-waste annually, and this number is expected to double by 2050. The UN fourth Global e-waste monitor, 2024, reveals that a record 62 million tonnes (Mt of e-waste) was produced in 2022, up to 82 % from 2010; on track to rise another 32 % to 82 million tonnes in 2030. Billions of dollars' worth of strategically-valuable resources squandered. Less than one-quarter (22.3 %) of the year's e-waste mass was documented as having been properly recycled in 2022, leaving US$ 62 billion worth of recoverable natural resources unaccounted for and increasing pollution risks to communities worldwide.(The Global E-waste Monitor, 2024).

Compared to conventional municipal wastes, certain components of electronic products contain toxic substances which can generate a threat to the environment and human health. This is a major concern that stems from improper disposal of these electronic devices. For instance, television and computer monitors usually contain hazardous materials such as lead, mercury, brominated flame retardants and cadmium which can contaminate the environment and pose a threat to human health. For example, when electronic devices are burned, toxic fumes are released, which can cause respiratory problems and other health issues. When these products are placed in landfills, or incinerated, they pose health risks due to the hazardous materials they contain. As more e-waste is placed in landfills, exposure to environmental toxins is likely to increase resulting in elevated risks of cancer and developmental and neurological disorders. A major cause of e-waste problem is the short lifespan of most electronic products — less than two years for computers and cell phones. This high obsolescence rate spells a major issue (Choudhary, 2016). On the other hand, e-waste may contain precious metals such as gold, copper, nickel, cobalt, lithium and beryllium, rare metals of strategic value such as indium and palladium can be recovered, recycled and used as valuable sources of secondary raw materials (Sambarmurthy *et al.*, 2021; Saha *et al.*, 2021). This is to say that in addition to the environmental and health concerns associated with e-waste, there is also a significant economic impact. Many of these materials used in electronic devices, such as gold, lithium, cobalt, nickel, copper, palladium, etc. are valuable resources that could be re-used if the devices were properly recycled. However, much of the c-waste generated in developed countries is shipped to developing countries, where it is often dismantled in unsafe and unregulated conditions, exposing workers to hazardous materials and releasing pollutants into the environment.

To address the e-waste problem, there have been efforts to promote responsible management and disposal of electronic devices such as recycling and designing devices that are more easily repairable and recyclable (Gonzalez-Salazar *et al.*, 2023), including awareness on sustainable practices (Adeniran and Abdulkarim, 2012; Sambarmurthy *et al.*, 2021; Saha *et al.*, 2021).

This aim of this study is to discuss the WRB management issues in Nigeria and estimate recoverable metals and the forex that can be earned from it. This study mined data from the UN Comtrade database for battery importation into Nigeria from 1999 – 2022 and used the mean metal levels determined in WRB. Data on metal contents of WRB is from Nnorom and Nwachukwu (2024a; b).

MATERIALS AND METHODS/APPROACH

Data sources

Data was mined from UN Comtrade Database for the importation of batteries into Nigeria. This provided data on the quantities of rechargeable batteries imported into Nigeria from various countries (Nwachukwu, 2024a; b). It was assumed that at some points, these batteries became waste and were disposed. Since the waste rechargeable batteries (WRB) contain valuable scarce critical raw materials (CRM), the study estimated the recoverable metals from the WRBs. Information on the market values of the recoverable metals were obtained from international raw material sites/market and thereafter used to estimate the recoverable values (in monetary terms) of the valuable metals using the average metal contents of the batteries as determined using AAS (Nwachukwu and Nnorom, 2024a; b).

Estimation of Recoverable CRMs from WRBs

For a given year, the recoverable values were estimated using the relationship:

$$R_m = Q_b \times Mc \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 1$$

Where R_m is the recoverable metal; Q_b is the quantity of battery imported; and Mc is the mean metal concentration (a given metal).

The amount of recoverable metals and their value (in Dollars) are presented in this section. For a given year, the recoverable values were estimated using the equation:

$$Value_{\$} = R_m \times Unit\ Market\ Value_{\$} \quad \ldots 2$$

RESULTS AND DISCUSSION

CRM Contents of Waste Rechargeable Batteries

The summaries of the metal contents of Li-ion batteries, Li-polymer batteries and NiMH batteries are presented in Figure 1. The mean concentrations (range) of the sample lithium-ion batteries are 28899 mg/kg (33397-14076 mg/kg) for Co, 65961 mg/kg (81159-47132 mg/kg) for Li, 18310 mg/kg (32549-8821 mg/kg) for Mn and 24329 mg/kg (35857-3808 mg/kg) for Ni. The mean concentrations (range) of the sample lithium-polymer batteries are 29753 mg/kg (33555-177436 mg/kg) for Co, 65477 mg/kg (73284-55494 mg/kg) for Li, 21287 mg/kg (30260-8461 mg/kg) for Mn and 20159 mg/kg (32706-2766 mg/kg) for Ni. The distribution of mean concentrations (range) of the sample nickel metal hydride batteries are 66287 mg/kg (71581-60993 mg/kg) for Co, 13851 mg/kg (15587-12115 mg/kg) for Li, 32899 mg/kg (54605-11192 mg/kg) for Mn and 82735 mg/kg (84580-80889 mg/kg) for Ni.

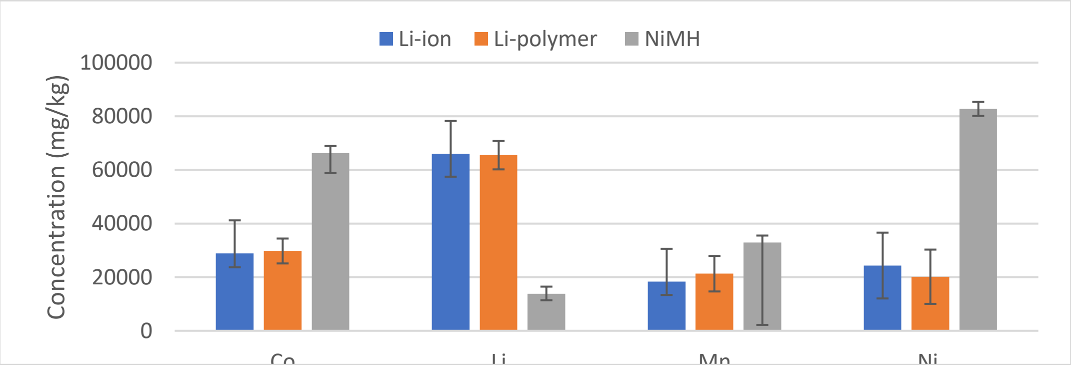

Figure 1: Summary of metal levels of waste rechargeable batteries.

Data for rechargeable batteries used in other devices that are imported as separate items (not installed in any electronic devices) from 1999-2022 are presented in Table 1. Recoverable metals and values from these batteries also show that lithium batteries imported into Nigeria from 1999-2022 had 75.9 tonnes of recoverable Co with an estimated recoverable value of $2.2 Million at a unit price of $28,550. Also, 173.7 tonnes of recoverable Li, which at a unit price of $15,343.30 was estimated at a recoverable value of $2.7 Million. Furthermore, 48.3 tonnes of recoverable Mn, having a unit price of $1,690 was estimated at a recoverable value of $81,347. In addition, 64 tonnes of recoverable Ni, at a unit price of $16,863 was estimated at a recoverable value of $1.1 Million. Li had the highest recoverable value followed by Co, then Ni and Mn. The total recoverable value of the metals was $6 Million.

Presented in Table 2 is the recoverable quantities of CRM from waste batteries that were imported fixed in mobile phones and the values (in Dollars) for the period 1999-2022. The percentage weight of battery in a mobile phone is estimated at 5.304 % (Annamalai and Gurumuthy, 2020). 5.304 % of 82,100 tonnes (Nwachukwu, 2024a) being the quantity of mobile phones imported gave 4351.3 tonnes as the quantity of battery in the mobile phones produced from1999-2022. Table 2 shows that 0.1 tonne of Co is recoverable from 4351.3 tonnes of the mobile phones imported from 1999-2022 which had a recoverable value of $3,590 at the mineral market. Also, 0.3 tonne of Li was estimated which had a recoverable value of $4,406. Mn was estimated at 0.08 tonne which had a recoverable value of $135 while Ni was estimated at 0.1 tonne and its recoverable value was $1,783. The total recoverable value of these metals was $9,914.

Table 1: Recoverable values of WRB's imported from 1999-2022

Metal	Qty of battery imported (t)	Recoverable metal (t)	Average metal content (g/t)	Market value ($/t)	Total value ($M)
Co	2630319	75.9	28.9	28550	2.17
Li	2630319	173.7	66	15343	2.66
Mn	2630319	48.3	18.3	1690	0.08
Ni	2630319	64	24.3	16863	1.08
Sum					**5.99**

Table 2: Recoverable value (in $) from batteries installed in mobile phones imported between 1999 to 2022

Quantity of battery (t)	Metal	Concentration (g/t)	Recoverable metal (t)	Unit price ($/t)	Market value ($)
4351.3	Co	28.9	0.1	28550	3,590
4351.3	Li	66	0.3	15343	4,406
4351.3	Mn	18.3	0.08	1690	135
4351.3	Ni	24.3	0.1	16863	1,783
Total value					**9,914**

DISCUSSION

Waste Rechargeable Batteries (WRB) – a cause for concern

Among the key components of rechargeable batteries are valuable metals such as lithium, cobalt, nickel, and rare earth elements (Roy *et al.*, 2021). These metals play a pivotal role in the functionality and performance of batteries, making them indispensable for various applications (Mrozik *et al.*, 2021). However, the conventional disposal methods of e-waste, often characterized by incineration and landfilling, not only squander these precious resources but also contribute to environmental pollution and resource scarcity (Sambarmurthy *et al.*, 2021; Melchor-Martinez *et al.*, 2021). As society moves towards more sustainable practices, there is a pressing need to develop efficient and environmentally sound methods for the recovery of valuable metals from waste rechargeable batteries (Roy *et al.*, 2021). The field of battery recycling and metal recovery has gained momentum in recent years, driven by concerns over resource depletion, environmental impact, and the economic potential of recycling these materials (Othman *et al.*, 2020; Pathak and Chabhadiya, 2022). Also, health problems such as central nervous disorder, prostate and lung tumors, kidney disorders, pre-mature births, cardiac hypertrophy and illnesses of anaemia and osteomalacia which are prevalent in Nigeria at large are linked but not limited to environmental pollution due to the presence of lithium, nickel and manganese (Adedeji *et al*., 2019). Despite the growing importation of batteries in Nigeria, there is a lack of comprehensive data on the metal levels present in discarded rechargeable batteries (Ajisegun *et al*., 2023). The absence of recycling facilities exacerbates the issue, hindering the recovery of valuable metals from these batteries (Manhart *et al*., 2022).

Global Depletion of CRMs and Importance of Urban Mining

Some of the key battery tech manufacturing countries include China, Japan, South Korea, the United States, Germany and India. Chile has the largest known reserves of lithium in the world, with a total of 8 million tons. This puts it ahead of other countries with significant reserves, such as Australia (2.7 million tons). In Europe, Portugal also has smaller deposits of lithium. The global battery technology market size is expected to grow from $95.7 billion in 2022 to $136.6 billion by 2027 at a compound annual growth rate of 7.4 % (Kabir, 2023).

It is projected that between 2020 and 2030, the global demand for lithium-ion batteries will increase eleven-fold reaching over two terawatt-hours in 2030. The global lithium-ion battery market, while valued at about 40.5 billion U.S dollars in 2020, the market should reach the size of around 91.9 billion U.S. dollars in 2030. The production capacity, worldwide is thus projected to significantly grow from almost 300 gigawatt-hours in 2018 to over two terawatt-hours in 2028 (Statista Research Department, 2023).

Urban mining aligns with the urgent need to address resource scarcity by recycling and recovering valuable metals from discarded batteries, minimizing the pressure on natural resources and mitigating environmental impact. Secondly, urban mining contributes to a sustainable waste management approach, reducing the burden of e-waste and promoting responsible disposal practices. Thirdly, it encourages the concept of a circular economy which emphasizes the importance of retaining the value of products and materials by promoting reuse, recycling, and resource recovery. Furthermore, it aligns with regulatory goals, complies with current environmental standards and responsible resource management.

Local Production of Rechargeable Batteries & WRB Management in Nigeria

The Federal Government of Nigeria, on October 12, 2023 inaugurated a $250 Million Lithium Battery factory in Endo Community, Nasarawa Local Government Area, Nasarawa State to encourage local production of batteries and to end the of exportation of raw materials. The plant will handle 18,000 metric tons of lithium per day with annual processing capacity of 4.5 Million tons providing 2,500 jobs directly and 15,000 jobs indirectly (Sunday, 2023)

One of the major challenges in waste management in Nigeria is the prevalence of informal waste disposal practices, such as open dumping and indiscriminate burning. The burning of waste releases harmful pollutants into the air, contributing to air pollution and posing serious health risks to residents, especially children and the elderly causing respiratory illnesses, skin conditions, and other health issues. Furthermore, the lack of public awareness regarding waste disposal, leads to littering and improper waste segregation. However, empowering local residents through education and capacity-building initiatives can help promote sustainable behavior change and mitigate the adverse impacts of informal waste disposal on both the environment and public health (Francis, 2024).

Despite the challenges, Nigerian cities are increasingly turning to innovative solutions to address the waste management crisis and pave the way for a cleaner and more sustainable future. One such approach is the implementation of integrated waste management systems used by the Lagos Waste Management Authority (LAWMA) initiative that encompass waste reduction, recycling, and resource recovery. This involves the promotion of waste segregation at the source, whereby households and businesses separate recyclable materials from non-recyclables. This reduces the volume of waste sent to landfills and facilitates the recycling process, thereby conserving valuable resources and mitigating environmental pollution. By embracing innovative solutions, fostering collaboration, and promoting civic responsibility, we can overcome these challenges and pave the way for a future where waste is no longer a burden but a valuable resource for sustainable development (Francis, 2024).

Review of Options in WRB Recycling

To ensure a circular economy and protect the environment, collection and recycling of WRB should be prioritized. This starts with collection and pre-treatment of WRB. The ultimate goal of pretreatment is to separate as much as possible, the components of the battery, so these materials do not interfere with the leaching process (Zhou *et al.*, 2021). It is necessary also to passivate the batteries (Bae and Kim, 2021). Pre-treatment reduces impurities, facilitates the subsequent recovery process and enhances overall efficiency (Nan *et al.*, 2005).

Discharge or Passivation: Battery discharge before dismantling prevents short-circuiting and self-ignition of battery rolls of anodes and cathodes (Hua *et al.*, 2020). Discharge is achieved by soaking the spent rechargeable batteries in a salt solution, with NaCl being the most popular. Na_2SO_4 is also common, but leaching efficiency has been shown to be as effective as NaCl (Du *et al.*, 2022).

Dismantling or Disassembly: In manual disassembly, wear masks, protective glasses, and gloves and adopt scissors, knives and pliers to disassemble the batteries into different components. Automatic dismantling involves the use of machines to carry out this process. In the process, different metal components of the battery cell including outer metal casing, plastic materials, separators, cathode, anode and other materials (glue, binders, electrolytes, wires, etc.) are separated and taken for further treatment (Du *et al.*, 2022; Yang *et al.*, 2021). As an alternative to dismantling, crushing and shredding the battery can be employed to make the process simple. Fires and emission of toxic gases are also dangers associated with crushing and shredding of batteries (Zhou *et al.*, 2023).

Component Separation: This may involve solvent dissolution which entails the use of alkalis or organic solvents to separate the components (Vascconcelos *et al.*, 2023). On the other hand, heat treatment using decomposition temperature of 350^{o}C-600^{o}C can be applied. Researchers often apply organic solvents to dissolve binders such as dimethyl formamide (DMF), N-methyl-2-pyrolidine (NMP), dimethyl sulfoxide (DMSO), ethanol and ionic liquids.

Processing/Extraction Methods for WRBs

Pyrometallurgy (Thermal Processing): Pyrometallurgy (thermal processing) is a high temperature (500 ^{o}C – 1000 ^{o}C) thermal treatment which converts metal-containing battery components into metallic alloy (Liu, *et al.*, 2023). Here, metals are converted into metal oxides. The pyrometallurgical process involves three main steps including pre-heating, plastic burning and metal reducing (Zhou *et al.*, 2021). Although pyrometallurgical process is industrially viable for large scale recycling of spent batteries (Li-ion, Li-polymer and Ni-MH), it shows poor perfornance towards lithium recovery. Other drawbacks of pyrometallurgy are high temperature and energy consumption, high capital cost (Roy *et al.*, 2021), hazardous gas emissions (Liu *et al.*, 2023) and high cost of recovering elements from slag.

Hydrometallurgy (Aqueous Processing): In hydrometallurgical method (aqueous processing), the valuable metals present in the battery are dissolved into a liquid at low temperature of about 60 ^{0}C, followed by separation and purification to recover valuable metals (Bae and Kim, 2021). In the metal leaching, various types of inorganic acids (HCl, HNO_3, H_2SO_4 and H_3PO_4) or alkaline e.g. (NaOH) are employed (Du *et al.*, 2022; Chen and Ho, 2018). It results in recovery of highly pure-grade Li but it produces a high amount of waste water which could damage the receving water bodies if discharged without proper treatment (Du *et al.*, 2022). In hydrometallurgical process, H_2O_2 is mostly used as a reductanct (Bae and Kim, 2021).

Bioleaching (Bio hydrometallurgy): Bioleaching is a microbial-based process used in the mining industry to extract valuable metals from ores and concentrates (Zhou *et al.*, 2021 Specific types of bacteria or microbial consortia such as *Acidithiobacillus ferroxidans* or *Acidithiobacillus thiooxidans* are selected for their ability to selectively leach metals from the battery components (Roy *et al.*, 2021). These microorganisms are often acidophilic, meaning they thrive in acidic environments, which is suitable for bioleaching. Fungi such as *Aspergillus niger* can also be used (Biswal and Balasubramanian, 2023; Zhou *et al.*, 2021). The metal-rich battery components are exposed to the selected bacterial culture and a suitable leaching solution. The bacteria then interact with the metal components, facilitating the dissolution of valuable metals into the solution.

Electrochemical Extraction: This method can achieve high recovery efficiency without producing impurities. When a potential is provided by the external energy source and applied to the two electrodes of the electrolyser, a redox reaction of ions in the leaching solution is induced which results in the reduction of metal ions to metal on the cathodes (Zhou *et al.*, 2021

Environmental Considerations and Potential Risks of WRB Mismanagement: Improper disposal of waste rechargeable batteries can lead to the release of toxic chemicals and heavy metals into the air, soil and groundwater, posing great risk to plants, animals and humans when they spread through large areas, potentially entering the food chain leading to diseases such as cancers, diseases of the central nervous system, kidney disorders, respiratory diseases, visual impairments, nausea, retarded cell growth, impairment of the reproductive system, cardiac arrest, etc. (Bolan *et al*., 2021; Melchor-Martinez *et al*., 2021). Recycling, which helps to reduce the environmental pollution caused by the improper handling of these WRBs has some demerits such as the emission of harmful gases from pyro metallurgy and the production of harmful waste during hydrometallurgy (Bae and Kim, 2021). Rechargeable batteries can pose a fire hazard if not properly handled. To mitigate these environmental hazards, it’s essential to promote battery collection programs to encourage proper disposal, increase public awareness about the environmental impacts of WRBs and the importance of recycling (Nnorom and Osibanjo, 2009).

CONCLUSION AND RECOMMENDATIONS

The improper management of these waste batteries in Nigeria has the tendency of exposing residents and the entire ecosystem to health hazards. However, the implementation of a well-coordinated management system can reduce the level at which large doses of toxic chemicals are released into the environment. Implementation of Extended Producer Responsibility, introduction of an effective collection strategy and application of environmentally sound management and metal recovery practices will make for resource conservation and generate a lot of money (foreign exchange) at the mineral market, thereby contributing to circular economy and economic growth.

Individuals, companies and government can invest in resource recovery by siting local recycling industries. This can enhance job creation, reduce environmental pollution and generate huge foreign exchange. Extended Producer Responsibility (EPR) laws that hold electronics manufacturers responsible for the entire life cycle of their products including collection, recycling and disposal of electronic waste should be implemented. Advance Recycling Fee (ARF) can be introduced. Products should be designed for durability, reparability and recyclability as well as promoting reuse to extend their lifespan. This helps to promote the principles of circular economy. Training programs and capacity-building procedures, recycling techniques and environmental regulations should be invested in.

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Full Length Research Paper

PHYSICOCHEMICAL QUALITIES AND MINERAL CONTENTS OF BOREHOLE WATER FROM UMUANA, UMUAHIA NORTH L.G.A, ABIA STATE

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ABSTRACT

The annual mean variation in the physicochemical quality and mineral content of borehole water obtained from Umuana area in Umuahia North Local Government Area of Abia State, Nigeria was studied. Standard methods of analyses were adopted in the study. From the results, the average pH values ranged from 6.09 to 7.24. These values were found to be within the standard permissible limits as stipulated by NSDWQ and WHO. The colour intensity of the water sample had higher values during dry the seasons (Nov. to Feb.) and lower values during the wet seasons (March to Oct). The values for turbidity (0.112 to 2.194 NTU), hardness (31.98 to 186.12 mg/L), fluorides (0.069 to 0.477 mg/L), chlorides (14.00 to 44.31 mg/L), nitrates (0.427 to 1.540mg/L), sulphates (0.920 to 2.240mg/L), ammonium ions (1.08 to 2.146mg/L), BOD (1.160 to 7.280 mg/L), DO (1.057 to 10.120 mg/L) were found to be within the permissible limits prescribed by WHO and NSDWQ with the exception of phosphate (0.022 to 1.056 mg/L) which showed slight deviation in the rainy seasons; Mar/April and May/June. All other metal ions such as calcium, magnesium, potassium, aluminum, sodium fell within the permissible limits as stipulated by NSDWQ and WHO. The values obtained for the heavy metals: copper, zinc, chromium, iron, nickel and lead were found to be below the standard permissible limits for the various metals except for cadmium, which exceeded the WHO limit. The results suggest that Umuanna borehole water is free from the toxicity of copper, zinc, chromium, iron, nickel and lead but susceptible to phosphate and cadmium toxicity.

Keywords: Borehole, water, physicochemical, heavy metal, quality

INTRODUCTION

Water is an essential factor that has multipurpose functions for both living and non-living things. Water is found mostly in oceans and other large water bodies having about 1.6% of water below ground. The oceans hold about 97% of the surface water on earth, with the other 3% being distributed throughout lakes, streams, rivers, ponds, seas, springs and underground. These water bodies are threatened by pollution as a result of increased human population, industrialization, agricultural practices and human influence. Globally, an estimated 1.10 billion people get water from lakes, rivers and open wells (WHO/UNICEF, 2008) which is usually not very safe for human consumption. According to Hutton and Chase (2018) unsafe drinking water quality accounts for 80 percent of illness in underdeveloped areas. Thus, lack of safe

drinking water supply, basic sanitation and hygienic practices are associated with high morbidity and mortality rates from excreta related diseases. Water-borne pathogens infect around 250 million people each year resulting in 10 to 20 million deaths annually across the globe. The provision of good quality water is often regarded as an important means of improving health care system. Clean water is such rare resource in the world that only a tiny fragment of the aquatic is available as fresh water. The major sources of water we use are mainly from surface and underground waters (Onwughara *et al*., 2012). The ground water is a major and important source of water for domestic, life stock, industrial and agricultural activities globally (Shivasharanappa *et al.*, 2020). Quality drinking water is essential for all forms of life. Drinking unsafe or contaminated water affects human health due to the presence of various dissolved chemical constituents which get into the water through various processes emanating from human activities, natural influence, animals and in addition to biological processes (Abida and Harikrishna, 2008). Depending on their levels, which are impacted by seasonal variations, the physical and chemical properties of ground water also have an impact on its quality (Likambo, 2014). The fact that water is life to every living organism implies that portable water devoid of contaminants that affects health of the organism is made accessible and available to all. Most pathogens are most commonly spread
through drinking water (Saati and Faidah, 2013). .
This study therefore, focuses on the physicochemical properties and mineral contents of water from boreholes within Umuana area in Umuahia North Local Government Area of Abia State, Nigeria to ascertain the quality.

MATERIALS AND METHODS

Sample Collection: The water samples were collected from six different commercial boreholes within Umuana Community using previously washed 2L polyethylene sample bottles. The water samples were collected bi-monthly over a period of twelve months starting from July/August, 2022 to May/June, 2023 covering both the rainy and dry seasons. The water samples from the six boreholes were pooled together to form a representative water sample for each of the months within the area.

Methods of analyses: Turbidity (NTU) and colour were determined using the various methods described by Skandaraja (2015). Dissolved Oxygen (DO) and Biological Oxygen Demand (BOD) were determined using the titrimetric method (Wrinkler) as clearly described by Dubey and Maheshwari (2004). Chemical Oxygen Demand was carried out using closed reflux method as described by Ademoroti (1996). Nitrates, fluorides, ammonium ion and phosphates were determined by spectrophotometric method as described by Tan *et al.* (2011). Chloride was determined by argentometric titration method as described by Greenberg *et al.* (1992). The pH and heavy metals were determined using various methods described by APHA (1998). Sulphate was determined by turbidimetric method as described by Sharma and Kaur (2016). Total hardness, calcium, magnesium, potassium and sodium were determined using various titrimetric methods as described by APHA (2005).

RESULTS AND DISCUSSION

Table 1 shows the results of the bimestrial seasonal variations in the physicochemical properties of the underground water samples derived within Umuana, in Umuahia North Local Government Area, Abia state, Nigeria.

The pH values range from 6.09 ± 0.9150to 7.24 ± 0.0300. These values are within the standard permissible limits of 6.0 – 9.0 (NSDWQ, 2017). However, except for the pH value of the water in July/August, there is a slight shift at the lower pH range of the water for the other months when compared to the standard permissible limit of 6.5 to 8.5 (WHO, 2018). These slight shifts account for the higher concentrations of dissolved acid salts which usually occur mostly during the dry season of the year (Amangabara and Ejenma, 2012). The colour intensities of the water samples show higher values during dry season (Nov. to Feb.) due to higher dissolved solids originating from inorganic salts and organic compounds and lower values during wet season (March to Oct) subsequent to dilutions from rainfall. The absence of colour could indicate purity of a water sample as stipulated by WHO (2018). The turbidity values (0.112 ± 0.0010 -2.384 ± 0.0072) fall within the permissible limits prescribed by WHO, 2018 (5.0 – 10.0 NTU) and the NSDWQ, 2017 (5.0 NTU) suggesting that the water samples across the seasons contain lower level of suspended solids. The mean value of hardness of the water samples ranged from 31.98 ± 1.0889 to 186.12 ± 7.206 mg/L. These values fall within the acceptable limits of WHO (2018) standard (100 – 250 mg/L).

The borehole water sample in July/August has the peak value (186.12 ± 7.206 mg/L) of hardness. The result reveals that hardness of wter is more prominent during wet season than in the dry season. The mean BOD values for the whole season range from 1.160 ± 0.0070 to 7.280 ± 0.2905 mg/l. These values fall within the acceptable limit of < 10.0 mg/l (NSDWQ, 2017).

The mean values for ammonium ion concentration range from 1.240 ± 0.0148 mg/l to 2.146 ± 0.0091 mg/l. The values fall within the permissible limit throughout the whole year. The mean values for the nitrate concentrations range from 1.240 ± 0.0148 mg/l to 2.146 ± 0.0091mg/l which are below the permissible limit 50 mg/l for nitrate ion (WHO, 2018). Nitrates are essential plant nutrients, but in excess amounts they can lead to significant problems to water quality. In addition, with phosphorus, excess amounts of nitrates can increase the tendency of eutrophication which causes sporadic increases in the growth of microbes which negatively affect BOD, COD and DO levels in the water sample (APHA, 1992).

However, the values in March/April (7.280 ± 0.2905 mg/l) and May/June (6.940 ± 0.1179 mg/l) are higher than the WHO (2018) acceptable standard limits for drinking water. This spike in the BOD can be accounted for by increase in rainfall and humidity which increase biochemical activities of microorganisms in water, thus causing an increase in the BOD. The mean COD values range from 0.906 ± 0.0806 to 403.33 ± 1.113 mg/l. However, the deviations from the standard from March/April through May/June imply that the underground water is at risk of being unsafe for drinking during these periods of the year. The reason for this could be due to anthropogenic activities within these periods of the year. COD values are higher between May and June which falls between the end of the dry season and the early periods of the wet season.

The mean values for dissolved oxygen (DO) range from 1.635 ± 0.0056 to 3.479 ± 0.372 mg/l. The threshold limit for DO is set at > 4.0 mg/l (WHO, 2018) for drinking water.

The DO, as well as the BOD and COD, show lower values which are below the permissible limit for drinking water except for the month of Nov/Dec which shows higher values of dissolved oxygen, suggesting a better water quality during these periods.

The mean values of chlorides range from 14.00 ± 10.392 to 44.31 ± 0.6755 mg/l. These values are seen to fall within the permissible limits of < 100 mg/L (NSDWQ, 2017) and < 250 mg/L (WHO, 2018) for drinking water. The dip value in chloride observed around May/June during the wet season can be attributed to an increased dilution of dissolved chloride contents of the water. The mean fluoride values range from 0.069 ± 0.0026 to 0.477 ± 0.5852 mg/l.

Table 1: Mean Values of the Physicochemical Properties of Borehole Water sample within Umuana Community.

	Jan/Feb	Mar/Apr	May/Jun	Jul/Aug	Sept/Oct	Nov/Dec	p-value	NSDWQ (2017)	WHO (2018)
pH	6.26 ± 0.3704	6.09 ± 0.9150	6.28 ± 0.6144	7.24 ± 0.0300	6.32 ± 0.0624	6.10 ± 0.0265	0.09291	6.0-9.0	6.5-8.5
Turb (NTU)	2.194 ± 0.0987^{b}	2.384 ± 0.0072^{a}	0.546 ± 0.0934^{d}	0.536 ± 0.0075^{d}	0.112 ± 0.0010^{e}	0.802 ± 0.0020^{c}	5.96E-15	5	5.0-10.0
T-Hard (mg/L)	31.98 ± 1.0889^{e}	69.98 ± 1.0018^{d}	79.68 ± 0.606^{cd}	186.12 ± 7.206^{a}	149.98 ± 9.669^{b}	90.12 ± 0.9035^{c}	8.13E-13	150	100-250
BOD (mg/L)	1.538 ± 0.0104^{c}	7.280 ± 0.2905^{a}	6.940 ± 0.1179^{a}	1.160 ± 0.0070^{c}	2.150 ± 0.0265^{b}	1.411 ± 0.0026^{c}	2.34E-16	10	6
COD (mg/L)	0.906 ± 0.0806^{f}	403.33 ± 1.113^{a}	225.68 ± 0.52^{b}	39.51 ± 0.9850^{d}	48.06 ± 1.9500^{c}	35.140 ± 0.880^{e}	2.20E-16	-	20-200
Cl^- (mg/L)	31.90 ± 1.030^{ab}	42.54 ± 1.0313^{a}	44.31 ± 0.6755^{a}	14.00 ± 10.392^{c}	39.00 ± 1.000^{ab}	28.36 ± 0.6161^{b}	1.68E-05	100	250
F^- (mg/L)	0.084 ± 0.0072	0.084 ± 0.0072	0.014 ± 0.0020	0.477 ± 0.5852	0.122 ± 0.0026	0.069 ± 0.0026	0.2303	1	1.5
PO_4^{3-}(mg/L)	0.173 ± 0.0134^{c}	0.534 ± 0.0087^{b}	1.056 ± 0.0072^{a}	0.052 ± 0.0069^{d}	0.022 ± 0.0053^{e}	0.056 ± 0.0017^{d}	2.20E-16	-	0.3
Mg^{2+} (mg/L)	4.86 ± 0.3422^{d}	4.86 ± 1.2439^{d}	9.73 ± 1.1377^{b}	7.30 ± 0.0500^{c}	17.02 ± 0.9902^{a}	7.30 ± 0.0100^{c}	3.28E-09	-	50
K^+ (mg/L)	0.655 ± 0.0132^{a}	0.481 ± 0.0095^{b}	0.525 ± 0.033^{ab}	0.611 ± 0.1005^{ab}	0.490 ± 0.0178^{b}	0.510 ± 0.0026^{b}	0.001843	-	1.1
Al^{3+} (mg/L)	0.016 ± 0.0026	0.009 ± 0.0026	0.010 ± 0.0100	0.114 ± 0.0053	0.009 ± 0.0036	0.335 ± 0.438	0.2342	0.2	0.2
Col (ppm)	20.26 ± 1.051^{ab}	20.84 ± 2.1029^{a}	19.50 ± 1.712^{ab}	19.20 ± 1.3865^{ab}	16.20 ± 0.9000^{b}	20.00 ± 0.5575^{ab}	0.01936	Colorless	colorless
DO (mg/L)	1.138 ± 0.0096^{c}	3.500 ± 1.0965^{b}	4.000 ± 0.1411^{b}	1.057 ± 0.0147^{c}	1.060 ± 0.0458^{a}	10.120 ± 0.925^{c}	1.63E-09	-	>4
NH_4^+(mg/L)	1.526 ± 0.0053^{b}	2.146 ± 0.0091^{a}	1.320 ± 0.0125^{c}	1.539 ± 0.0805^{b}	1.084 ± 0.0017^{d}	1.240 ± 0.0148^{c}	1.31E-12	-	2
NO_3^- (mg/L)	1.540 ± 0.0180^{a}	1.246 ± 0.0055^{b}	1.108 ± 0.0045^{c}	1.486 ± 0.0318^{a}	0.427 ± 0.0976^{d}	1.028 ± 0.0026^{c}	7.05E-12	50	50
SO_4^{2-}(mg/L)	1.173 ± 0.008^{ab}	1.067 ± 0.0095^{ab}	2.240 ± 1.0000^{a}	0.920 ± 0.0819^{b}	2.049 ± 0.01^{ab}	1.158 ± 0.0017^{ab}	0.006768	100	250
Ca^{2+}(mg/L)	12.02 ± 0.2425^{e}	20.04 ± 0.9700^{d}	28.10 ± 0.9550^{b}	28.06 ± 0.9901^{b}	36.07 ± 1.6803^{a}	24.05 ± 0.965^{c}	7.13E-11	70	75
Na^+ (mg/L)	0.305 ± 0.1025^{a}	0.296 ± 0.0087^{a}	0.256 ± 0.0060^{a}	0.200 ± 0.0265^{a}	0.221 ± 0.0860^{a}	0.232 ± 0.0026^{a}	0.2099	200	200

Table 2: Mean Values of the Heavy metal Contents of the Borehole Water sample within Umuana Community.

	Jan/Feb	Mar/Apr	May/Jun	Jul/Aug	Sept/Oct	Nov/Dec	p-value	NSDWQ (2017)	WHO (2018)
Cd	0.103 ± 0.0056^{a}	0.021 ± 0.0026^{b}	0.022 ± 0.0026^{b}	0.015 ± 0.0043^{b}	0.018 ± 0.0046^{b}	0.014 ± 0.0052^{b}	4.89E-11	-	0.03
Cr	0.019 ± 0.0017^{b}	0.046 ± 0.0036^{a}	0.028 ± 0.0026^{ab}	0.020 ± 0.0026^{b}	0.010 ± 0.009^{b}	0.021 ± 0.0113^{b}	0.0003478	0.05	0.05
Cu	0.009 ± 0.0135^{c}	0.169 ± 0.0025^{a}	0.108 ± 0.0062^{b}	0.01 ± 0.0026^{c}	0.003 ± 0.001^{c}	0.019 ± 0.0053^{c}	2.26E-12	-	1.00-2.00
Fe	0.226 ± 0.001^{a}	0.015 ± 0.001^{c}	0.017 ± 0.0036^{c}	0.141 ± 0.0060^{ab}	0.189 ± 0.0527^{ab}	0.114 ± 0.0753^{bc}	5.05E-05	3.0	5.0
Zn	0.033 ± 0.0017^{a}	0.017 ± 0.001^{a}	0.023 ± 0.0026^{a}	0.031 ± 0.0046^{a}	0.026 ± 0.008^{a}	0.028 ± 0.01^{a}	3.27E-05	3.0	5.0
Pb	Traces	Traces	Traces	Traces	Traces	Traces		0.01	0.01
Ni	Traces	Traces	Traces	Traces	Traces	Traces		-	0.01

The values fall below the permissible limits of < 1.00 mg/l (NSDWQ, 2017) and <1.50 mg/l (WHO, 2018) indicating that the water samples require some remedial actions. The mean values of the phosphates range from 0.022 ± 0.0053 mg/l to 1.056 ± 0.0072 mg/l. The mean value of phosphates in the water sample for May/June is higher than the standard permissible limit of < 0.3mg/l for phosphates in drinking water (WHO, 2018). The mean values for the sulphates concentration range from 0.920 ± 0.0819 mg/l to 2.240 ± 1.0000 mg/l. These values are quite below the standard permissible limit (250 to 500 mg/l) for sulphates in drinking water (WHO, 2018). The low contents of sulphate observed in this study is an indication that there is little or no source of pollution of the groundwater from anthropogenic activities. However, the values of the sulphates in this study are comparable to the values reported by Etesin *et al.* (2021). The mean values of the calcium ion concentration range from 12.02 ± 0.2425 to 36.07 ± 1.6803 mg/l. These values fall below the permissible limit of 75 mg/l (WHO, 2018). This may be an indication that the water samples may not be prone to hardness or considered hazardous to human consumption due the lower concentrations of calcium ion.

It can be observed that calcium and magnesium have similar trends in their variation across the seasons as they have their peak values in September/October. The mean values of magnesium ion concentration range from 4.86 ± 1.2439 mg/l to 17.02 ± 0.9902 mg/l. These values fall below the permissible limit of 50 mg/l (WHO, 2018). This may be an indication that the water samples may not be prone to hardness due to the lower concentrations of magnesium. The mean values of potassium ion concentration range from 0.481 ± 0.0095 mg/l to 0.655 ± 0.0132 mg/l. These values fall below the permissible limit of 1.10 mg/l (WHO, 2018). Thus, the water may not pose any risk of health complications associated with potassium when consumed. The range of values for sodium ion, 0.200 ± 0.0265 to 0.305 ± 0.1025 mg/l, falls far below the permissible limit of 200 mg/l (WHO, 2018). Thus, the water may not pose any risk of health complications associated with sodium when consumed. However, higher concentrations of sodium are found around January/February. This may be due to the dry season period. It is worthy to note that sodium, potassium, calcium and magnesium levels correspond with lower total hardness observed during the study periods. The mean values of aluminum ion range from 0.009 ± 0.0026 to 0.335 ± 0.438 mg/l. The value of aluminium (0.335 ± 0.438 mg/l) in Nov/Dec. falls above the permissible limit of 0.200 mg/l (WHO, 2017). Iroha *et al.* (2020) reported a mean aluminium content of 0.22 ± 0.02 mg/l in water samples from Abakaliki Local Government Area of Ebonyi State. Aluminum in a very high dose can alter the normal function of blood–brain barrier (Lee, 2009; Bingham and Cohrssen, 2012).

The result of heavy metal contents (including cadmium, chromium, copper, zinc iron, nickel and lead) of the water sample is tabulated in tables 2.

The mean values for the heavy metals; chromium (0.010 ± 0.009 to 0.046 ± 0.0036mg/l) falls within NSDWQ (2017) and WHO (2018) standard limits while the values for copper (0.003 ± 0.001 to 0.169 ± 0.0025 mg/l), Zinc (0.017± 0.001 and 0.031 ± 0.0046mg/l) and iron (0.015 ± 0.001 to 0.226 ± 0.001 mg/l) are less than their various permissible limit. Nickel and Lead have only trace amounts. Considering the variability of the mean values of the heavy metals in the borehole water, it becomes necessary to conclude that the water samples from the study area, though good for consumption still requires constant monitoring to avoid contamination and hazardous effect to humans when consumed.

CONCLUSION

The study on the variations in the physicochemical properties and heavy metal contents in the borehole water from Umuana area in Umuahia North Local Government area has revealed generally that borehole water from Umuanna area is safe for consumption. Most of the physicochemical properties and the mineral contents were found to fall within the World Heath Organizational Standard limit for drinking water (WHO, 2018) and the Nigerian Standard for Drinking Water Quality (NSDWQ, 2017). Such values include; pH, turbidity, total hardness, chloride, nitrates, sulphates, calcium, magnesium, potassium, sodium and aluminum. The values for the BOD, COD and DO observe between March/April and May/June suggest a possible risk for microbial contamination within these periods. The heavy metals like chromium, copper, zinc and iron were found to be below the permissible limits. Nickel and lead were found in trace amounts. However, the value cadmium was found to be a little above the permissible limit for drinking water. Thus, it can be deduced that the borehole water from Umuana area is safe for consumption and other domestic purposes, though with frequent monitoring to avoid contamination through anthropogenic activities.

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