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Edo State University Uzairue (EDSU)
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SN 1 THE IMPACT OF POULTRY WASTE ON BIOREMEDIATION OF SOIL CONTAMINATED WITH SPENT ENGINE OIL

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Abstract

Bioremediation is the use of living organisms and their enzymes to return contaminated environment to their original condition. This study determined the bioremediation effects of poultry dung (PD) on spent engine oil (SEO) contaminated soil. Loamy soil were sun-dried and divided into 5 different sacks (2 kg each), labelled (control I, II and treatment I, II and III) respectively. Each sample except control I was mixed vigorously with 400 ml SEO, PD was sun-dried, grinded into powder, constituted into 0.2 g/ml, 0.5 g/ml and 0.75 g/ml and then mixed with treatment I, II and III respectively. Physicochemical, elemental (CHN) composition, microbial enumeration (using gram staining, catalase and coagulase activities) and ecotoxicity were determined. At the end of the experiment, treatment III was found to have the highest pH value; all the samples had temperature values within 31°C. Microorganisms observed include *Staphylococcus aureus*, *E. coli* and *Bacillus* among others. Catalase and coagulase activities were observed in all samples. Treatment III was found to have the highest values for CHN and highest proximate composition % when compared to other samples. Control I and II were found to have the lowest and highest % of Nitrate reductase respectively. Treatment III was found to have the highest % of Chlorophyll while Control II had the lowest. It can be concluded from this study that poultry dung is an effective source of bioremediant.

Keys: Bioremediation, microbial enumeration, Poultry dung, spent engine oil

1.0 INTRODUCTION

The human population and rapid demand of industrial expansion for the economic development are increasing continuously day by day and putting a pressure on our decreasing natural resources (air, water, and land). Thus a global rise in environmental pollution has been seen in the past few decades due to the increasing population, fast industrialization, increasing anthropogenic activities, and unregulated and unsafe agricultural activities, which have caused the accumulation of hazardous waste, such as plastic, agricultural, domestic, rubber, metallic, and industrial waste, in the environment (Megharaj *et al.*, 2011). This hazardous waste may contain heavy metals, petroleum oil, pesticides, hydrocarbons such as aliphatic, aromatic, and polycyclic aromatic hydrocarbons, nitroaromatic compounds, chlorinated hydrocarbons such as polychlorinated biphenyls (PCB) and perchloroethylene, organophosphorus compounds, organic solvents (phenolic compounds), and phthalates (Megharaj *et al.*, 2011). More than 450 million kilograms of toxic wastes are discharged into the air, water, and land on a global scale according to the third world network reports (Tiwari and Singh, 2014). The contaminated ecosystem or environment adversely affects the soil composition (structure and fertility), soil microbial growth and metabolic activities, plants and aquatic organisms, and the biogeochemical cycle of the elements present in the environment that further affects the ecosystem and its functioning as well as human health. As the quality of life is intricately related to the quality of the environment,

there is a global need to improve and sustain the quality of the environment. Some advancement in remediation techniques has been seen in terms of the cost of the techniques, their eco-friendly approach, and effectiveness to restore the polluted environment (Harekrushna and Kumar, 2012).

2.0 Materials and methods

2.1 Soil Materials

Loamy soil was gotten from Kwara state polytechnic campus at the back of Institute of Environmental studies, Ilorin Kwara State on 11th of March, 2023.

2.2 Poultry Dung

Poultry dung was gotten from Oke-Oyi Ilorin Kwara State on 27th of March 2023.

2.3 Spent Engine Oil

Spent engine oil was gotten from Offa garage at Automobile shop.

2.4 Plant Material

Tefairia occidentalis seeds were gotten from Challenge at Ilorin Kwara State on 9th of April, 2023. The seeds were gotten from the same source and their viability was tested before planting.

2.5 Chemicals, Reagents, Nutrient Agars and other Materials

Potato dextrose agar(PDA), lactophenol, phenol red indicator, Normal saline, mercury chloride, methylated spirit, peptone water agar, starch agar, 70% ethanol, antibiotics (gentamicin), distilled water, Nutrient agar (NA), liquid soap, Hydrochloric acid, urea fertilizer, hydrogen peroxide were all obtained from Microbiology Laboratory.

3.0 RESULTS AND DISCUSSION



Plate 1: Germination of *T. occidentalis* for Control 1



Plate 2: Germination for Control 2



Plate 3: Germination of *T. occidentalis* for Treatment 1



Plate 4: Germination of *T. occidentalis* for Treatment 2 Source: (Self)

The soil, oil and bioremediant on the first day were found to be slightly acidic and alkaline respectively. In line with (Pichtel, 2007) the soil buffering capacity should be evaluated prior to application of

amendments. Microbial metabolism is substantially affected by temperature. Most microorganisms grow well in the range of 10 to 38°C (Rike, 2008). Although temperatures within the top 10 m of the subsurface may fluctuate seasonally, subsurface temperatures down to 100 m typically remain within 1° to 2°C of the mean annual surface temperature suggesting that bioremediation within the subsurface would occur more quickly in temperate climates (Freeze *et al.*, 1979). Poultry was observed that the pH of Treatment III was very high both after contamination and during bioremediation. The pH increased from slightly acidic to alkalinity across all the Controls and Treatments. The pH range in which most bioremediation works most efficiently is nearly 5.5 to 8.0. Additionally, as biological processes proceed in the contaminated media, the pH may shift and therefore must be monitored regularly. The pH can be adjusted to the suitable range by the addition of acidic or basic substances (i.e., mineral acids or limestone, respectively). However changes in soil pH will influence dissolution or precipitation of soil metals and may increase the mobility of hazardous materials. Therefore, the soil buffering capacity should be evaluated prior to application of amendments (Pichtel, 2007). The average temperature for all the samples from Control I II, Treatment I, II and III was 31°C. Thus this result corresponded to Freeze *et al.* (2002) where most microorganisms grows well in the range of 10 to 30°C. Also supported by Rike, (2008), microbial metabolism is substantially affected by m

At the end of microbial staining, microorganisms majorly dominated were *cocci* (*Staphylococcus aureus*), *rod* (*E. coli*), *Spirilla*, *Diplococcic*, *Baccilla* and *Spirilla cocci*. Gram staining differentiates bacterial base on the differential staining properties of bacterial cell wall. Bacterial with thick peptidoglycan layer stains blue to purple and are treated as gram positive, while bacterial with thin peptidoglycan can layer stains red to pink and are treated a gram negative (Smith *et al.*, 2005).

CONCLUSION

It can be concluded from the result of the study that poultry dung was an effective bioremediant of soil contaminated with spent engine oil, having decrease the acidity level to nearly alkaline. The growth of the *Telfairia occidentalis* seeds in the samples shown it ability to

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SN 2 MECHANOCHEMICAL SYNTHESIS AND CHARACTERIZATION OF ZINC COORDINATION POLYMER USING N-DONOR LIGAND

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ABSTRACT

Synthesis of metal-organic frameworks using 4,4-bipyridine ligand via mechanochemical and solvent-based methods is reported. The mechanochemical product was obtained by grinding a stoichiometric amount of zinc acetate with 4,4-bipyridine. Solvent-based synthesis of the MOFs was done by reacting zinc acetate with 4,4-bipyridine at 700°C in methanol using the reflux method. The mechanochemical product was characterized by comparing the melting, elemental analysis, and spectroscopic data (IR, UV-visible, and ¹H-NMR). Metal ion coordinates through the nitrogen of bipyridine and two oxygen of the carbonyl and hydroxyl group of carboxylate ligand. The MOFs exhibit polymeric chains.

Keywords: Mechanochemical, 4,4bipyridine, solvent-based metal-organic frameworks

1.0 Introduction

The evolution of a new class of coordination polymers known collectively as metal-organic framework materials (MOFs) has emerged in recent years (Chenet *al*, 2007). Coordinate bonds form these materials from multidentate ligands to mono- or polynuclear metal centers. They may have extensive open-framework structures, resulting in the inclusion of guest species (usually solvent) during synthesis. These species can be removed via desolvation, and the resulting empty framework may maintain structural integrity, giving a porous MOF material with a sizeable apparent surface area. The original solvent or other guest molecules can then be adsorbed into this porous structure (Freiberg and Zhu, 2004). The MOF connectivities and topologies are controlled by the coordination preferences of metal and ligand, with the templating role of pore species being less pronounced in structure direction than it is in zeolitic aluminosilicate and metallophosphate systems governed by template-directed assembly of purely tetrahedral building units. Porous media have potential applications in many fields, including separation, heterogeneous catalysis, and gas storage. Porous networks are also of interest because of adsorption properties, where confined species may alter the physical properties of the host material (Qiu *et al.*, 2007).

2.0 Experimental

All materials were used as received from commercial sources (Sigma-Aldrich or Fisher Scientific); solvents were purified and dried according to standard methods.

2.1 Mechanochemical Synthesis of MOFs [Zn(OAc)₂(bipy)₂] 1a

4,4-bipyridine (0.156g) and Zincacetate (0.109g) were weighed into a mortar and pestle previously washed and dried. The reactants were ground for 30 minutes to a fine paste at room temperature.

2.2 Solvent based Synthesis of [Zn(bipy)₂(OAC)₂] 1b

A solution of 4,4-bipyridine (0.156 g) in methanol was added to a clear colorless solution of zinc acetate (0.109 g) in methanol. The resulting solution was refluxed for two hours at 700°C. A white precipitate

was formed and evaporated for three days at room temperature. A white crystal was obtained as a product,

3.0 Results and Discussion

Metal-organic frameworks of $[\text{Zn}(\text{bipy})_2(\text{OAC})_2]$ 1a

The mechanochemical product was characterized by comparing analytical data, spectral data, and XRPD with those of free ligands and solution-based products. The elemental analyses (CHN) were found to be consistent with the formula unit of the product. It also appears in our result that both methods (mechanochemical and solvent-based) gave similar spectral data compared to the free ligand bipyridine. The comparison of solubility and melting point of the sample synthesized via the two methods shows that there is no difference in their value. It can be seen from Table 1 that the product of mechanochemical is white powder, while the solvent-based product gives off-white crystals. The products are non-hydroscopic. The percentage yield of the mechanochemical product is higher than the solvent-based product, and the melting point of the complexes is higher than the parent ligand.

FT-IR spectroscopy result of $[\text{Zn}(\text{bipy})_2(\text{OAC})_2]$ (1a) and (1b)

Figure 1: compares the FT- IR. spectrum of the free 4, 4 bipyridine ligand with the MOFs obtained via mechanochemical and solvent-based methods.

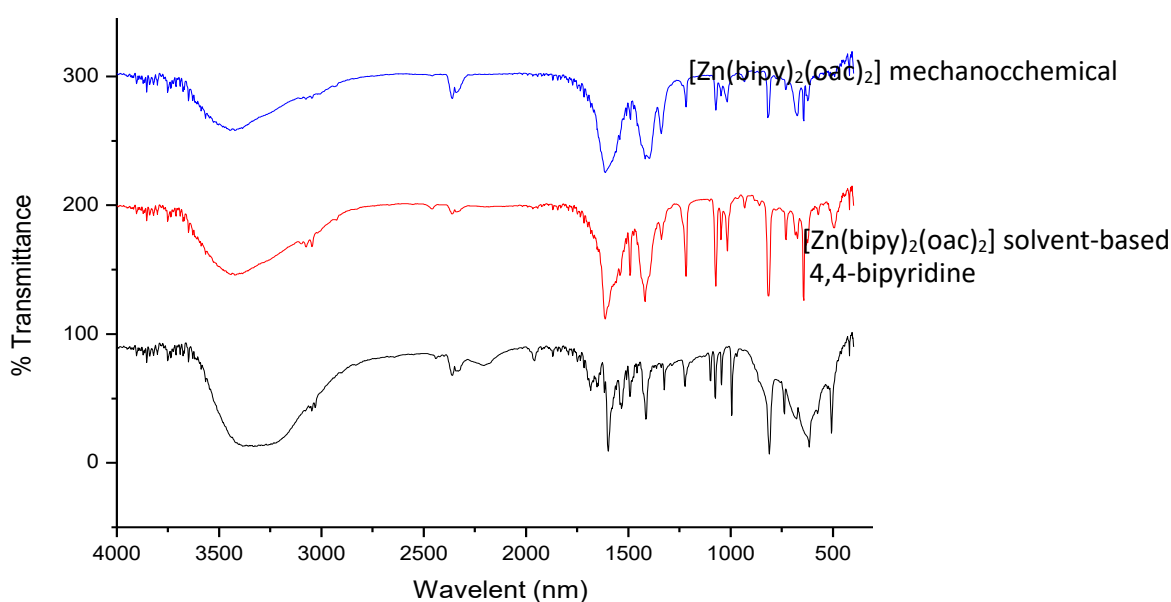


Figure 1. Comparison between the FT- IR. spectrum of the free 4, 4 bipyridine ligand with the MOFs obtained via mechanochemical and solvent-based methods.

FT-IR spectrum includes bands at 1597cm⁻¹, corresponding to the stretching vibrations of the C=N group, and the bands in the range 1617-1325cm⁻¹ were associated with the pyridine ring stretching vibrations

In the solid-state I.R. spectra, MOFs [Zn(bipy)2(oac)2] 1a and 1b possess similar spectra for the V_{asy}(COO) and V_{sy}(COO) bands, supporting similar structures. The carbonyl asymmetric and symmetric stretching frequencies are observed at 1612cm⁻¹ and 1417cm⁻¹, respectively. The ΔV value (V_{asy}(COO) - V_{sy}(COO) = 195cm⁻¹) suggests that the acetate group is bidentatively coordinated to the central metal ion.

The positions and separation between these frequencies are similar to those associated with classical carboxylate bridges [Cu-O-C-O-Cu]. These I.R. spectra results are consistent with the proposed structures of these MOFs in which two acetates are bridging two Zinc atoms and one bipyridine is coordinated as a monodentatively bind to each zinc atom.

The pyridine breathing frequently appearing at 995cm⁻¹ in the free ligand is shifted to 1014cm⁻¹ for the complex. This splitting proves the coordination of 4, 4-bipyridine to the metal atom by nitrogen.

UV-Visible Spectroscopy Result of 4,4-bipyridine ligand and its MOFs

The selected UV-visible spectral data of 4,4-bipyridine and 3a and 3b are shown in Table 3. It can be seen in Table 3 that the UV visible of both MOFs synthesized via the two methods are identical. The UV-visible spectral of 4,4-bipyridine presents one absorbance band at 268, assigned to π - π^* transition within the organic ligand. The two compounds in the visible region produced broadband at 619 and 616, respectively; this is attributed to the d-d transition.

Table 1: Selected UV-visible Spectroscopy data of 4,4-bipyridine and its MOFs

Ligand/MOFs	Wavelength(nm)	Energy(cm ⁻¹)	Absorbance	Assignment
4,4-bipyridine	268	37313	0.368	π - π^*
[Zn(bipy)2(oac)2]	619	16155	1.089	2Eg-2T2g
mechanochemical	637	15698	1.072	4T1g-4A2g
[Zn(bipy)2(oac)2]	619	16155	1.320	2Eg-2T2g
solvent base	637	15698	1.307	4T1g-4A2g

Table 1. above shows that UV-visible spectra of free oxalic, 4,4-bipyridine ligand in solid state form present one absorption band at 268 and 268nm assigned to π - π^* transition, respectively, for the two complexes. The visible region produced bands at 616 and 619 assigned to d-d transition (2Eg-2T2g), typical of octahedral geometry. This result agrees with those described by Sara et al. 109.

¹H-NMR Spectroscopy Result of [Zn(bipy)2(oac)2] [1a & 1b]

Figure 2 below shows the comparison of the H-NMR spectral of the mechanochemical product and solvent-based product of [Zn(bipy)2(oac)2] with the free ligand (4,4-bipyridine) are identical. The ¹H-NMR spectrum of the mechanochemical product after 30 minutes of grinding in the mortar with a pestle shows there is little or no change in the chemical shifts of each proton signal.

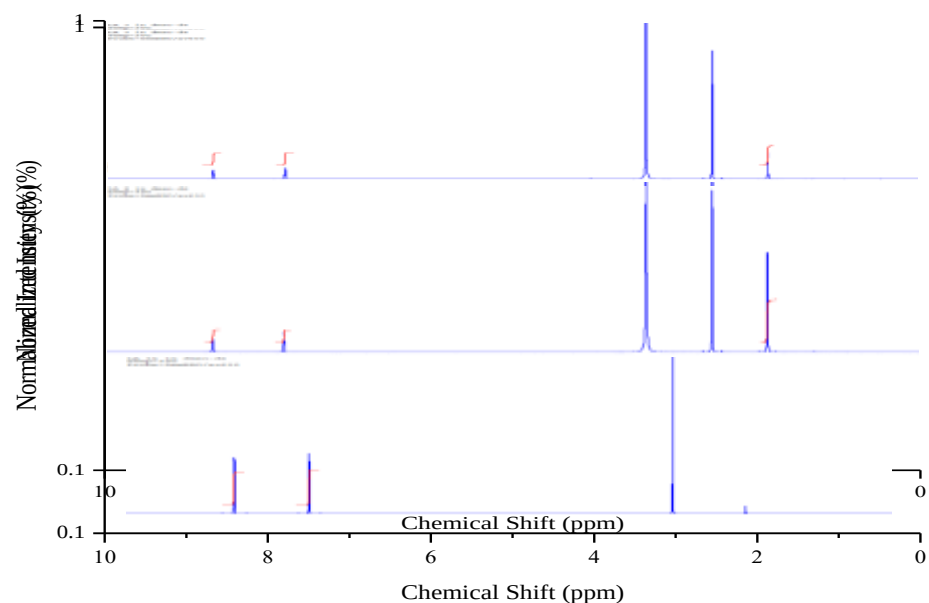


Figure 2 below shows the comparison of the H-NMR spectral of the mechanochemical product and solvent-based product of $[\text{Zn}(\text{bipy})_2(\text{oac})_2]$ with the free ligand (4,4-bipyridine)

Figure 4: Comparison of H-NMR spectral of mechanochemical product (3a) and solvent-based (3b) product of $[\text{Zn}(\text{bipy})_2(\text{oac})_2]$ with the free ligand (4,4-bipyridine)

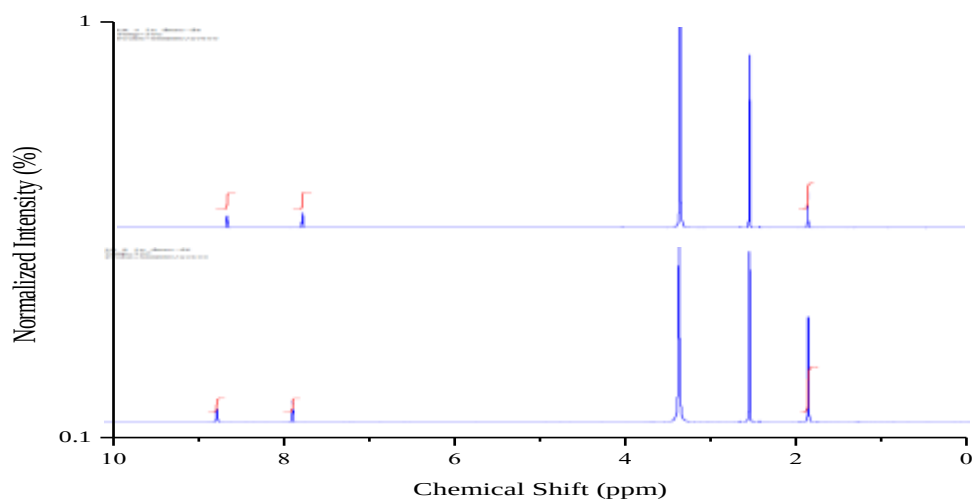


Figure 5: Comparison of H-NMR spectral of mechanochemical (3a) and solvent-based (3b) product of $[\text{Zn}(\text{bipy})_2(\text{oac})_2]$

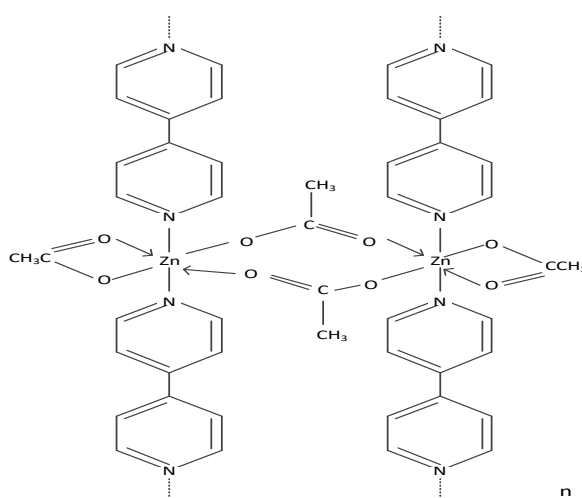
From the figure 4, it can be seen that the ^1H -NMR spectra of the complex synthesized via the two methods are similar but different from that of the free ligand. All the chemical shifts and the assignment of the individual ^1H resonance of 4,4-bipyridine and its MOFs in DMSO are listed in Table 14.

Table 2: Chemical shifts and the assignment of the individual ^1H resonance of 4,4-bipyridine and its MOFs in DMSO. [3a&3b]

Ligand/MOFs	C1-H	C2-H	Ca-H
4,4-bipyridine	7.81	8.72	-
[Zn(bipy)2(OAC)2]			
Mechanochemical 3a	7.85	8.74	1.82
[Zn(bipy)2(OAC)2]			
Solvent-based 3b	7.85	8.74	1.82

It can be seen from Table 3.10 that $^1\text{H-NMR}$ spectra of Zn(II)bipyridyl signals are slightly shifted downfield in comparison with the appropriate signals in the spectra of 4,4-bipyridine. A decrease in the chemical shifts in spectra of MOFs points to an increase in the screening of aromatic protons as a consequence of the circular current weakening. The differences in chemical shifts are 0.03-0.05ppm. The $^1\text{H-NMR}$ spectrum of 4,4-bipyridine in DMSO shows the appearance of duplets of proton signals at $\delta(\text{C1-H})$ 8.72ppm,d, and $\delta(\text{C2-H})$ 7.81ppm, The signals in the 7-8ppm range is typical of the hydrogen attached to the aromatic ring.

3.3 Figure 6: Proposed Structure of [Zn(bipy)2(OAC)2] MOFs [3a&3b]



Conclusion

Metal-organic frameworks of zinc acetate using the mechanochemical method have been achieved. The mechanochemical product was characterized by comparing elemental analysis, UV-visible spectrum, I.R., and H-NMR spectroscopy with the product obtained from the solvent-based method. The MOFs from the two different methods were identical, suggesting that the products are the same.

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SN 3 SENSORY PROPERTIES OF MANGO (*MANGIFERA INDICA L.*) FRUIT CV. 'BROKEN' AND 'DAUSHA' PRESERVED WITH 1-METHYLCYCLOPROPENE
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Abstract

The study was undertaken to determine the effect of 1-methylcyclopropene (1-MCP) and storage conditions on the sensory attributes of two mango cultivars namely Broken and Dausha grown in Gboko, Benue State, Nigeria. The two mango cultivars were harvested at the green-mature stage and treated with four concentrations of 1-MCP (0, 1000, 3000 and 5000 ppb) in closed air-tight plastic containers for 24 h. The samples were stored for 90 days at 11oC. Treatments were laid out in factorial arrangement in randomized complete design (RCD) with three replications. The results of the sensory evaluation of both treated and untreated mango samples showed that Dausha treated with 5000 ppb 1-MCP (D5) scored higher for flavour, texture and general acceptability than the other treatments (1000 and 3000 ppb). Relatedly Broken mango samples scored treated Dausha stored for more than 90 days while Broken for 75 days. The research findings clearly showed that 1-MCP treatment at reduced temperature can extend the shelf life and maintain the quality and sensory attributes of mango fruit for 90 days.

Key words: 1-methylcyclopropene, Mango fruit, sensory properties, Broken and Dausha mangoes

1.0 Introduction

The *Mangifera* is a tropical fruiting tree of the family *Anacardiaceae*. It has about 30 species worldwide. It is a tropical and sub-tropical fruit tree which originated in India and Burma [1]. Mango is a climacteric fruits which displays high postharvest losses due to its highly perishable nature thus, requires special postharvest treatments to extend its shelf life. It is one of the most popular fruits liked for its nutritional value, juice, flavour, fragrance and colour [2]. Due to these characteristics; it is known as the King of fruits in the Indian sub-continent [3].

Mango production has also increased in some countries like Asia, West Africa, Australia, South America and Mexico [4]. The annual mango production in Nigeria is estimated at around 8.5 million metric tonnes. The main mango-producing states in Nigeria include Benue, Jigawa, Plateau, Yobe, Kebbi, Niger, Kaduna, Kano, Bauchi, Sokoto, Adamawa, Taraba and Federal Capital Territory (FCT), Abuja [5].

There are about 1000 mango varieties grown worldwide, but the varieties common in Nigeria and particularly in Benue State include Hindi, Dausha, Peter, Julie, John, Broken and local mango [6]. Mango fruits are highly nutritious containing carbohydrates, proteins, fats, fibre, minerals and vitamins. The most common vitamins in mango are vitamin A (β -carotene), B1, B2 (riboflavin) and vitamin C (ascorbic acid) [7]. Because of these attributes, mango is highly demanded both locally and internationally. However, mango manifests high postharvest losses and hence short shelf life. This is due to the high endogenous and exogenous ethylene development which accelerates respiration, ripening and consequently maturity. This is followed by softening and senescence of the fruit, thereby decaying a few days after postharvest storage under ambient temperature [8]. To overcome these problems it is necessary to find techniques that would extend the shelf life of the fruit and maintain the quality. Therefore, the development of technologies to extend the postharvest life of mango fruit requires approaches aimed at blocking the ethylene receptor site. This subsequently leads to a delay in ethylene-dependent responses. Several methods/technologies are in use to inhibit ethylene for the

preservation of fruit and vegetables. Among these, 1-methylcyclopropene (1-MCP) is the most potent. 1-MCP is a gas at room temperature and pressure. The strength to which 1-MCP binds to the ethylene receptor cell is about 10 times that of ethylene itself and is more active at low concentrations and refrigerated/low temperatures. It has no detectable odour and has not been reported to have any toxic properties [9]. 1-MCP is known to have no residue within 24 hours of application [10]. It has been known to extend the shelf life and maintain the quality of various climacteric fruit such as apples, tomatoes, kiwis, bananas and melons. This is achieved by blocking the ethylene receptor sites, thereby preventing the binding of endogenous and exogenous ethylene and its negative effects [11]. Mango is among the crops registered for 1-MCP treatment [12] and positive effects of 1-MCP on several cultivars have also been reported [13]. The application of 1-MCP at different concentrations, storage durations and refrigerated temperatures to extend shelf life and delay quality deterioration processes in tropical fruit has also been reported [14]. The use of 1-MCP to preserve mango had been on cultivars that are not found in Nigeria most specifically in Benue State. In Nigeria, there is limited information and experience in the postharvest handling of mangoes in general particularly in the use of 1-MCP as postharvest technology to extend the shelf life of mangoes. Also, there have been no standard refrigerated systems in the Nigerian mango industry. Hence, there is a dearth of information about the performance of our local mango cultivars under standard refrigerating systems during extended storage/shipping conditions. Therefore, the present research was initiated to evaluate the separate or combined effects of 1-MCP and low temperature on the shelf life and sensory quality attributes of Broken and Dausha mango fruit.

2.0 Materials and Methods

2.1 Study Area

The study area Gboko, lies within latitude 6° 28' to 8° 13' N and longitude 8° 04' to 9° 16' E. It is located in the North Central Zone of Nigeria. This area produces mango fruit varieties of interest in this study in very large quantities.

2.2 Sample Collection

A sample size consisting of 32 mature green mango fruit was collected from the two orchard farms, MtswenenTyo farm, behind the new GRA and TseApev compound, both in Gboko Local Government Area of Benue State using hand picking method with the stalk intact. Each cultivar was collected and labelled. Fruit was considered mature green if firm with no depression when thumb-pressed and visual appearance as determined by the size, shape (fullness of cheeks), skin colour (dark green to light green) and specific gravity (ratio of mango density to the density of water) [15]. Clean open-air plastic containers were used in transporting samples to the Chemistry laboratory, at Benue State University, Makurdi, Nigeria.

2.3 Sample treatment and storage

The 32 mango fruits were labelled according to variety (Broken and Dausha) and concentration of 1-MCP (1000, 3000 and 5000 ppb and control 0ppb). Broken 0ppb (B0), Broken 1000ppb (B1), Broken 3000ppb (B3), Broken 5000ppb (B5) and Dausha 0ppb (D0), Dausha 1000ppb (D1), Dausha 3000 (D3) and Dausha 5000ppb (D5). Thereafter, they were grouped into three equal lots of 8 fruit. These lots with equal numbers of Broken and Dausha fruit were placed inside the corresponding labelled air-tight lidded plastic containers together with a beaker containing a known amount of 1-MCP needed to generate the required concentration (1000, 3000 and 5000 ppb) of the gas. The containers were covered immediately and sealed after adding 20 mL of distilled water into the beaker to release the 1-MCP gas and were kept at 18 °C for 24 h for the reaction to complete. The control fruit (B0 and D0) were kept

on the laboratory bench till after 24 h to be stored at the same time as the treated fruit. The treated and untreated (control) were stored for ninety (90) days at 11 °C for sensory evaluation. The sensory evaluation was performed 4 times on days 15, 45, 60 and 90 of storage.

2.4 Sensory Evaluation

The sensorial evaluation of two mango varieties was performed in the Postgraduate Research Laboratory, Department of Chemistry, Benue State University, Makurdi, using 9-point hedonic scale [16]. The mango samples were coded and presented to a twenty (20) member-trained panel of judges. The judges were selected based on their ability to discriminate and scale a broad range of different attributes. An orientation program was organised for the panel members to brief them on the objectives of the study. The panellists scored the colour, flavour, texture and overall acceptability in the four Mango samples of each variety. The judges were provided with prescribed questionnaires to record their observations. The information contained on the hedonic scale was 9 = Like extremely; 8 = Like very much; 7 = Like moderately; 6 = Like slightly; 5 = neither like nor dislike; 4 = Dislike slightly; 3 = Dislike moderately; 2 = Dislike very much; 1 = Dislike extremely. The panellists expectorated the pulp and rinsed the mouth using ozonized bottled water between samples. Data generated were analyzed using one-way analysis of variance (ANOVA) without blocking. Means separation was done using the Least Significant Difference (LSD) test for multiple means comparison. The GenStat statistical package was conducted using The GenStat Release 10.3DE, PC/Windows 7, Edition 17th, VSN International Ltd, Rothamsted Experimental Station. All tests of significance were at $p \leq 0.05$. Results were expressed as mean $\pm$ standard deviation.

3.0 Results and Discussion

The results of the sensory evaluation of Broken and Dausha for the period of study; 15, 45, 60 and 90 days using sensory parameters such as colour, flavour, texture and general acceptability are presented in Figures 1 to 4.

Colour

Visual examination by the consumers is of significant importance as it attracts the eyes of a consumer, so the product colour is one of the important quality parameters. Panellists' rating of mango fruits during storage revealed a significant decrease in colour with the advancement of storage time. Among the treatments imposed, Broken control (B0) was considered to have the significant maximum colour score of 8.5 while that of Dausha (D0) control was 7.8 on day 15 of storage (Figure 1). The difference in colour between them could also be due to varietal and genetic composition. The colour changes in the two control samples (Dausha and Broken) occurred within the first 15 days of storage thus resulting in to increase in carotenoid.

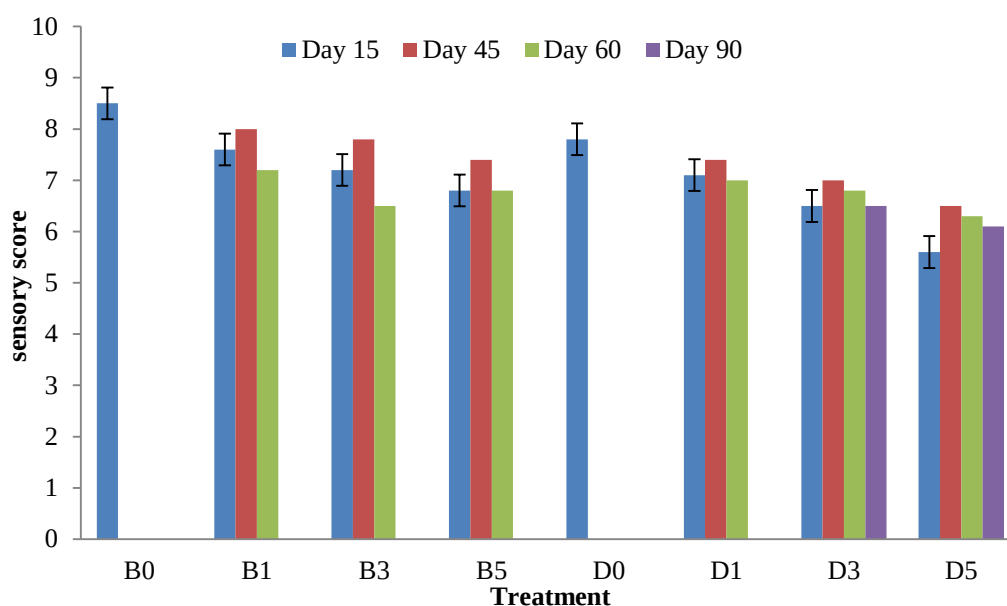


Figure1: Colour sensory score of Broken and Dausha treated and stored at 11°C for 90 days. Broken control (B0), Broken 1000 ppb (B1), Broken 3000 ppb (B3), Broken 5000 ppb (B5), Dausha control (D0), Dausha 1000 ppb (D1), Dausha 3000 ppb (D3) and Dausha 5000 ppb (D5)

The fast colour change was due to chlorophyll degradation favoured by the high ambient temperature and absence of 1-MCP treatment. During ripening, the peel colour of mango changed from green or light green to yellow or light yellow due to the breakdown of chlorophyll and synthesis of carotenoids [17]. The principal agents responsible for this degradation might be the oxidative system, pH change and enzymes like chlorophyllases. These results compared favourably with those of Durrani *et al.*, [18]. However, the colour of the 1-MCP treated mango was lower and less preferred than the untreated fruit. The low colour scores indicate a delay in ripening as a result of the inhibition of ethylene action by 1-MCP. These findings are further supported by Yahia and Hernandez [19] who observed that fruit stored in an open atmosphere lost their green colour faster, while those stored in a controlled atmosphere remained green. This means that fruit stored at low oxygen concentrations showed a decrease in respiration rate, ethylene production, flesh firmness and colour losses [20].

The results also revealed that the skin colour score increased up to day 45 and decreased gradually to the end of the storage period (90 days) (Figure 1).

Flavour

The flavour is the total of taste and aroma. Taste is comprised of five primary components namely sweet, salty, sour and bitter. Mastication of food products generates secondary products and the compounds that impart aroma in foods are known to be secondary compounds [21]. It was observed from the result that the flavour scores for Broken mango fruits treated with 1-MCP increased up to day 45 and then decreased gradually to day 60 (Figure 2). A similar observation was made for Dausha, but the increase rose to day 60 before decreasing with storage time. The controls for broken recorded the highest flavour scores (7.1) on day 15, while, that of Daushahad 6.9 (Figure 2). Ripening may have started in the control samples with fast biochemical changes in volatile compounds originating from proteins, carbohydrates, lipids and vitamins in the fruit. These findings are in line with the report of Hayat *et al.*, [22] who reported that organoleptic evaluation such as taste/flavour of *bankyapple* and *alphonso* mangoes significantly decreased with the increase in storage period when stored at 32 to 36 °C and relative humidity of 70 to 75%.

Although at the early stage of preservation (15 days) the flavour score for both Dausha and Broken was low. However, at 45 days of storage, Daushamango had more flavour acceptability compared to Broken (Figure 2). This was due to biochemical activities which were slower in the fruit treated with 1-MCP at the initial stage but tend to increase as the effect of 1-MCP decreases. Also, the conversion of complex organic compounds into esters, aldehydes, acids, alcohols, ketones and ethers which contribute significantly to the aroma and flavour were fully developed at the later stage of storage. It has also been reported that the characteristics of ripe fruit and their flavour intensity increased with storage time [23]. Abbasiet *al.*, [24] attributed the change in the taste of mango to the storage period and reported that the taste score of mango increased from 3.54 to 8.42 after four weeks of storage. The aroma of fruit improves with ripening and the characteristic aroma of fruit is usually derived from the production of different volatile compounds. Mono- and sesqui-terpen hydrocarbons are known to be the major aroma compounds in mango [25]. Similar findings were reported, by Kader [28].

Medicottet *al.*, [27] reported that the changes in mango flavour are proportional to storage temperature and that mangoes stored at relatively low temperatures exhibited higher flavour scores, which agrees with the findings of this study. Malundoet *al.*, [28] reported that sugar and acids are primary taste compounds that enhance human perception of specific flavours in mango, including aroma but pH, titratable acidity and total soluble solids are also related to sourness and astringency. Also, it is evident from the result obtained in the present investigation that the flavour of mango pulp deteriorates with the advancement of the storage period (Figure 2). The decrease in the flavour of mango samples treated with 1-MCP at the end of storage was due to the oxidation process of the flavouring compounds such as esters, aldehydes, acids, ketones, tannins and ethers. A similar result was reported in guava nectar by Weichmann[29].

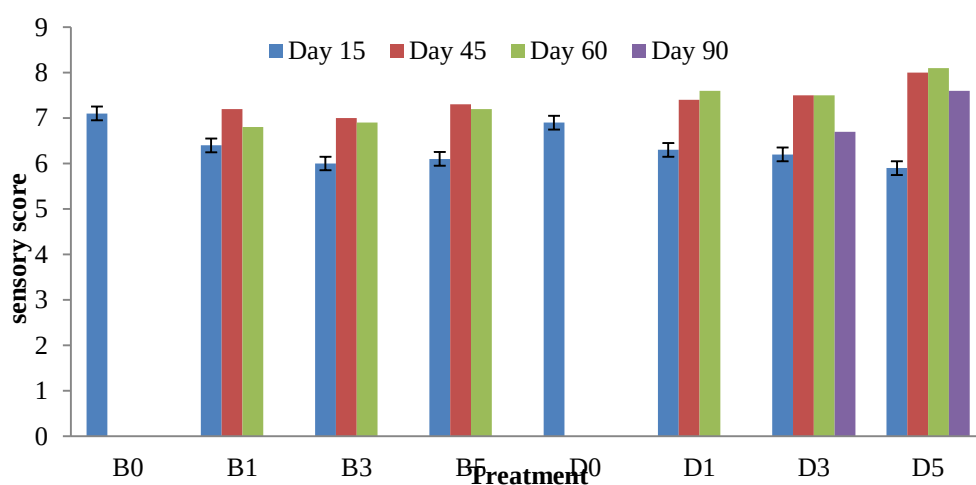


Figure 2: Flavour sensory score of Broken and Dausha treated and stored at 11oC for 90 days. Broken control (B0), Broken 1000 ppb (B1), Broken 3000 ppb (B3), Broken 5000 ppb (B5), Dausha control (D0), Dausha 1000 ppb (D1), Dausha 3000 ppb (D3) and Dausha 5000 ppb (D5)

Texture

Texture is one of the important quality parameters in sensory evaluation, which plays an important role at the time of selection of fruit by the consumer. The texture of fruits is mainly attributed to cell wall integrity and stored carbohydrates such as pectin and starch. Pectin substances are structural polysaccharides responsible for firmness. Softening of fruit occurs when these pectin polymers become less tightly bound in the cell walls during ripening. Firmness could therefore, be used as an index for fixing the optimum stage of maturity for harvest [30].

Figure 3 showed lower textural values for the controls Broken (B0, 0 ppb) and Dausha (D0, 0 ppb) and higher values for the treated. However, a decreasing trend in the textural score of mango fruit treated with 1-MCP was observed from day 45 to 60 and a significant decrease thereafter as the storage period progressed. The untreated fruit scored low (1.8 and 2.3) for Broken and Dausha respectively in textural scores, and the fruit spoiled after 15 days of storage. Dausha (D5, 5000 ppb) recorded a maximum textural score ranging from 10.0 to 8.1 for days 15 to 90, while Broken (B5, 5000 ppb) had lower scores of 7.9 to 6.8 (days 15 to 60); and got spoiled. Dausha expressed better firmness, which indicates its potential for extended shelf life.

The ability of 1-MCP to maintain fruit texture after 90 days of storage may be due to the non-breakdown of insoluble pectin substances and this shows the efficacy of 1-MCP in fruit preservation. Therefore, the reduction in texture score during storage could be due to the breakdown of insoluble pectin substances into soluble forms.

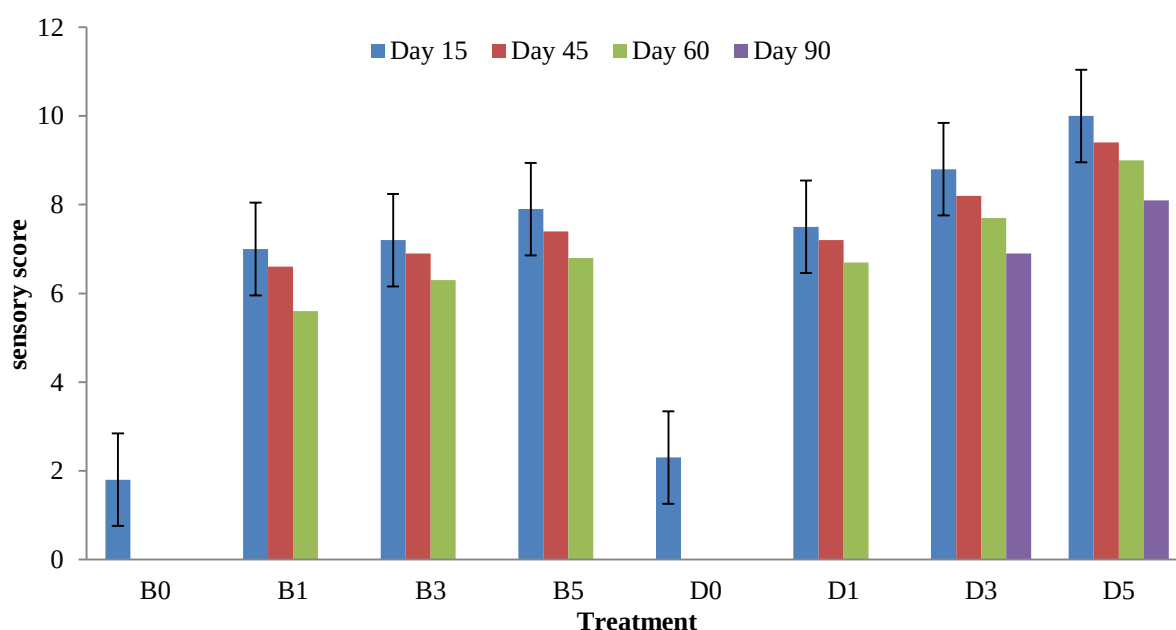


Figure 3: Texture sensory score of Broken and Dausha treated and stored at 11°C for 90 days. Broken control (B0), Broken 1000 ppb (B1), Broken 3000 ppb (B3), Broken 5000 ppb (B5), Dausha control (D0), Dausha 1000 ppb (D1), Dausha 3000 ppb (D3) and Dausha 5000 ppb (D5)

The rapid reduction in texture score in the control sample might also be a result of accelerated ripening in the free ambient temperature. These findings are supported by the report of Opara *et al.*, [31] in Vietnam, that the firmness of *buoi* mango was highly dependent on storage temperature. Doreyappa-Gowda and Huddar [32] reported similar observations in green mature *alphonso* and other 7 varieties of mango that firmness decreased from 28.96 to 17.46 lbs/sq.inch at 18 to 34 °C. Similar findings were also observed by Shinde *et al.*, [33] in *Alphonso*, *Kesar*, *Desi* and *Dasher* mango varieties grown in the Saurashtra region of Gujarat and Deka *et al.*, [38] for mango and pineapple.

General acceptability

The general acceptability test revealed that Dausha (D5, 5000 ppb) at day 60, with a rating of 8.9, was the most preferred to other samples, closely followed by Dausha (D3, 3000 ppb) day 60, Dausha (D1, 1000 ppb) day 60 and Dausha (D5, 5000 ppb) day 45 (Figure 4). The degree of ripeness at which fruit is tested plays a major role in the assessment of its sensory qualities and acceptability [34].

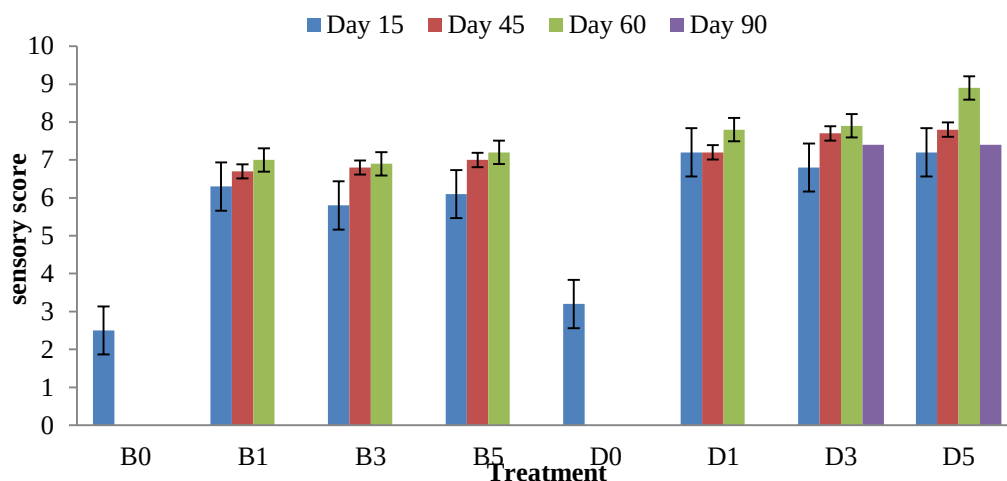


Figure 4: General acceptability sensory score of Broken and Dausha treated and stored for 90 days. Broken control (B0), Broken 1000 ppb (B1), Broken 3000 ppb (B3), Broken 5000 ppb (B5), Dausha control (D0), Dausha 1000 ppb (D1), Dausha 3000 ppb (D3) and Dausha 5000 ppb (D5)

Conclusion

The 9-point hedonic scale taste panel scores revealed a significant difference at ($p < 0.05$) in both treated and untreated mango samples. The panellists showed a clear preference for Dausha treated with 5000 ppb 1-MCP (D5) in flavour, texture and general acceptability than the other treatments (D1, 1000 ppb and D3, 3000 ppb). Relatedly, Broken mango samples scored higher in colour but lower in flavour, texture and general acceptability under the same treatment.

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SN 4 RESPONSE OF PZT-ROD PERIODICITY IN PIEZOELECTRIC POLYMER STRUCTURE BASED ON DENSITY OF THE COMPOSITE AND VOLUME PERCENT PZT IN COMPOSITE

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Abstract

Response of PZT-rod periodicity in piezoelectric polymer structure to the density of the composite and volume percent PZT in composite was evaluated using the derived empirical model: $\lambda = \beta \rho^{-\epsilon} + N \chi^{-\eta} - \eta$. The validity of the model is strongly rooted in the core model structure: $\lambda - N \chi^{-\eta} \approx \beta \rho^{-\epsilon} - \eta$, both sides of which are correspondingly near equal. The model-predicted results agree with previous research on the inverse relationship between the PZT rod periodicity and density of composite and the volume fraction of PZT rod in composite. The correlations between the periodicity of PZT-rod in polymer structure, volume percent of PZT in composite, and density of composite were all > 0.99 . The standard error incurred in predicting the model-based PZT rod periodicity relative to the actual results was $< 0.023\%$, implying an over-99% model confidence level. The periodicity of PZT rod per unit volume fraction of PZT rod in composite and per unit density of the composite were -0.042 and -0.043 mm/% and -0.533 and -0.546 mm/(gm/cc), using experimental and model-predicted results, respectively. The overall maximum deviation of the model-predicted periodicity of the PZT rod from the actual results was 2.56% . The derived model will predict the periodicity of PZT rod within the actual results range. On substituting values of the density of composite and volume fraction of PZT rod in composite, provided the boundary conditions are considered.

Keywords: PZT-rod periodicity, piezoelectricity, polymer structure, density, PZT volume percent, composite

1. Introduction

Research has been conducted on some designed and fabricated composite materials optimized for a special application. The applications range from electronic devices to mechanical structures. During composite material design, prime importance is given to the way in which the proper choice of component phases is interconnected to maximize the merit of the expected outcome. It has been reported [1–7] that piezoelectric ceramic-polymer composite transducers are a family of an important new class of materials. These reports indicate that current research on piezoelectric ceramic-polymer composite materials focuses on hydrophone applications in the low-frequency (less than 40 KHz) range, where the dimensions of the transducer are much smaller than the acoustic wavelength.

Until now, there has not been any indication of studies geared towards the usefulness of these composites at higher frequencies (1–10 MHz) for medical diagnostic and non-destructive testing applications. At these frequencies, the acoustic wavelength is comparable to the scale of the composite microstructure. The acoustic impedance, bandwidth, and radiation patterns of the composite transducer can be controlled in a manner so sophisticated that it is impossible to control single-phase materials. The systematic investigations [8] of the composite materials made from piezoelectric lead zirconate titanate (PZT) ceramics and piezoelectrically inactive polymers have focused on the understanding of the electromechanical properties of the composite materials in resonant configurations. The knowledge of the high-frequency dynamic behaviour of the composite was then used to evaluate the composite materials for ultrasonic transducer applications, with an emphasis on medical diagnostic applications.

The PZT rod-polymer composites have been prepared [8] with 5 to 30 volume percent PZT, using 0.28 mm and 0.45 mm rods. In a disc of the PZT rod-polymer composite material, there are three principal types of resonance: the planar mode, the thickness mode, and various lateral modes caused by the regular periodicity of the PZT rod in the composite. These resonance modes have been studied with the following techniques: electrical impedance measurement as a function of frequency and laser probe dilatometry of the dynamic displacement as a function of frequency and position in the composite lattice. The observed resonance behaviour was found to be a result of lateral interactions in the composite through the epoxy medium. It has been shown [8] that the periodicity of PZT rods in a polymer structure, which also affects the highlighted resonance behaviour, is the distance between the centres of neighbouring PZT rods.

Investigation [9] has shown that among all the different composites, only those with PZT rods embedded in Spurr's epoxy matrix with regular periodicity (1-3 connectivity) appeared to be very promising for the ultrasonic transducer application. The research revealed that PZT polymer composites have shown several remarkable advantages over conventional piezoceramic materials for ultrasonic applications. Findings from the investigation further revealed that 70–90% PZT in most composites is replaced by a low-density polymer, bringing in a better acoustic impedance matching that of the human body.

Previous research [8, 9] shows that the volume fraction of the PZT rod in the composite, the density of the composite, and the periodicity of the PZT rod in the composite are related. Until now, no existing mathematical expression has established this relationship. This unknown stance, therefore, prompted the need for the present work to fill in the gap.

The present work aims at mathematically deriving the dependence of PZT rod periodicity in the composite on the PZT rod volume fraction in the composite and the density of the composite. It is strongly believed that the model, if derived, will be able to predict the PZT rod periodicity within the actual range by just substituting into the model the PZT rod volume fraction and density, provided the boundary conditions are considered.

2. Materials and Methods

2.1. Sample Preparation

PZT powder of grain size between 1 and 3 μm was used in this work to make rods of 1 mm diameter. The powder was supplied by the Shanghai Institute of Ceramics, having properties similar to the Vernitron (Morgan Matroc Ltd.) PZT-4 composition. The rods were extruded through a home-made die and sintered at 1300°C for about 6 hours. To measure the piezoelectric properties of the ceramic component, a rod sample of length 0.78 mm was cut from a long-fired rod. [10].

A series of holes of 1 mm diameter were drilled in already-cast epoxy sheets, used as the matrix, in a square pattern with centre-to-centre periodicity noted. The fired PZT rods were inserted into these holes to glue the PZT rods to the polymer. After curing the composites, they were cut into disks of about 0.7 mm thick and 12 mm in diameter. The PZT rod volume percentage in the composite was 5%. The experiment was repeated for a PZT percent volume range of 7–30%, and the density of the composite and the associated periodicity of the PZT rod in the composite were evaluated. [10].

2.2. Composite Density Evaluation

The various densities of the PZT rod and epoxy resin were measured using the Digital Density Meter, after which the density of the PZT rod-epoxy resin composite (gm/cc) was calculated using the expression [11].

$$\rho_c = V_r \times \rho_r + (1-V_r) \times \rho_m \quad (1)$$

Where;

ρ_c = Density of composite

V_r = Volume fraction of Reinforcement

ρ_r = Density of Reinforcement

ρ_m = Density of matrix

2.3. Model Derivation

Table 1: Variation of PZT rod periodicity in polymer structure with the density of the composite and volume percent PZT ceramic in composite

(λ)	(ρ)	(γ)
1.78	1.11	5
1.57	1.32	7
1.26	1.64	10
1.19	1.77	12
1.08	1.97	15
0.90	2.29	20
0.82	2.69	25
0.73	2.99	30

Computational analysis of the actual results shown in Table 1, gave rise to Table 2 which indicate that;

$$\lambda - N\gamma - \beta \approx \beta\rho - \epsilon - \eta \quad (2)$$

$$\lambda = \beta\rho - \epsilon + N\gamma - \eta \quad (3)$$

The derived expression in (3) is an empirical model which predicts the periodicity of PZT-rod in piezoelectric ceramic-epoxy structure based on the density of the composite and volume percent PZT in composite. The model is a sum of two power functions. Comparative analysis of 1 and Table 2 indicates that λ , γ and ρ are periodicity of PZT-rod in polymer structure (mm), density of composite (gm/cc) and volume concentration of PZT in composite (%) respectively. The equalizing constants; N , β , ϵ and η are 2.0292, 0.4991, 0.9862, 0.8962 and 0.001 respectively. They were generated using software [12].

3.0 Results and discussion

3.1 Boundary and Initial Conditions

Consider a cylindrically shaped PZT rod as the composite, interacting with the matrix, which is epoxy. The wave velocity is assumed to be affected by the volume fraction and density of the PZT rod in the composite. The considered range of the volume fraction of PZT in composite, range of density of the composite, and PZT rod periodicity are 5–30%, 1.11–3.08 cc/gm, and 0.73–1.78 mm, respectively.

Table 2: Variation of $\lambda - N\gamma - \beta$ with $\beta\rho - \epsilon - \eta$

$\delta - N\alpha - \beta$	$\beta\rho - \epsilon - \eta$
0.8711	0.8971
0.8017	0.7679
0.6169	0.6320
0.6030	0.5902
0.5548	0.5361
0.4451	0.4683
0.4129	0.4053
0.3585	0.3589

3.2 Model Validity

In view of the derived model in equation (3), the validity is strongly pivoted on the core model structure in equation (2), expressed as $\delta - N\alpha - \beta \approx \beta\rho - \epsilon - \eta$, both sides of which have close corresponding point values. The computational analysis of the experimental results in Table 1 gave Table 2, which is the confirmed mathematical outcome of the model structure following the closeness of the corresponding structure component values. Furthermore, the derived model was validated by comparing the derived model-predicted results with experimental results by carrying out deviational analysis and statistical analysis, involving evaluation of the correlations and standard errors.

3.2.1 Statistical analysis

3.2.1.1 Correlation

The correlation between the periodicity of PZT-rod in polymer structure and volume percent of PZT in composite & density of composite were calculated as 0.9994 and 0.9979, using model-predicted and experimental results respectively. This was based on the coefficient of determinants on the actual and model-predicted results, shown in Figs. 1 and 2, evaluated using equation (4).

$$R = \sqrt{R^2} \quad (4)$$

3.2.1.2 Standard Error (STEYX)

Statistical analysis of generated results indicates that the overall standard error on predicting the periodicities of PZT-rod in polymer structure (relative to the experimental results) is 0.023%, for every change in the volume percent of PZT in composites and density of composite. This translates into a model confidence level above 99%.

3.2.2 Graphical Analysis

Graphical analysis of Fig.1 and Fig. 2 show closely fitted and aligned curves of periodicities of PZT-rods in composites, relative to volume percent of PZT and its density in composite respectively.

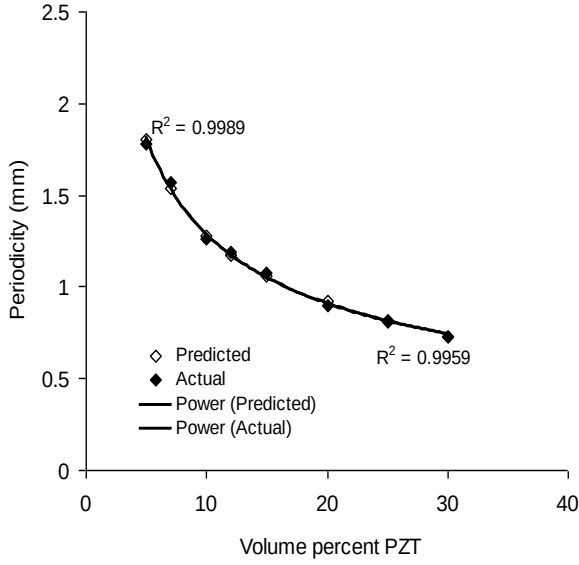


Fig.1: Comparison of the periodicities of PZT-rod in polymer structure (relative to the volume percent PZT in composite) from the actual and model prediction.

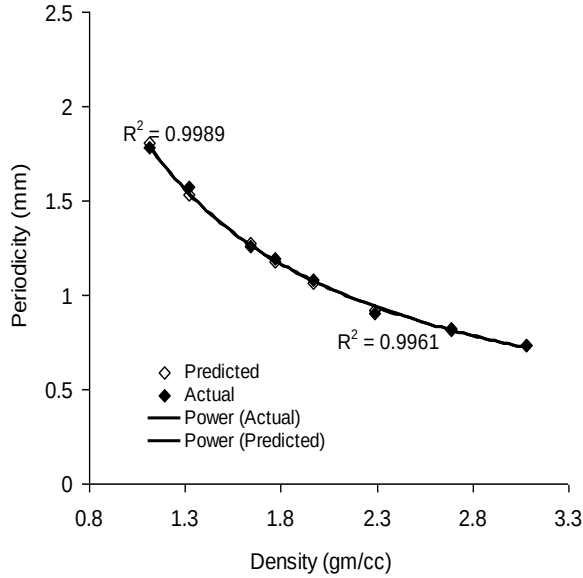


Fig.2: Comparison of the periodicities of PZT-rod in polymer structure (relative to the density of composite) from actual and model-prediction

These curves represent experimental and model-predicted results. Each set of curves from the figures, excellently show similar trend & spread of results point distribution, and well fitted corresponding point values.

Curves from the figures indicate negative orientation, and will likely prompt negative slopes, barring the inverse variation of periodicities of PZT-rods in composites with volume percent of PZT in composite and density of composite respectively.

3.2.3 Deviation Analysis

The functionality and acceptability of a derived model largely depends on the deviation of model-predicted result from corresponding experimental value. Fig. 3 indicates sets of points on the curves, each of which gives the percent deviation between the experimental and the corresponding model-predicted

results. The figure gives 2.56% as the overall maximum deviation of model-predicted periodicity of PZT-rod in polymer structure (from corresponding experimental results). This translates into over 97% operational model confidence level. The figure also shows that the least and highest deviations of the model-predicted periodicity of PZT-rod in polymer structure are 2.56 and 0.0 % respectively. Furthermore, these deviations correspond to periodicities of PZT-rod in polymer structure: 0.923 and 0.73 mm, volume percents PZT: 20 and 30% & densities of composite: 2.29 and 3.08 gm/cc respectively. The overall model confidence level therefore places between 93-99%, following evaluations from standard deviation, correlations and maximum deviation. Introduction of correction factors to the model-predicted results are necessary, to overcome the deviation and realize the experiment results.

The deviation D_v , of model-predicted PZT rod periodicity from the corresponding actual result was given by

$$D_v = \left(\frac{\lambda_m - \lambda_E}{\lambda_E} \right) \times 100 \quad (5)$$

Where; λ_m and λ_E are periodicities of PZT rod in polymer structure evaluated from actual and model-predicted results respectively

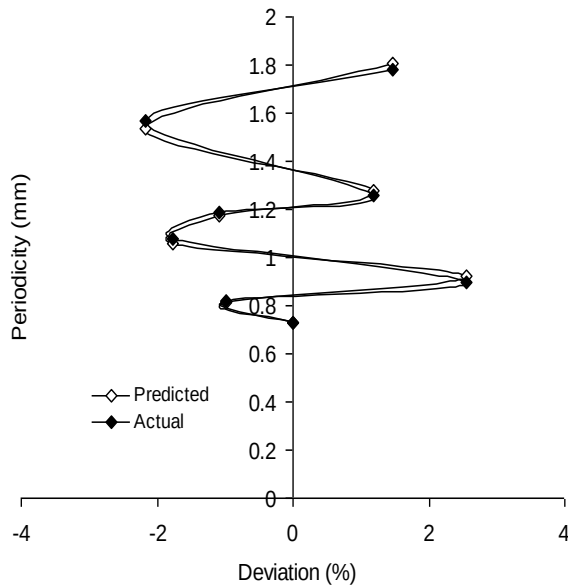


Fig. 3: Variation of model-predicted periodicity of PZT rod in composite with its corresponding deviation from experimental results

It is instructive to state that the model results deviation from corresponding experimental values prompted from, non consideration during model formulation, the effects of surface properties of the PZT rod and physicochemical interaction between the PZT rod and the epoxy matrix, all of which play vital roles during the polymer reinforcement process with PZT rod. This necessitated the introduction of correction factor, to bring the model-predicted PZT rod periodicity to those of the corresponding experimental values.

Periodicity of PZT-rod in polymer structure per unit volume percent PZT.

Periodicity of PZT-rod in polymer structure per unit volume percent PZT λ_v mm/% was calculated from the expression;

$$\lambda_v = \lambda / v \quad (6)$$

Re-written as

$$\lambda_v = \Delta\lambda / \Delta v \quad (7)$$

Equation (7) is detailed as

$$\lambda_v = (\lambda_2 - \lambda_1) / (v_2 - v_1) \quad (8)$$

Where; $\Delta\lambda$ = Change in the periodicities of PZT-rod in polymer structure λ_2, λ_1 at two volume percents PZT v_2, v_1

Plotting points (5, 1.78) & (30, 0.73) and (5, 1.806) & (30, 0.73) as shown in Fig.1, designated as (v_1, λ_1) and (v_2, λ_2) for experimental and model-predicted results, and substituting them into equation (8) gives the slopes: -0.042 and - 0.043 mm/%, as their respective periodicity of PZT-rod in polymer structure per unit volume percent PZT.

Periodicity of PZT-rod in polymer structure per unit density of composite

Periodicity of PZT-rod in polymer structure per unit density of composite λ_ρ mm/(gm/cc) was calculated from the expression;

$$\lambda_\rho = \lambda / \rho \quad (9)$$

Re-written as

$$\lambda_\rho = \Delta\lambda / \Delta\rho \quad (10)$$

Equation (10), is detailed as

$$\lambda_\rho = (\lambda_2 - \lambda_1) / (\rho_2 - \rho_1) \quad (11)$$

Where;

$\Delta\lambda$ = Change in the periodicities of PZT-rod in polymer structure λ_2, λ_1 at two densities of composite ρ_2, ρ_1

Similarly, on plotting points (1.11, 1.78) & (3.08, 0.73) and (1.11, 1.806) & (3.08, 0.73) shown in Fig. 2, designated as (ρ_1, λ_1) and (ρ_2, λ_2) for experimental and model-predicted results, and substituted into the (11), gives the slopes: -0.533 and - 0.546 mm/ (gm/cc), as their respective periodicity of PZT-rod in polymer structure per unit density of composite.

The negative signs preceding the respective periodicities of PZT-rod in polymer structure, per unit volume percent PZT and density of composite, just indicate that their respective curves as shown in Fig 1 and Fig. 2 are positioned in the negative plane. Their real values are the magnitudes of the respective slopes.

4. Conclusion

Response of PZT-rod periodicity in piezoelectric polymer structure to the density of the composite and volume percent PZT in composite was evaluated using a derived empirical model: $\lambda = \beta\rho^{-\epsilon} + N\gamma\eta - \eta$. The validity of the model is strongly rooted in the core model structure: $\lambda - N\gamma\eta \approx \beta\rho^{-\epsilon} - \eta$, both sides of which are correspondingly near equal. The model-predicted results agree with previous research on the inverse relationship between the PZT rod periodicity and density of composite and the volume fraction of PZT rod in composite. The correlation between the periodicity of PZT-rod in polymer structure, volume percent of PZT in composite, and density of composite were all > 0.99 . The standard error incurred in predicting the model-based PZT rod periodicity relative to the actual results was $< 0.023\%$, implying an over-99% model confidence level. The periodicity of PZT rod per unit volume fraction of PZT rod in composite and per unit density of the composite were -0.042 and -0.043 mm/% and -0.533 and -0.546 mm/(gm/cc), using experimental and model-predicted results, respectively. The overall maximum deviation of the model-predicted periodicity of the PZT rod from the actual results was 2.56% . The derived model will predict the periodicity of PZT rod within the actual results range. On substituting values of the density of composite and volume fraction of PZT rod in composite, provided the boundary conditions are considered.

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SN 5 THE EFFECTS OF FILLER LOADING ON THE MECHANICAL PROPERTIES OF UNSATURATED POLYESTER RESIN/CASSAVA PEEL COMPOSITE

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ABSTRACT

The research examines the effect of filler loading on the mechanical properties of cassava peels/unsaturated resin composite. Cassava peels are wastes with the potential of being one of the raw materials for environmentally friendly bio plastic, filler in unsaturated polyester resins. The resins have good properties and are cheap alongside reducing the environmental pollutions. Exactly 150 microns of cassava peel powder with unsaturated polyester resin composites were prepared using hand layup technique. The filler loading ranges from 0%-10% filler to resin ratio at 2% increase rate. The effect of cassava peels on the mechanical properties of unsaturated polyester were investigated. The flexural strength with lowest value 27.15MPa at 10% filler loading and highest value of 43.64MPa at 4% filler loading. Also, hardness test ranged from 21.6 to 54.5 as the filler content increases from 2% to 10% increases with increased filler content. The impact strength values were 0.25, 0.21, 0.25, 0.21, 0.28 and 0.23 for 0%, 2%, 4%, 6%, 8%, and 10% respectively. It was observed that the Hardness values increases from 21.6 to 54.5 as filler loading is increased from 0% to 10% and flexural strength decreases and increases at different filler loading. Filler loading at 4% has the highest flexural strength value of 43.64

(N/mm²). The result show that the less filler loading had better result of voids and agglomerate formation which weakens bonding of poor inter-facial adhesion between the filler and the matrix, causing fluctuations in results obtained. Water absorption test for 30 days' period shows increase in percentage of water absorption with increasing filler content and increase in number of days.

Keywords: Unsaturated Polyester Resin (UPR), Cassava peel, Composite, Cobalt naphthate

INTRODUCTION

Presently, various synthetic polymers are being prepared and combined with various reinforcing fillers in order to improve the mechanical properties along with the characteristics demanded in actual application. The need for materials that are non-toxic with appropriate characteristics for specific purposes is ever increasing due to the lack of resources and increasing levels of environmental pollution. Natural fillers are being sought since the production of composites using natural substances as reinforcing fillers is not only inexpensive but also able to minimize environmental pollution due their biodegradability. Thus, enabling these composites to play an important role in resolving future environmental problems (Premalal *et al.*, 2002).

Unsaturated polyesters are a family of polyesters characterized by vinyl unsaturation in the polyester backbone. Unsaturated polyester is thermosetting polyester that is cross-linkable by reaction with an unsaturated monomer or pre-polymer by virtue of the presence of carbon-to-carbon double bonds in its polymer chain. This research is more interested in preparing a composite made of abundantly available and cheaper natural materials as fillers as compared to synthetic products which need to be processed and made up of chemicals to gain the required property of composites. These natural fibers yield better mechanical strength when added to thermosets or thermoplastics. The mechanical properties of particulate filled polymer composites depend strongly on the particle size, particle-matrix interface adhesion and particle loading (ishiaku *et al.*, 2007). In the recent years, polymer matrix composites are gaining more importance compared to monolitical materials because they more reliable and cheaply available. With the advancement of polymer matrix composites (PMC) their properties have been increased by one. The addition of one more fibre as hybrid composites boost the property of the PMC. The single fibre composite lags polymeric composite materials in a variety of uses such as automotive, sporting goods, marine, electrical, industrial, construction, house hold application etc. polymeric composites have high strength and stiffness, light weight and high corrosion resistance (Madhusudhana *et al.*, 2014).

The utilization of cassava peel as a filler in UPR composites presents an eco-friendly alternative and an innovative approach to waste valorization, in addition to potential enhancements in material properties. Cassava peel is an agricultural byproduct, rich in cellulose and other natural fibers. Incorporating cassava peel into UPR matrices offers an opportunity to improve the sustainability of composite materials while potentially modifying their physical and mechanical characteristics. The filler loading, or the proportion of cassava peel added to the composite, plays a pivotal role in determining the final properties of the material (smith *et al.*, 2020). The aim and objectives of this research is to study the effects of filler loading on the mechanical properties of unsaturated polyester resin/cassava peel composite. To achieve this, cassava peels were used as fillers at different filler loading in unsaturated polyester resin to obtain composites. Thereafter, mechanical and physical properties of the unsaturated polyester composites alongside the effect of different filler loading properties of the cassava peels reinforced in unsaturated polyester composite were examined.

MATERIALS EQUIPMENT'S AND METHODS

Materials

UPR (unsaturated polyester resin), Cobalt naphthate (accelerator), *Methyl ethyl ketone peroxide* (MEKP) (catalyst), Glass mould, Foil paper, Plastic disposable container, Mould releasing agent (paraffin wax), Hand kerchief, Detergent, Weighing balance. and Sieve (150 micron)

Equipment's

Hounsfield Monsanto Tensiometer Model No. S/N 8889 (For Tensile Strength), Universal Materials Testing Machine Cat. Nr. 261 (Flexural Strength), Charpy Impact Testing Machine Cat. Nr.412 (Impact), Indentec Universal Hardness Testing Machine (Model: 8187:5 LKV) and Weighing Balance

Methods

Matrix polymer: Unsaturated polyester resin was used in this research with accelerator (cobalt naphthenate) and hardener (methyl ethyl ketone peroxide).

Reinforcing filler: Grounded cassava peels sieved into the particle size of 150 microns. The sieving was done at the department of civil engineering, faculty of engineering ABU, Zaria

Preparation of cassava peels

The cassava peel particles that were used as reinforcement in this research were obtained from a market in Kakuri Kaduna South. The sample was washed and dried for Three days, pounded using mortar and pestle before grinding with electric grinding machine so as to get uniform and fine particles. Thereafter, the sample was taken to the department of civil engineering of ABU Zaria where it was sieved into the particle size of 150 microns so as to obtain more finer particles.

Unsaturated polyester resin

An Unsaturated polyester resin is the most important polymer for the production of composite materials, mainly glass fiber-reinforced plastic (FRP), but also for casting resins (non-reinforced), Fiber-reinforced plastic composites are consumed primarily by the construction, marine, and land transportation industries, although they find use in a variety of other applications in the field of engineering. The Unsaturated polyester resin used was obtained from Department of Polymer and Textile Engineering Ahmadu Bello University Postgraduate research laboratory. Alongside the required promoters, accelerators (cobalt) and catalyst (methyl ethyl ketone peroxide).

Cassava peels/Unsaturated Polyester Resin Composite

The required amount of unsaturated polyester resin, accelerator (cobalt) and catalyst (MEKP) 2% to the resin volume were weighed out and thoroughly mixed. Glass mould of $120 \times 120 \times 3$ mm dimension is used. The cassava peels were mixed with the unsaturated resin in their respective proportions. The mixing is done by simple mechanical stirring. Aluminum foil was placed on the surface of the glass mould to conform to the shape of the mould, after which the mold releasing agent which is the paraffin oil was rubbed on the aluminum foil. The aim is to prevent the composite from sticking to the glass surface, thus, aid easy removal of the composites from the mold after curing. The cassava peels were then poured into the unsaturated resin alongside methyl ethyl ketone peroxide and cobalt naphthate and stirred to have a uniform mixture. The mixtures were poured in series of glass moulds of the same dimension. This method is referred to as hand lay-up method of reinforcing. The air trapped is removed by sliding a roller as well as compressing the mould with a heavy weight object after covering the mould with flat glass plate. It is then kept at a room temperature to cure for about 2 hours. The control sample of unsaturated polyester and cobalt with methyl ethyl ketone peroxide was first prepared with no filler alongside with five other samples of each cassava peels powder in weight fractions was made. After curing, the samples are then cut into suitable dimensions with the help of diamond cutter for mechanical tests based of the ASTM standards. The corresponding amount of cassava peels were weighed out as shown in the table 3.1 and added to the UPR. The mixture was thereafter, thoroughly mixed to ensure even distribution of the filler. The formed composites according to the filler volume were removed and allowed to cure under laboratory conditions before subjecting them to the physical and mechanical tests.

Characterization of Composites

The characterizations were carried out according to ASTM standards for testing materials.

Mechanical Test Such as; Tensile Test (ASTM D638) Strength, Modulus and Elongation at break. Flexural Test (ASTM D790) Strength, Modulus Hardness Test (ASTM 2240) and Impact Test (ASTM D256)

Table 3.1 Chemical Composition

S/N	% of cassava peels (g)	% of UPR	Mass of cassava peels (g)	Mass of UPR (g)	Mass of accelerator (cobalt naphthate)	Mass of catalyst (methyl ethyl ketone)	Total mass
1	0%	98%	0g	98	1	1	100
2	2%	96%	2g	96	1	1	100
3	4%	94%	4g	94	1	1	100
4	6%	92%	6g	92	1	1	100
5	8%	90%	8g	90	1	1	100
6	10%	88%	10g	88	1	1	100

Mechanical Tests:

After the fabrication of the composites, the samples were subjected to the following tests.

Tensile Strength Test

The tensile test of the composite samples depends on the strength of the material, the length of the material and the material matrix interaction. The tensile test was carried out at the Mechanical Engineering department where the Hounsfield (Monsanto) tensiometer (Universal Testing Machine) (Model No: S/N 8889) was used to determine the elastic modulus, ultimate tensile strength and percentage elongation in length of the materials. The specimen geometry was in dumb-bell shape and the dimension were ascertained using a Vernier calipers. Uni-axial load was applied to each ends of the respective samples until it fails. Stress-strain curves were plotted from the force extension data obtained on a special graph paper during the tests and the required mechanical properties were determined on the curve. The test was repeated on all the other samples of the composites and the average value was recorded. The test result as well as the tensile parameters were determined according to following equation;

Ultimate tensile strength (σ) = $F(N) / A(mm^2)$,

Where; F = Applied load at breaking x Gravity, A = Cross- sectional Area in (m^2),

Tensile Strain (ϵ) = $\Delta L / L$

Where; ΔL = Increase in gauge length up to the breaking point (mm), L = Gauge length in (mm)

Modulus of Elasticity (E) = σ / ϵ

Where; ϵ = Tensile Strain

Impact Strength

The impact strength tests of the composite samples were carried out using the charpy impact testing machine according to ASTM D 256 and ISO 180 standards. Samples were tested in a replicate of two each at room temperature by a single swing of the pendulum hammer using Resil Impactor impact tester (cad.nr 412 a capacity of 15joules). The specimen size was 50mm were each sample was placed on the vice and clamped firmly. The pendulum hammer was raised to the required height and then released to strike the sample at once. Then the impact energy absorbed by the specimen is recorded.

Hardness Test

The indented universal hardness testing machine model 8187.5 LKV –BL Rockwell HRF (1/161 steel ball) with minor load 10kg and major load 60kg was used in measuring the hardness using the shore scale according to ASTM D2240. It consists of an indenter, a graduated circular tube and a flat surface which the sample / material to be tested are mounted or laid on. The sample was placed on the flat surface and the indenter was forced on the surface of the specimen, the load was maintained at maximum time of 10 to 15 seconds and the test was repeated three times and the average of each test result were recorded accordingly.

Flexural strength

Flexural strength also known as modulus of rupture, bend strength or fracture strength is a material property, known as the stress in a material just before it yields in a flexure test (Hodgkinson, 2000). The three-point bending test was conducted according to ASTM D790 with Cat Nr.261 Universal Material Testing Machine-100KN. At least three rectangular beam samples were tested at a support span length of 70mm, the width and thickness was measured correctly using Vernier caliper. The samples were centre loaded in 3-point bending as a simply supported beam, using 3mm diameter supports and loading bar. The deformation in mm and load in KN were recorded and tests were repeated six times and the average values recorded accordingly. The flexural stress under the modulus of rupture and the modulus of elasticity was determined using the equation below;

Flexural Stress;

$$\sigma_f = 3FL / 2bd^2 \text{ (N/mm}^2\text{)}$$

Modulus of Elasticity

$$E_f = FL^3 / 4bd^3D \text{ (N/mm}^2\text{)}$$

Where; F= Applied Load in (N), L= Gauge length in (mm) b= Width (mm), d= Thickness (mm) D= Deflection (mm)

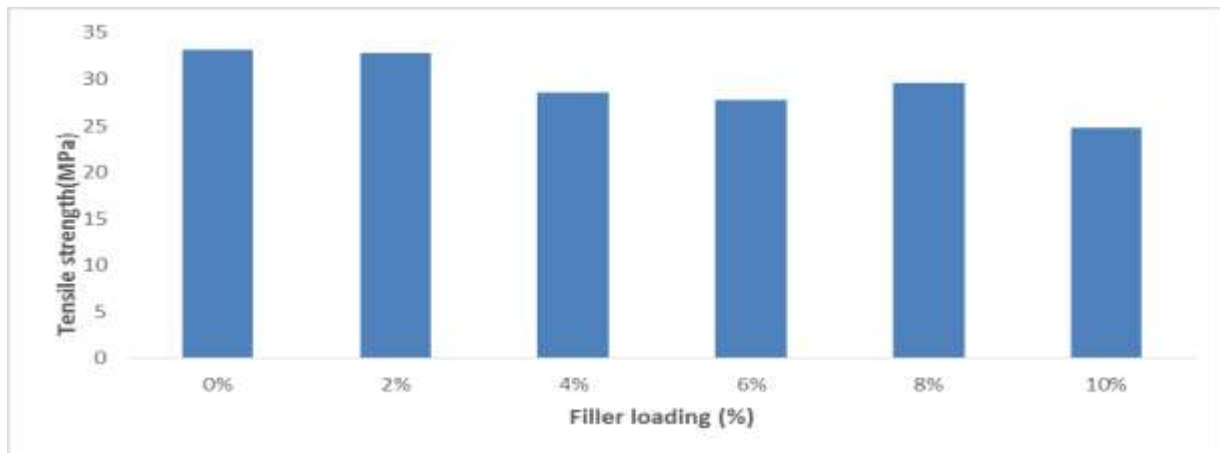
RESULTS AND DISCUSSION

Mechanical Tests

TENSILE TEST

Table 4.1 Tensile test of cassava peels/UPR resin composite

S/N	% of cassava peels	% of UPR	Tensile strength of cassava peels/ unsaturated polyester resin composite (Mpa)
1	0%	98%	33.204
2	2%	96%	32.843
3	4%	94%	28.505
4	6%	92%	27.729
5	8%	90%	29.642
6	10%	88%	24.728

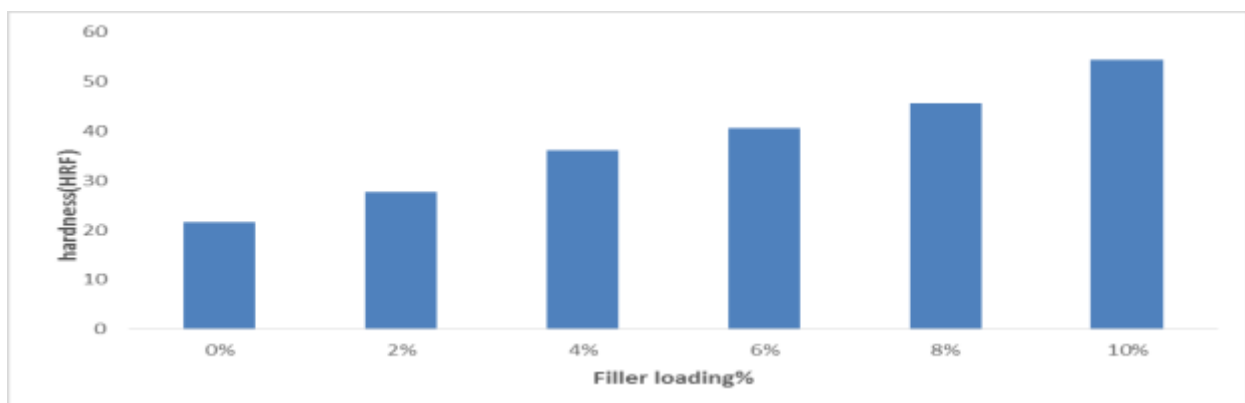


Tensile strength is the maximum amount of tensile stress a material can withstand before failure i.e. before it breaks. From the above table it can be seen that the tensile strength decreases in cassava filler sample with 2% filler loading has the highest tensile strength of 32.843MPa after 0% UPR, 4% with 28.505MPa, 6% with 27.729MPa, 8% with 29.642 and 10% with the least tensile strength of 24.728.

Hardness Test

Table 4.2 Hardness Test

S/N	% of cassava peels	% of UPR	Hardness test of cassava peels/ unsaturated polyester resin composite (HRF)
1	0%	98%	21.6
2	2%	96%	27.7
3	4%	94%	36.1
4	6%	92%	40.7
5	8%	90%	45.6
6	10%	88%	54.5



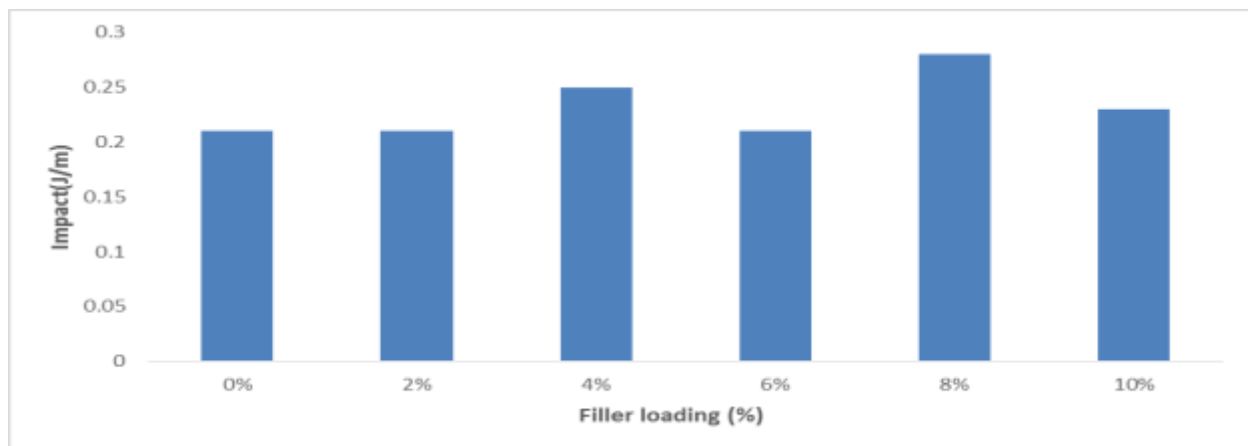
Hardness is the measure of a material's resistance to surface indentation, it is also a function of the stress required to produce some specific types of surface deformation (Swamy *et al.*, 2011). Table 4.2 shows the variation of hardness with percentage filler loading for cassava peels/UPR composites. It was observed that the hardness value increases with increased filler loading.

Impact Test

Table 4.3 impact test

S/N	% of cassava peels	% of UPR	Impact test of cassava peels/ unsaturated polyester resin composite (j/m)
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1	0%	98%	0.21
2	2%	96%	0.21
3	4%	94%	0.25
4	6%	92%	0.21
5	8%	90%	0.28
6	10%	88%	0.23

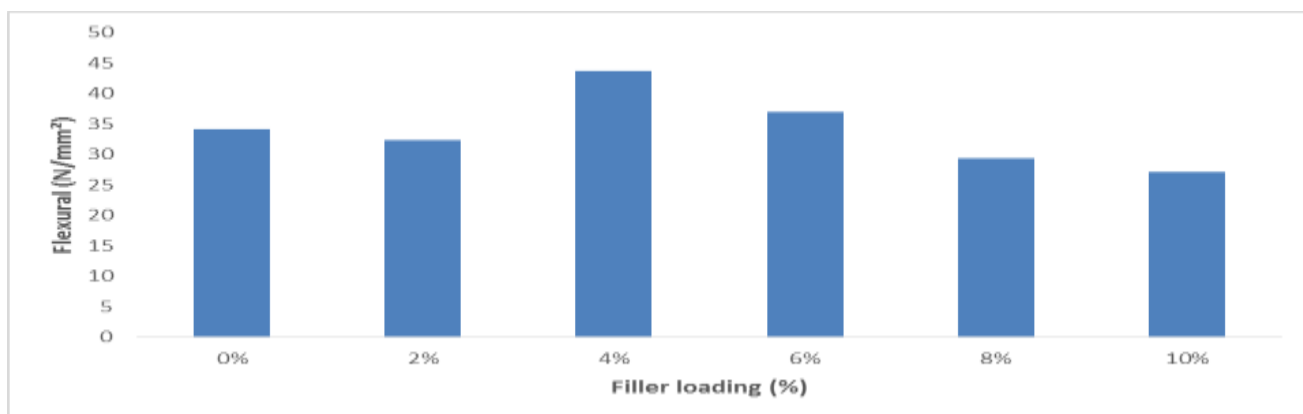


Impact strength is the ability of the composites material to withstand shock loading or the ability of a material to absorb mechanical energy in the process of deformation and fracture under impact loading. Presence of longitudinal fibres at the loading points contributes to increase in the resistance and invariably better mechanical properties. This can only take place if the interfacial adhesion between the matrix and the filler will not result into a crack, lowering the impact strength of the composites. As filler loading increase there is a disturbance in the three dimensional network of the polymer matrix resulting into decrease in mobility of matrix molecules. The decrease in impact strength can be attributed to saturation of the UPR by fillers, thus, preventing proper bonding of the fillers to form strong composites.

Flexural Test

Table 4.4 flexural test

S/N	% of cassava peels	% of UPR	Impact test of cassava peels/ unsaturated polyester resin composite (N/mm ²)
1	0%	98%	34.21
2	2%	96%	32.33
3	4%	94%	43.64
4	6%	92%	36.96
5	8%	90%	29.32
6	10%	88%	27.15



Flexural strength is also known as bend strength or fracture is defined as materials ability to resist deformation under load. It was observed from the table above that the filler loading at 4% has the highest bend strength value while sample with 10% filler loading has the lowest bend strength value of 27.14N/mm². During introduction of fillers into matrix, air may be trapped in the material. After curing micro voids maybe formed in the composites along the individual fillers due to the fibre spacing in between the composite, which has adverse effect on the mechanical properties of the composites (Kabir *et al.*, 2011).

CONCLUSION

This work was carried out to study the effect of filler loading on mechanical properties of cassava peels/unsaturated resin composite. The waste cassava peels obtained from cassava can also be used as filler in unsaturated polyester resins. The effect of cassava peels on some mechanical properties of unsaturated polyester were investigated. The flexural strength with lowest value was 27.15MPa at 10% filler loading while the highest value was 43.64MPa at 4% filler loading. The hardness test gave values ranging from 21.6 to 54.5 as the filler content increases from 2% to 10% increases with increased filler content. The values of the impact strength were 0.25, 0.21, 0.25, 0.21, 0.28 and 0.23 for 0%, 2%, 4%, 6%, 8%, and 10% respectively. It was observed that the control sample and the 4% filler loading have the same impact value of 0.25 so also the filler loading at 2% and 6% have the same impact value of 0.21. The result also show that the filler loading at 8% has the highest impact value of 0.28J/m. It is recommended that further studies should be carried out on the preparation of composites using other polymer matrices, with cassava peels of different particle sizes and other composite moulding techniques instead of local hand mix should be used in the production of these composites. Also the physical tests like water absorption and density can also be carried out.

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SN 6 SURFACE CHARACTERIZATION OF BIOCHAR FROM AGRICULTURAL RESIDUES FOR THEIR APPLICATION AS SOIL AMENDMENT

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Abstract

Bio-waste materials; banana (*Musa Balbisiana*) leaves, cassava (*Manihot Esculenta*) peels, mango (*Mangifera Indica*) leaves, plantain (*Plantago Lanceolata*) leaves and peels were pyrolyzed at different temperatures; 300, 400, 450, 500 and 600 °C using a muffle furnace. The biochar samples obtained were characterized and properties evaluated for their potential application in soil for agronomic and environmental benefits. The measured physico-chemical properties; pH, bulk density, percentage yield and electrical conductivity varied with temperature of pyrolysis and somewhat with the source of the bio-waste. Surface morphology and elemental composition were determined from Scanning Electron Microscopic (SEM) and Energy Dispersive X-ray (EDX) measurements. There were variations in texture, porosity and elemental composition with pyrolysis temperature. The results obtained suggest that biochar samples obtained at lower temperatures 300 and 400 °C will be better suited for agronomic applications, while biochars obtained at higher temperatures with better structure and porosity may be more suited for pollutant adsorption.

Keywords: Bio-waste materials, pyrolysis, biochar, environmental applications

Introduction

Bio-wastes from agricultural residues which are abundant, inexpensive and readily available are a valuable resource used in the preparation of biochar, a carbon – rich product obtained from the pyrolysis of biomass in the absence or a limited supply of oxygen (O'Connor *et al.*, 2018; Xiao *et al.*, 2018). Biomasses from agricultural residues, some of which are by-products of the agricultural crops, raw materials from the forest, municipal solid waste, animal and human wastes are affordable source of energy and materials derived from them which include bio-oil, biochar, fuel and chemicals amongst others have been reported to have potential benefits to agriculture and the environment (Bardalai and Mahanta, 2018). Biochar has been reported to be an effective and environmentally friendly material in the agricultural sector for soil amendment and enhancement processes due to its large specific surface area, possession of surface functional groups such as hydroxyl, carboxyl, etc., microporous structure, high cation exchange capacity (CEC) amongst many others (Pattnik *et al.*, 2018; Yang *et al.*, 2017).

The use of biochar from different agricultural residues for environmental applications abound in literature (Adesemuyi *et al.*, 2020; Wang *et al.*, 2020; Safian *et al.*, 2020) as biochar – related materials remain pillars for sustainable growth and development considering Nigeria's estimation of agricultural wastes production of approximately 998 million tons annually which has potential of producing biochar on commercial basis for environmental applications (Obi *et al.*, 2016). Biochar from varieties of biomass such as bamboo leaves, rice husk, nutshells, pine wood, orchard pruning biomass, etc., have been exploited as feedstock and reported to produce efficient sorbents used in immobilizing heavy metals in aqueous environments, soils and sediments, remediate soil from pollutants such as petroleum hydrocarbons and pesticides, improve soil fertility and plant growth amongst many others (Guo *et al.*, 2020; Xu *et al.*, 2021; Kumar *et al.*, 2023).

Agricultural residues (wastes) are being churned out in large quantities all over the world in general and Nigeria is not left out as population increases and some of these wastes are indiscriminately disposed in the environment which ultimately results in pollution with its attendant health effects on man. With the global call for sustainable practices which offer an eco – friendly approach to waste management, converting agricultural residues into valuable resource materials would no doubt enhance sustainability with the development of soil amendment materials for agronomic and environmental applications as well as reducing diverse health issues arising from the indiscriminate disposal of waste. Biochar have

been reported to be prepared from different renewable resources and the general characteristics which are somewhat similar have also been shown to be effective in the removal of pesticides and other contaminants in the environment (Singh *et al.*, 2022). This present study seeks to investigate the quality of biochar obtained from banana (*Musa Balbisiana*) leaves, cassava (*Manihot Esculenta*) peels, mango (*Mangifera Indica*) leaves, plantain (*Plantago Lanceolata*) leaves and peels obtained over a range of pyrolytic temperatures in terms of pH, elemental analysis, bulk density, electrical conductivity, surface morphology and functional groups present so as to provide important baseline information for the production of biochars from agricultural wastes with desired properties for environmental applications and management.

Materials and Methods

Five different biomasses were collected from nearby farmlands around the Ugbomoro village where the Federal University of Petroleum Resources, Effurun, Delta State, Nigeria, is situated. Prior to pyrolysis, the biomasses were cleaned and washed severally with deionized water to remove surface contamination, crushed (> 1 cm), air – dried for approximately twenty – one (21) days and oven – dried at 60 oC for six (6) hours. The pyrolysis was carried out in a laboratory scale using muffle furnace coupled with a glass condenser and a nitrogen (N₂) gas cylinder using low and high temperatures at 300 – 450 oC and 500 – 600 oC respectively. In a typical pyrolysis experiment, 60g of the biomass was placed in the muffle furnace, which had been heated to the desired temperature, in an inert atmosphere. Each sample was heated for one hour at a constant heating rate and biochar was the product obtained after pyrolysis which was collected and stored in air – tight containers for further analysis. The percentage yield (%) for each biochar sample was obtained as a ratio of the mass of the dry biochar (M₂) to the mass of the dry biomass (M₁) using the equation:

$$\% \text{ Yield} = \frac{M_2}{M_1} \times 100 \dots\dots\dots (1)$$

Five biochar samples were obtained for each biomass: BL 300, BL 400, BL 450, BL 500 and BL 600 for biochars obtained from banana leaves; CP 300, CP 400, CP 450, CP 500 and CP 600 for cassava peels; ML 300, ML 400, ML 450, ML 500 and ML 600 for mango leaves; PL 300, PL 400, PL 450, PL 500 and PL 600 for plantain leaves; PP 300, PP 400, PP 450, PP 500 and PP 600 for plantain peels in addition to control samples for each biomass which did not undergo pyrolysis for comparison purposes.

Physico-chemical analyses and Surface Characterization of Biochar Samples

To assess the quality of the biochar obtained from the different biomasses, standard methods as described (Singh, *et al.*, 2010; Adesemuyiet *al.*, 2020) were used to determine the physico-chemical composition of each homogenized and ground (> 1 mm) biochar sample. The pH and electrical conductivity (E.C) of all the biochar samples was determined as a 1:10 biochar: deionized water ratio (w/v) slurry after vigorous shaking for two hours on a mechanical shaker using a Metrohm 744 pH meter and a Model S 213 compact conductimeter. The bulk density and exchangeable cations were determined as described previously (Singh, *et al.*, 2010). All the experiments were carried out in triplicates and average values recorded.

The microstructure and elemental composition of the biochar samples were carried out using a TESCAN Scanning Electron Microscope (TE-SEM) equipped with Energy Dispersive Spectroscopy (EDS), Oxford Instruments, Czech Republic. The gold sputtering technique was used to coat the samples before analysis. To identify the functional groups, JASCO FTIR 4100 Fourier Transform

Infrared Spectrophotometer was used to record the spectrum of the biochar samples over a scanning range of 400 – 4000 cm⁻¹.

Results and Discussions

Physicochemical analyses of biochar samples

The pyrolysis temperature has been reported to be strongly correlated with changes in the structure and physicochemical properties of biochar (Jindoet *al.*, 2014). Data on these relationships are presented in Table 1.

Table 1: Physicochemical characteristics of biochars derived from different biomasses: banana leaf (BL), cassava peel (CP), mango leaf (ML), plantain leaf (PL) and plantain peel (PP)

Biochar Sample	Temperature (oC)	Yield (%)	pH	EC (μS/cm)	Bulk density (g/cm ³)	CEC (cmol/kg)
Control BL	Banana Leaf	100.0	7.15	40000	0.19	283.1
	300	84.6	7.34	71000	0.18	319.9
	400	44.7	8.38	92000	0.18	399.3
	450	41.5	8.73	70900	0.14	376.4
	500	33.5	8.91	102400	0.18	328.5
	600	30.9	10.83	368300	0.18	817.1
Control CP	Cassava Peel	100.0	4.4	15.6	0.37	201.7
	300	72.5	5.5	10.6	0.41	195.2
	400	53.5	8.4	7.4	0.29	175.0
	450	50.5	8.5	7.8	0.27	319.5
	500	46.5	8.7	9.0	0.30	239.6

	600	39.7	8.9	9.9	0.26	333.6
Control	Mango Leaf	100.0	6.4	47900	0.31	354.6
ML	300	32.3	8.4	76300	0.20	311.2
	400	31.8	8.7	94000	0.21	318.7
	450	31.1	8.8	97200	0.21	335.9
	500	21.1	9.0	120300	0.24	231.5
	600	16.1	9.1	119600	0.22	311.9
Control	Plantain Leaf	100.0	6.5	10.1	0.30	272.9
PL	300	54.1	7.5	55.4	0.14	240.8
	400	38.8	8.1	51.1	0.13	230.5
	450	38.0	9.2	128.3	0.13	260.5
	500	30.1	9.5	106.2	0.15	274.1
	600	2.2	10.1	122.6	0.11	339.4
Control	Plantain Peel	100.0	6.8	26.4	0.46	217.3
PP	300	61.2	7.4	27.4	0.27	360.1
	400	45.5	7.7	52.1	0.23	258.1
	450	37.0	9.7	54.4	0.21	220.3
	500	36.9	9.7	50.8	0.22	332.6
	600	22.1	10.0	67.1	0.22	272.1

Generally, at the end of pyrolysis, the biochar yield decreased with an increase in temperature for all the biochar samples, however, the percentage decrease, $\geq 60\%$ was lower for BL and CP biochars produced at low temperatures (300 – 400 oC) when compared with those produced at higher temperatures (450 – 600 oC), ML, PL and PP biochars with $\geq 80\%$. Biomasses have been reported to contain different proportions of lignocellulose components which vary and decompose differently due to the differences in the relative abundance of cellulose, hemicellulose and lignin present in them (Somparnet *et al.*, 2020; Yang, *et al.*, 2017). Plant biomasses such as BL, ML and PL used in this study have been reported to have main components as carbohydrates and lignin: the carbohydrates which are mainly cellulose or hemicellulose fibers gives strength to the plant structure and lignin holds the fibers together (Ucar and Ozkan, 2008).

It has been reported that a good number of biochars from different biomasses used for soil amendment are alkaline as a result of carbonization during which acidic functional groups are removed and salts of alkali and alkaline earth metals become enriched (Singh, *et al.*; 2017). The pH of the biochars increased as the temperature increases for all the biochar samples as shown in Table 1. With the exception of BL, all the biomasses were acidic having pH values < 7 but after pyrolysis, the biochars became alkaline as a result of reduced acidic groups and an increase in the salts of alkali metals which would make them suitable for improving acidic soils (Bardalai and Mahanta, 2018). Two effects of pyrolysis temperature on pH have been reported to be based on two aspects: an increase in pyrolytic temperature increases the formation of biochar ash which contains alkaline minerals and biochar produced at lower pyrolytic temperatures may contain greater densities of phenolic and carboxyl groups which are acidic thereby decreasing the pH (Zhao, *et al.*, 2018).

The electrical conductivity (EC) of a biochar sample is a measure of the quantity of soluble salts present and is an important property to consider when used for soil amendment as it affects the salinity of the soil. Some authors have reported high EC values for biochars produced at higher pyrolysis temperatures (Kloss *et al.*, 2012) and the values of EC obtained for the biochars in this study vary considerably with BL and ML having the highest values.

Carbonization through slow temperature have been reported to enrich the carbon content, create a porous structure and less dense biochar generally. This is attributed to the decomposition of organic matter thereby leading to the transformation of biomass matrices into a lighter and porous structure (Amupam *et al.*, 2016). The bulk density for all the biochar samples generally decreased with an increase in pyrolytic temperature indicating an increase in the porosity of the biochar samples. PL biochar samples had the lowest values for bulk density and may appear to a highly porous surface.

The cation exchange capacity (CEC) which is an indication of carboxyl groups present and the ability of a soil or substrate to hold exchangeable cations and supply nutrients for plant uptake is of agronomic advantage. The application of biochar has been reported to increase the cation exchange capacity of soils thereby improving soil fertility (Wang, *et al.*, 2020). The CEC obtained for the biochar samples from different biomasses varied: BL and PP biochar samples had CEC values increasing with an increase in temperature, CP and PL had higher CEC values at temperatures ≥ 450 oC while the CEC for ML biochar samples decreased with an increase in pyrolysis temperature. High CEC values for BL, CP, PL and PP biochar samples indicate their potential application in soil to hold cationic nutrients and retain cationic fertilizer.

Elemental Composition using EDX measurements

Surface elemental analysis was performed using energy dispersive X-ray spectroscopy (EDX). For accuracy in data analysis, each EDX analysis was repeated three times for the biochar samples and average values obtained for the different elements present are given in Table 2. The major elements detected included C, O and K accompanied by small amounts of other elements such as Cl, Si, P, Mg amongst others as presented. The carbon content increased exponentially with an increase in pyrolytic temperature for most of the biochar samples which has been reported to be associated with the loss of –OH functional groups caused by dehydration (Song, *et al.*, 2023). The oxygen (O) content in some cases, decreased with an increase in temperature. The decrease in oxygen concentration with increasing temperature can be explained by the fact that various oxygen functional groups are released as volatiles during carbonization (Wu *et al.*, 2016).

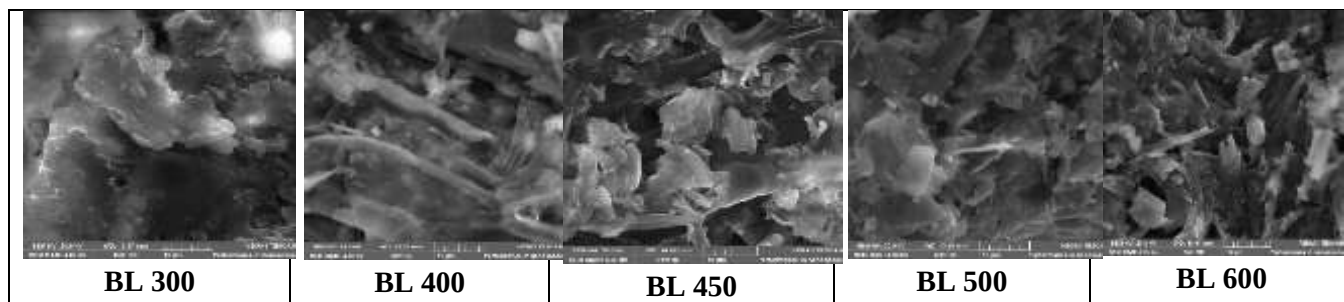
Table 2. EDX analysis of biochars derived from different biomasses: banana leaf (BL), cassava peel (CP), mango leaf (ML), plantain leaf (PL) and plantain peel (PP)

Biochar Sample	Temp (oC)	C	O	K	Si	Ca	Mg	Fe	Mn	P	Al	Cl
		Weight%										
BL	300	48.8	38.2	1.3	-	11.7	-	-	-	-	-	-
	400	75.4	20.5	1.5	0.5	1.0	0.8	-	-	0.2	0.3	-
	450	75.8	18.8	2.5	0.8	2.0	-	-	-	-	-	-
	500	66.9	18.4	4.5	-	7.8	1.4	-	-	0.9	-	-
	600	72.5	15.9	6.6	0.7	2.5	1.7	-	-	-	-	-
CP	300	56.5	37.1	0.6	2.2	-	-	0.9	-	-	2.6	-
	400	69.1	22.0	3.1	1.8	1.1	0.4	0.8	-	0.5	1.3	-
	450	71.7	23.0	1.7	0.7	0.7	-	1.0	-	-	1.1	-
	500	65.7	25.1	5.2	-	3.2	0.8	-	-	-	-	-
	600	72.0	15.7	4.6	2.4	1.5	-	1.4	-	0.7	1.6	-

ML	300	70.1	27.0	1.7	-	1.2	-	-	-	-	-	-
	400	17.0	34.0	7.9	7.9	27.1	0.4	-	5.7	-	-	-
	450	73.1	23.8	1.0	0.8	1.3	-	-	-	-	-	-
	500	43.0	35.8	2.2	4.7	12.5	0.4	-	-	0.4	0.9	-
	600	69.1	12.1	2.2	1.2	15.3	-	-	-	-	-	-
PL	300	65.0	25.4	4.1	-	4.0	-	-	-	-	-	1.6
	400	71.8	13.4	3.7	11.1	-	-	-	-	-	-	-
	450	68.3	15.4	8.3	2.6	3.4	0.8	-	-	-	-	1.3
	500	64.5	21.5	5.2	1.0	6.7	1.0	-	-	-	-	-
	600	69.9	18.3	5.6	0.9	3.4	1.4	-	-	-	-	0.6
PP	300	57.5	24.9	16.9	-	-	-	-	-	-	-	0.7
	400	61.3	20.8	15.1	-	-	-	-	-	-	-	2.7
	450	38.1	35.2	25.0	0.6	-	-	-	-	-	-	1.2
	500	69.7	19.0	9.2	0.5	-	-	-	-	0.4	-	1.3
	600	62.5	21.7	13.6	0.4	-	0.3	-	-	0.6	-	0.8

Scanning Electron Microscopic (SEM) measurements

Scanning electron micrograph (SEM) images are very useful in obtaining accurate details about the surface structure of biochar and the comparison of the images at various temperatures might provide more insight into the morphological changes taking place during pyrolysis. The micrographs obtained for the different biochar samples pyrolysed at different temperatures are shown in Fig. 1. All the biochars at various temperatures possess porous structures. Each micrograph shows a porous structure of the biochar with different shapes and scales of pores with cylindrical crevices interconnected by some large tubes, seeming honeycomb-like at higher temperatures. Temperature strongly influences the structure of different biochars and previous studies (Devenset *al.*, 2018) have shown that the porosity of biochar is mainly attributed to the intrinsic physical structure of the precursor biomass, and may be influenced by the sample pyrolysis temperature. The biochar samples contain several cracks and holes formed because of the evolution of volatile matter during carbonization. The morphology of the biochar samples pyrolysed at different temperatures varied from each other and the SEM scans showed the complex surface structure of the biochars which are heterogeneous. As the pyrolytic temperature increased, the biochar structures became more uniformed as the number of macropores increased and the number of micropores decreased thereby exhibiting a large degree of macro-porosity in the 1 to 10-micron scale.



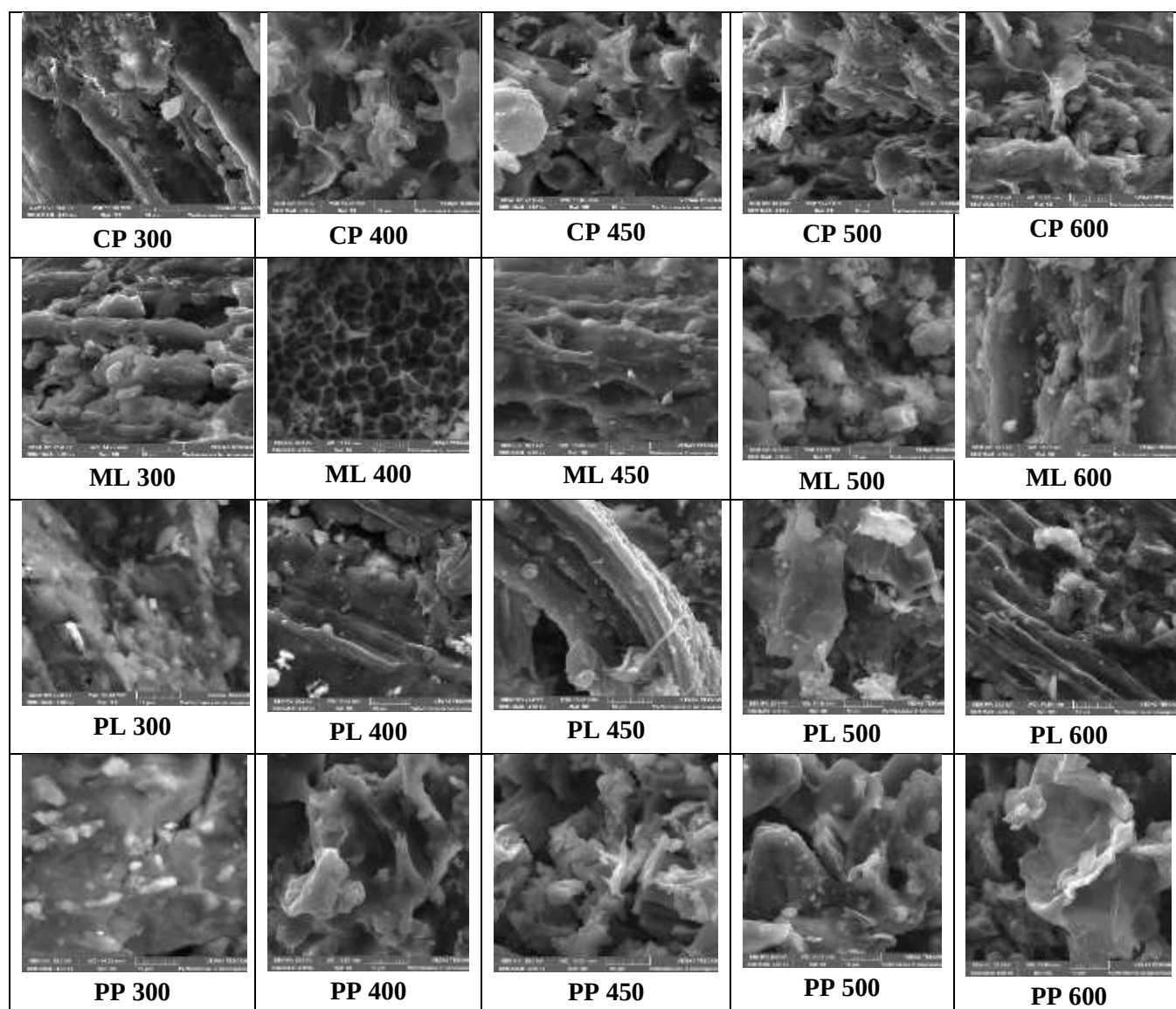


Fig. 1: Scanning electron micrographs (SEM) at 10 μ m magnification for all biochar samples

Infrared (IR) Spectral Analysis

The biochar samples were subjected to FTIR analysis to determine the functional groups present. A typical FTIR spectra of CP at 300 oC is shown in Fig. 2.

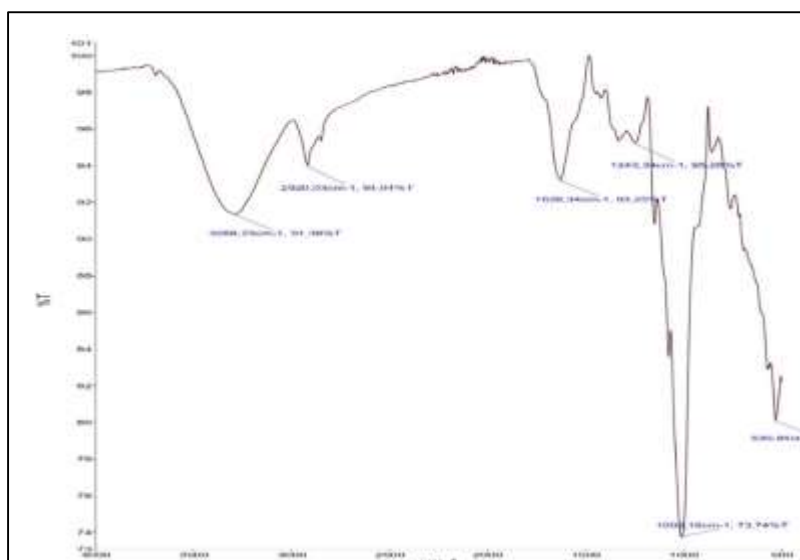


Fig. 2: Typical FTIR spectra for CP biochar sample at 300 °C

For all the biochar samples, the FTIR spectra were characterized by three principal absorption bands between 3305 – 3505, 2920 – 2927 and 1580 – 1630 cm^{-1} corresponding to the stretching vibration of –OH, –CH₂ and aromatic C=O ring respectively. It has been reported that biochar from biomass is dominated by functional groups typical of oxygenated hydrocarbons which reflect the carbohydrate structure of cellulose and hemicelluloses (Tomczyk, *et al.*, 2020). The production of biochar at various pyrolytic temperatures has been shown and reported to cause the disappearance of absorption bands characteristic of the raw material and the appearance of new bands typical of biochar samples (Ghani, *et al.*, 2013; Tomczyk, *et al.*, 2020). Typical FTIR bands reported for biochars ((Claoston *et al.*, 2014; Ghani, *et al.*, 2013; Liu, *et al.*, 2015; Tomczyk, *et al.*, 2020; Zhao, *et al.*, 2017), were present in all the biochar samples at different pyrolytic temperatures.

Conclusion

This study produced biochars from banana (*Musa Balbisiana*) leaves, cassava (*Manihot Esculenta*) peels, mango (*Mangifera Indica*) leaves, plantain (*Plantago Lanceolata*) leaves and peels at different pyrolysis temperatures – 300, 400, 450°C, 500 and 600°C. They were characterized using energy dispersive spectroscopy, scanning electron microscopy and Fourier transform infrared spectroscopy. The biochar yield, pH, electrical conductivity, bulk density and CEC were also determined using standard methods. The pH, bulk density, percentage yield and electrical conductivity of all the biochar samples varied with temperature of pyrolysis. The porosity of the biochar samples increased as they exhibited a large degree of macro-porosity in the 1 to 10-micron scale. The results obtained suggest that biochar samples obtained at lower temperatures 300 and 400 °C will be better suited for agronomic applications as the alkalinity of the biochar samples have potential for improving soil alkalinity, while biochars obtained at higher temperatures with better structure and porosity may be more suited for pollutant adsorption.

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SN 7 SYNTHESIS AND CHARACTERIZATION OF CHOLINE CHLORIDE – ETHYLENE GLYCOL DEEP EUTECTIC SOLVENT FOR THE EXTRACTION OF BTEX FROM SOIL

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Abstract

Benzene, toluene, ethylbenzene and xylene (BTEX) are among environmental pollutants of environmental concern. They are often found in industrial effluents, which when discharged into farmlands end up contaminating the soils. Such happenings warrant the remediation of the soil for environmental sustainability. Prominent among the techniques employed for this remediation is solvent extraction. However, this procedure is limited by the type of solvent used, as volatile organic solvents end up producing secondary pollutants. This study aims to synthesize and characterize a biodegradable and environmentally friendly solvent that will be used for the remediation of soils contaminated with BTEX. Deep Eutectic Solvents (DESs) are continuously gaining attention as alternatives to volatile organic solvents due to their tunable nature, ease of synthesis and the availability of biodegradable constituents. Choline chloride and ethylene glycol in a 1:2 molar ratios were synthesized and its functional group interactions as well as the variation of its physical properties- density, viscosity and surface tension – with temperature were measured. The density, viscosity and surface tension values range from 1.1181 kg m⁻³ – 1.0816 kg m⁻³, 36.03 cPs – 10.07 cPs, and 41.01 mN m⁻¹ – 34.65 mN m⁻¹ respectively over the temperature range of 303K – 353K. These values conform with the requirements for green solvents and appear suitable for application (as solvent) in the remediation of soils contaminated with hydrocarbons.

Keywords: Soil, contamination, Deep Eutectic Solvents, BTEX, solvent extraction.

1.0 Introduction

One of the major environmental problem faced by the Nigerian oil and gas industry is industrial pollution (Ekere *et al.*, 2015). Various contaminants such as oils, pesticides and heavy metals released by modern industrial, agricultural and mining activities affect soils by eventually leaching to the aquifer (Mukhopadhyay, 2016). These contaminants, when released, render the soil unsuitable for various activities (such as agriculture, housing and urbanization, as well as the development of basic infrastructural amenities) that require the use of land. The Niger-Delta region of Nigeria has been plagued with diverse environmental, socioeconomic and public health issues associated with petroleum hydrocarbon contamination (Amaize, 2016; Brevik *et al.*, 2013). These health issues include genetic mutation, cancer, birth defect, central nervous system disorder etc. Soil contaminants are chemicals or substances present in the soil in concentrations above Permissible limit (Rodríguez *et al.*, 2018). The effects of soil contamination depend in part, on soil properties because they control contaminants mobility, bioavailability, and residence time. Most petroleum contaminants, such as benzene, toluene, ethylbenzene, and xylenes (BTEX), aliphatics and polycyclic aromatic hydrocarbons (PAHs) are easily trapped in soils and sediment and this is a growing concern globally because of how toxic these contaminants can be to the ecosystem.

Several methods have been developed to remove hydrocarbon contaminants from soils. The performance of these methods depends on several factors such as amount of oil spill, oil penetration depth into the soil, soil type as well as age and level of contamination (Motshumi and Edison, 2014). These methods are grouped into two broad categories; Destructive techniques including biological, chemical and thermal remediation, and recovery techniques including extraction, adsorption, coagulation and sedimentation. Similarly, hydrocarbon contaminated environment can be remediated using various technologies. These are broadly classified as physicochemical, biological and thermal remediation technologies (Tewari and Sirvaiya 2015). Physicochemical method is the most diverse group of remediation technologies. It includes techniques such as solvent extraction, solidification/stabilization, chemical oxidation, soil vapor extraction, soil washing/flushing e.t.c (Wu *et al.*, 2011; Tewari and Sirvaiya 2015). Solvent extraction is an attractive technique for the removal of hydrocarbon contaminants from soil. The two steps involved in the extraction of hydrocarbon contaminants from a soil matrix are desorption from the binding site in (or on) the solid matrix followed by elution from the solid into the extraction fluid (Wu *et al.*, 2012). One of its favorable features is that it is implemented at mild operating conditions thereby reducing energy demand. An important issue of concern when adopting solvent extraction as a remediation technique is the type of solvent used in the process - various solvents ranging from volatile organic compounds (VOCs), alcohols, vegetable oils and supercritical/subcritical water are limited by low extraction efficiency and the problem of secondary pollutants (Gano *et al.*, 2015; Wu *et al.*, 2011).

A deep eutectic solvent is generally composed of two or three cheap and safe components which associate with one another, through the interaction of hydrogen bond, to produce a eutectic mixture (Zhang *et al.*, 2012). Deep eutectic solvents (DESs) have recently emerged as a new class of solvents - similar to ionic liquids - produced by complexing quaternary ammonium salts with metal salts or hydrogen bond donors (Smith *et al.*, 2014). DESs have been applied in a variety of extraction techniques, including but not limited to liquid- liquid extraction (Aleksandra *et al.*, 2015). Moreover, these solvents find use in analytical method development such as solid-phase (micro) extraction, microwave-assisted extraction, ultrasound-assisted extraction and pressurized liquid extraction (Pena-Pereira and Namiesnik, 2014), removal of environmental pollutants (Duan *et al.*, 2020), selective isolation and recovery of target compounds (Warrag, 2018), desulfurization of fuels (Gano *et al.*, 2015), and azeotrope breaking (Mulyono *et al.*, 2014).

One of the most promising technologies for the removal of hydrocarbon contaminants from soil is solvent extraction. This is a technique whereby petroleum hydrocarbons are removed from soil using a particular solvent or mixture of solvents (Wu *et al.*, 2011; Gan *et al.*, 2009). This work aims to synthesize a deep eutectic solvent using choline chloride and ethylene glycol in a 1:2 molar ratios and establish the variation of its physical properties with temperature. This relationship once established, along with the DESs structure, obtained from FTIR spectroscopy will be used to ascertain its application for the removal of BTEX from contaminated soil.

2.0 METHODOLOGY

2.1 Chemicals

Choline chloride (98% pure) was purchased from Macklin (Shanghai Macklin Biochemical Company Ltd, China) while ethylene glycol ($\geq 98\%$ pure) purity was purchased from Merck (Merck, Darmstadt, Germany) both chemicals are of analytical grade.

2.2 Methodology

2.2.1 Deep Eutectic Solvents (DESs) Synthesis and Characterization

DES synthesis was carried out according to procedure reported by Ibrahim *et al.*, 2018; Choline chloride (ChCl) was mixed with ethylene glycol (EG) in a 1:2 molar ratios, on a magnetic hot plate stirrer operated under atmospheric pressure at 280 rpm and a temperature of 70°C until a clear, homogeneous and colorless solution (that forms no precipitate after cooling) was formed.

Fourier transform infrared spectroscopy (FTIR) was performed on Agilent 5000a with attenuated total reflectance (FTIR-ATR) spectrometer manufactured by Agilent technologies. Its spectrum range is 4000-650 cm⁻¹ with a resolution of 8cm⁻¹. Physical properties of the DES which affect extraction - density, viscosity, and surface tension - were measured as a function of temperature in the temperature range 303K – 3553 K. sigma force tensiometer was used to measure density and surface tension while viscosity was measured using an NTV-E series intelligent touch viscometer at measuring range of 1 – 100,000 cP, and spindle rotation of 12 rad/min.

3.0 RESULTS AND DISCUSSION

FTIR spectra for Choline chloride, Ethylene Glycol and the synthesized DES are depicted in figure 3.1. The spectrum of choline chloride shows several functional groups; prominent among them are the peaks at 3219 cm⁻¹ and 3007 cm⁻¹ which corresponds to an N-H, and a symmetrical CH₃ stretches respectively (Hayyan *et al.*, 2015), peaks at 896 cm⁻¹ confirms the existence of the halide ion (Cl⁻) (Ibrahim *et al.*, 2019). The spectrum of ethylene glycol shows peaks at 3290 and 2980-2880 cm⁻¹ corresponding to an O-H stretch, and C-H stretch of sp³ hybridized bending (Delgado-Mellado *et al.*, 2018), O-H in plane bending at 1335 cm⁻¹, C-O-H bond bending at 1261-1208 cm⁻¹, C-O bond stretching at 1086 cm⁻¹, C-C-O asymmetric stretch at 1037 cm⁻¹ and C-C-O symmetric stretch at 884-861 cm⁻¹ (Ibrahim *et al.*, 2019). The spectrum for the DES 1:2 molar ratio ChCl:EG Peak appearing at 3290 cm⁻¹ refer to O-H stretching, at 2936 cm⁻¹ and 2873 cm⁻¹ refer to a shift in C-H stretching of sp³ hybridized bending. Peaks at 1484 cm⁻¹ to the bending of a CH₂ from an alkyl group. C-O-H bending appears at 1209 cm⁻¹, Others appearing at 1189 cm⁻¹, 1041 cm⁻¹, and 866 cm⁻¹ represent a shift in the C-O stretching, C-C-O asymmetric stretching, and C-C-O symmetric stretching functional groups respectively. These structural changes in functional groups agree closely with what is reported by Hayyan *et al.* for a CHCl: EG (1:2) thus confirming formation of the intended DES.

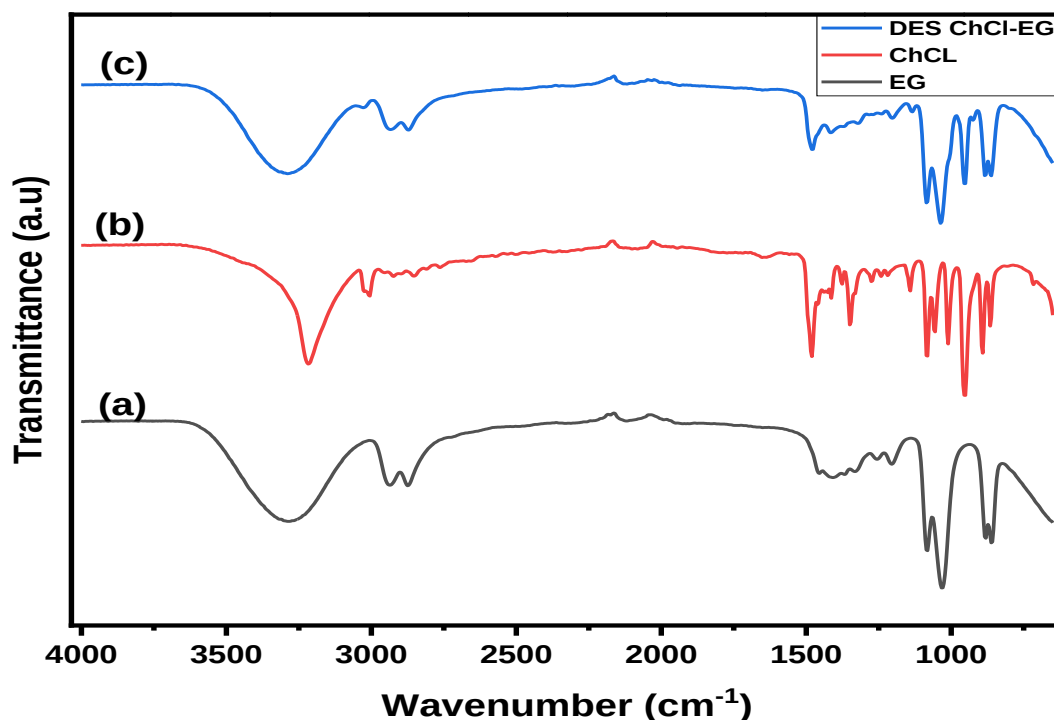


Fig.3.1: FTIR result for Choline Chloride, Ethylene Glycol and ChCl:EtG DES

Fig. 3.2, 3.3 and 3.4 shows the relationship between density/temperature., viscosity/temperature and surface tension/ temperature. All three physical properties show a behavior that is consistent with those reported by Ibrahim et. al confirming the formation of the DES (1:2 molar ratios, ChCl:EG). Also, these behaviors further inform the viability of the DES for the intended application for the following reasons; (1) the properties fall within the range of important transport properties for application in solvent extraction. (2) the viscosity relationship can be used to fix the extraction temperature in the region of minimal change with temperature, thereby limiting the factors to consider when designing the experiment.

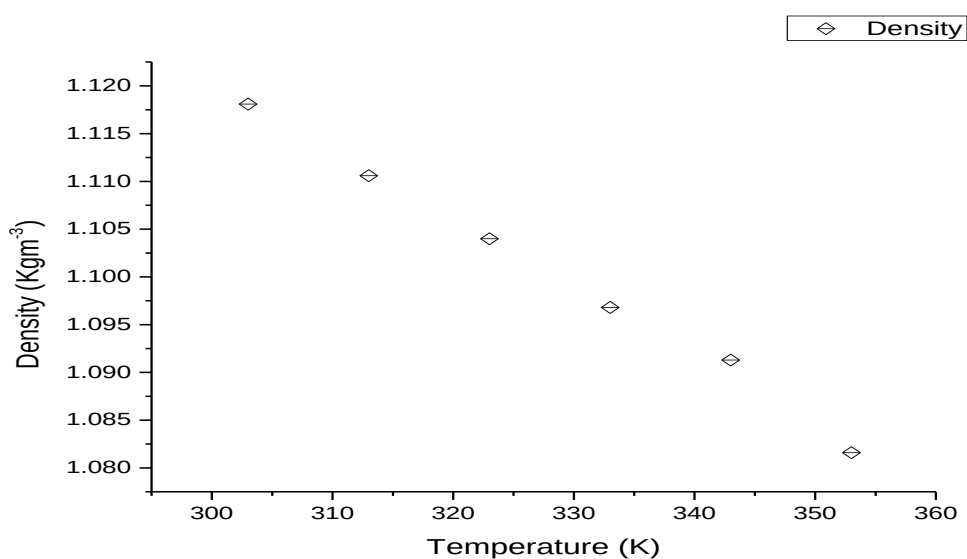


Fig 3.4: variation of DES density with temperature for the

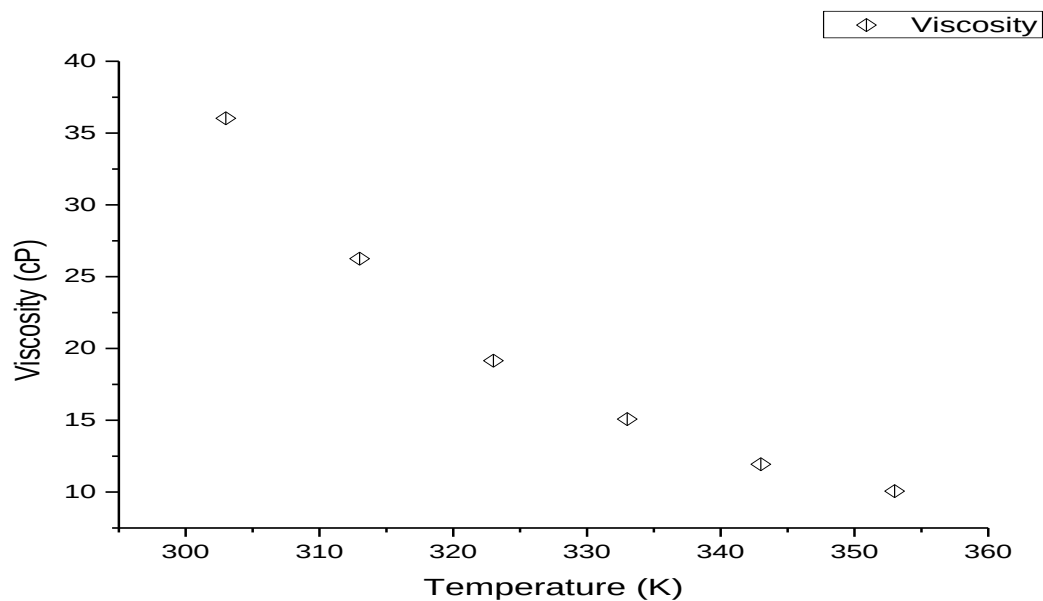


Fig. 3.3: variation of DES viscosity with temperature

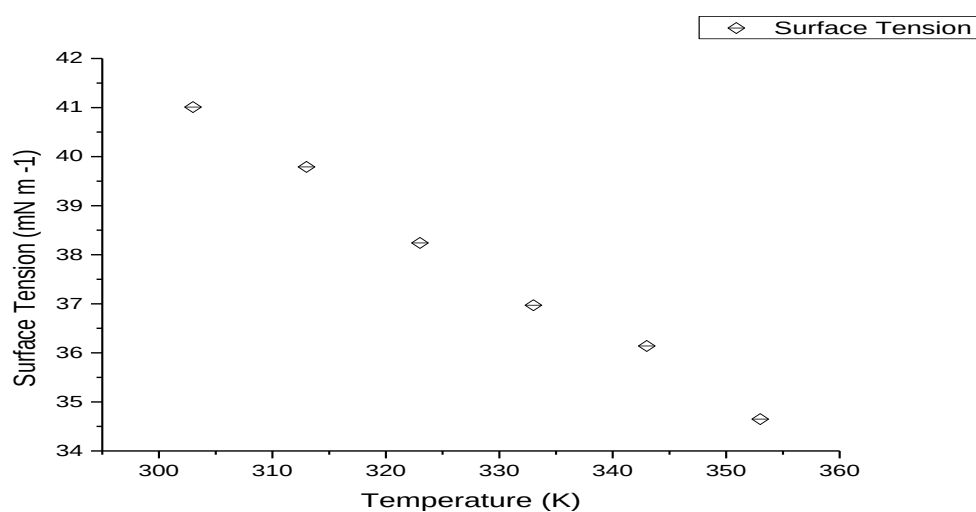


Fig.3.4: Variation of Surface tension with Temperature.

4.0 Conclusion

A 1:2 molar ratios deep eutectic solvent was successfully synthesized from choline chloride and ethylene glycol. Its functional groups and variations of its physical properties - density, viscosity and surface tension – with temperature were established. The density and surface tension show linear relationship with temperature while viscosity tends to follow an Arrhenius curve. The changes in functional groups, very low viscosity and a density range above that of water over the temperature range all support our aim of extracting BTEX contaminants from soil under mild operating condition. Hence, the synthesized DES is expected to perform favorably as an extraction solvent for the extraction of BTEX contaminants from soil.

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SN8 The Impacts of Hydroxyapatite on the Materials Properties of Titanium Alloys for Orthopaedic Applications – A Review

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ABSTRACT

The use of biomaterials for orthopaedic purposes has reached an advanced state. Notable among these biomaterials used as implants are titanium and its alloys. They possess several properties that make them one of the most reliable and durable metallic alloys used as implants. However, with the high demand for improved biomaterials for orthopaedic applications, various researches have been carried out to improve the general properties of titanium alloys as implant materials. One such is the use of hydroxyapatite (HAp). Hydroxyapatite is a naturally occurring form of calcium phosphate and is the main mineral component of bones and teeth. Research has shown that the application of hydroxyapatite to titanium alloys and other implant biomaterials tends to improve their general material properties. It also improves the osseointegration ability of the implant materials with the host tissues. In this paper, the impacts of hydroxyapatite on titanium alloys are reviewed. With the quest to keep improving the material properties of implants, hydroxyapatite will certainly play a vital role in the advancement of implant biomaterials.

Keywords: ***Biomaterials, Orthopaedic, Implants, Hydroxyapatite, Titanium***

Introduction

Hydroxyapatite, a naturally occurring form of calcium phosphate, is the main mineral component of bones and teeth. Natural hydroxyapatite and bone have similar physical and chemical characteristics that make them biocompatible. Its porous structure resembles native bone (Pokhrel, 2018). The chemical similarity of hydroxyapatite to the inorganic component of bone and tooth gives it a major advantage compared to other materials when it is used as a biomaterial or bio-ceramic. The biocompatibility, biodegradability and bioactivity make it extensively useful in interdisciplinary fields of sciences like chemistry, biology, and medicine. Chemically, hydroxyapatite is $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ but often written as $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ (Pokhrel, 2018).

Bones and teeth are living organisms made up of minerals and tissues, the latter consists of cells, fatty substances, natural polymers (such as polysaccharides, collagen and polyphosphates) and other substances. Bone is the major calcified tissue present in mammals and is a ceramic–organic bio nanocomposite that has a complex structure. Bone tissues contain about two-thirds of the weight of inorganic material and a third of organic material on average. So, bone tissue is composed of a mineral phase that occupies about 69% of its total weight, about 9% water and about 22% of an organic matrix, which consists, in turn, mainly of collagen (90-96%) (Rivera-Muñoz, 2011).

Titanium as an Implant Material

The history of using Titanium in medicine goes back to 1950 when a coincidence led a doctor from the US to notice its biocompatibility. However, it was in 1970 when Branemark introduced Titanium to dentistry as he observed and defined osseointegration. Since then, the use of Titanium as dental implants to replace missing teeth has become very popular among dentists and patients (Alhomsi, 2018). Titanium has gained prominent attention in its use as biomaterials for implants over the past few years.

This is because it has a favourable combination of mechanical strength, chemical stability, and biocompatibility. There are several alloys of titanium but the two most common titanium-based materials are commercially pure titanium (CpTi) and extra low interstitial Ti-6Al-4V (ELI). Pure titanium is a soft nonmagnetic material and when heated to 883°C, it undergoes a crystallographic change from α to β -phase. Phase stabilizers are added to improve the mechanical properties of titanium (Shrestha and Joshi, 2014). An example of phase stabilizers added is aluminium called the α -phase condition stabilizer, which functions to increase the strength and decrease the weight of the alloy and Vanadium called β -phase stabilizer is added to help increase the ductility. The most common alloy contains 6% aluminium and 4% vanadium called Ti-6Al-4V. Ti-6Al-4V alloys are light, strong, highly resistant to fatigue and corrosion, stiffer than bone and they possess elastic modulus (stiffness) that is closer to the bone than any other important implant metal. This property leads to a more even distribution of stress at the critical bone-implant interface as the bone and implant will flex more similarly with minimal load /stress shielding (Shrestha and Joshi, 2014).

Coating Titanium using Hydroxyapatite

The processes of coating titanium with hydroxyapatite (HA) include plasma spraying, Sol-gel, sputtering, ion implantation etc. (Rattan *et al*, 2012). With the ease of application, plasma spraying is widely commercially exploited in the production of hydroxyapatite coating on titanium implants (Jongprateep *et al*, 2019). HA-coated implants with plasma spraying show good bond strength as against uncoated implants. The coated implants provide earlier and stronger fixation (Rattan *et al*, 2012; Oonishi *et al*, 1989). Nevertheless, due to high-temperature application, the plasma spraying technique is reported to produce nonuniformity in coating thickness and density, phase impurity, low crystalline hydroxyapatite coating and weak adhesion (Jongprateep *et al*, 2019). Sol-gel is time-consuming and requires post-processing annealing, however, ion implantation has found its applications better than the plasma spraying and Sol-gel techniques (Rautray *et al*, 2011; Rattan *et al*, 2012).

Preparing Hydroxyapatite

Nano-hydroxyapatite can be prepared by any of the following processes namely, Sol-gel Method, Precipitation Method, Eggshells as Starting Material or Animal Bone as Starting Material (Pandey *et al*, 2021).

Osseointegration

Osseointegration was first described by Branemark *et al*. (1977) and the term was then defined in more detail by Albrektsson *et al*. as direct contact between living bone and implant (Albrektsson *et al*., 1981). Osseointegration is the functional and mechanical connection of living, natural bone to the load-bearing implant, titanium in this case (Souza *et al*, 2019). This property is critical for the stability of the implant. Titanium and titanium-based alloys are unique in their properties of osseointegration (Gibbs, 2020). Osseointegration is also histologically defined as the direct anchorage of an implant by the formation of bony tissue around the implant without the growth of fibrous tissue at the bone-implant interface. A 100% bone-to-implant contact does not occur and there is neither agreement as to the extent of bone-to-implant contact required for acceptance of the connection as osseointegration nor even on the criteria for definition of the term (Rautray *et al*., 2010). Properties are observed at the interface of the tissue and the implant. It is also important to note that osseointegration is a time-dependent healing process (Souza *et al*., 2019; Gibbs, 2020).

Hydroxyapatite and Osseointegration

Most titanium alloys are materials with great strength, low-slung modulus, inferior density, and a virtuous blend of mechanical and exceptional corrosion resistance. However, they do not offer good osseointegration and bone development properties (Asrar *et al.*, 2021). Conversely, hydroxyapatite (HA) is highly bioactive to binds with the nearby bone tissues when implanted in the host body and has been used in recent times as a bioactive implant coating because of its ability to increase osseointegration (Asrar *et al.*, 2021; Dewi *et al.*, 2020). This property of hydroxyapatite is due to its capacity to absorb protein, and increase osteoblast proliferation, to increase bone formation and reduce bone loss (Dewi *et al.*, 2020). Hydroxyapatite (HA) also can cause stronger bonds between bone and implants, make fixation faster, and enable uniform bone growth between the implant and bone (Narayanan *et al.*, 2008; Kilpadi *et al.*, 2001). When a material is coated with hydroxyapatite, the coating confines fibrous membrane formation and changes fibrous membranes induced by movement into bone anchors (Dewi *et al.*, 2020).

Previous Works

Asrar *et al.* (2021) carried out research to study the effects of facile coating of hydroxyapatite (HA) on Ti6Al4V for Osseointegration. In the research, HA was extracted from bovine bones by using the thermal decomposition method. This was then followed by its deposition onto the Ti6Al4V alloy using the Electrophoretic Deposition (EPD) technique. TiO₂ was used as a bond coat layer to increase the adhesion between HA and Ti6Al4V alloy substrates. It was discovered that after sintering the coated samples exhibited excellent adhesion. The characterization of the coated sample confirmed that the coating enhanced the osseointegration properties of the implant. A hardness test done on the coated Titanium alloy using a Vickers hardness tester confirmed the increase in hardness value of coated samples up to 35%. The corrosion rate for coated samples was found to decrease from 33.53×10^{-3} mpy to 11.95×10^{-3} mpy (Asrar *et al.*, 2021).

Łukaszewska-Kuska *et al.*, in 2019 investigated the effects on bone osseointegration in rabbits resulting from the application of an HA coating deposited on titanium endosseous implants using a modified electrochemical method. Titanium implants with HA coatings and controls with Al₂O₃ grit-blasted surfaces were embedded into rabbit tibiae. Implant stability tests were performed, and the Periotest value (PTV) and the implant stability quotient (ISQ) value for Osstell Mentor were done to evaluate the osseointegration. The results showed that the surface characterization of the implants revealed a microstructure with an arithmetical mean height (Sa) in the range of 0.71–1.04 μm. The HA coating was free of contamination, whereas the controls were enriched with corundum. After healing, a statistically significant increase in the mean ISQ and a decrease in the mean PTV for the HA-coated implants was observed. In the case of the control implants, only PTV decreased significantly with time. From the overall research, it was observed that implant surface properties affected implant stability as determined by Osstell and Periotest measurements and the HA coating was found to have chemical and physical properties which appear to improve osseointegration compared to grit-blasted implants (Łukaszewska-Kuska *et al.*, 2019).

Oskouei *et al.* (2016) investigated the wear resistance and fatigue behaviour of Ti-6Al-4V notched members coated with hydroxyapatite coatings. In the study, surface properties of Ti-6Al-4V alloy coated with hydroxyapatite coatings were investigated. Wear resistance and fatigue behaviour of samples with coating thicknesses of 10 and 50 μm as well as uncoated samples were examined. Wear experiments demonstrated that the friction factor of the uncoated titanium decreased from 0.31 to 0.06, through a fluctuating trend, after 50 cycles of wear tests. However, the friction factor of both the coated

samples (10 and 50 μm) gradually decreased from 0.20 to 0.12 after 50 cycles. At the end of the 50th cycle, the penetration depth of the 10 and 50 μm coated samples were 7.69 and 6.06 μm , respectively. Fatigue tests showed that hydroxyapatite coatings could improve the fatigue life of a notched Ti-6Al-4V member in both low and high-cycle fatigue zones. From fractography of the fracture surfaces, they observed that the fatigue zone of the uncoated specimens was generally smaller in comparison with that of the coated specimens. No significant difference was observed between the fatigue life of coated specimens with 10 and 50 μm thicknesses (Oskouei *et al*, 2016).

Alhomsi in 2018 reported a study successfully carried out in Taiwan where HA was sprayed on titanium using the applied plasma-spray technology to modify the surface of the titanium. The result indicated almost entirely and uniformly covered dental implants by HA coating and showed a high biocompatibility for bone regeneration and insulation against the ion release of titanium implants (Alhomsi, 2018).

Jeffcoat *et al*, 2003 carried out a study to compare the success of hydroxyapatite (HA)-coated and machined titanium (Ti) implants in a 5-year randomized, controlled clinical trial conducted at 2 centres. Each of the 120 edentulous patients received HA-coated threaded, HA-coated cylindric, and machined Ti-threaded implants in a randomized design using 5 or 6 implants. Digital radiographs were used for yearly measurements of bone loss. The criteria employed to assess implant outcome included the need for successful implants to lose less than 2 mm of bone support over the 5 years following placement of the prosthesis. This analysis revealed that 95.2% of machined Ti threaded implants and 97.92% of HA-coated threaded implants were successful, while 99.0% of HA-coated cylindric implants experienced less than 2 mm of bone loss ($P < .06$). Over 5 years, the success rate tended to favour HA-coated implants (Jeffcoat *et al*, 2003).

Cehreli *et al*, 2003 investigated the effects of hydroxyapatite-coated and commercially pure titanium oral implants on nerve conduction. Isolated rat sciatic nerves were placed between two suction electrodes in a bath containing a tyrode solution. The implants were brought into intimate contact with the nerves and evoked compound action potentials (CAPs) were recorded before and after contact with the implants. It was observed that the commercially pure titanium implants did not cause any change in CAPs and it was observed that there was a gradual reduction in CAPs for hydroxyapatite-coated implants. This reduction was however less than 50% after an application time of 120 min. Recovery of the CAPs in this group was recorded after approximately 60 min. The effects of the intimate contact with hydroxyapatite-coated implants led to a reduction in CAPs in nerves *in vitro*. It was however noticed that neither this surface nor a commercially pure titanium surface led to irreversible neurotoxic effects (Cehreli *et al*, 2003).

Conclusion

The use of biomaterials for orthopaedic purposes has seen numerous researches being carried out with discoveries leading to tremendous improvements in the material properties of the prostheses. However, there is still a long way in achieving implants that have general properties that meet the increasing demands of the present time. Titanium and its alloys which have been one of the standouts of medical implants widely used today, yet they are still deficient in several aspects of the materials properties. The application of hydroxyapatite has helped to improve the general properties of titanium alloys for orthopaedic applications. HA has been able to improve biocompatibility, corrosion resistance, adhesion to the host tissues, and properties like fatigue resistance, hardness, wear resistance etc. With more research, HA can be improved to meet the aspects where titanium alloys and other medical prostheses are deficient in meeting the requirements for orthopaedic applications.

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SN 9 SYNTHESIS, CHARACTERIZATION, AND APPLICATION OF CHEMICALLY TREATED WATER LILY LEAF POWDER FOR THE ADSORPTION OF METHYL VIOLET DYES FROM AQUEOUS SOLUTIONS

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Abstract

In this study, chemically treated water lily (AWL) leaf powders were prepared and used as adsorbents for the removal of methyl violet (MV) dye from an aqueous solution. The AWL was characterized using scanning electron microscopy (SEM) and Fourier transform infrared (FT-IR) spectroscopic methods. Different adsorption parameters that could affect the adsorption process, such as contact time, dosage, concentration, and pH, were studied and optimized using batch adsorption techniques. The results show that the best adsorption of MV onto AWL was at 90 minutes of contact time, 0.1g dosage, a concentration of 60.00 ppm, and alkaline pH, which were used as the optimized conditions. The equilibrium data generated shows that Dubinin-Rudushkevich (DRK) best described the adsorption process with a regression value of 0.9852. The mean free energy was estimated from the DRK model to be 0.088 kJ/mol, indicating the adsorption process to be a physisorption process. The kinetic data generated revealed that the adsorption process followed pseudo-second order with R² values greater than 0.9868 at different temperatures. The experimental (q_e) and calculated adsorption capacities (q_{cal}) were in agreement with each other. The thermodynamics studies conducted revealed that the adsorption was spontaneous, feasible, and exothermic, with Gibb's free energy (ΔG) values ranging from -9.81 to -10.81 kJ/mol, an enthalpy (ΔH) value of -2.22 kJ/mol, and an entropy change (ΔS) during the transfer of molecules between the solid and liquid phases, with the entropy being 24.95 J/mol. This study shows that AWL-derived adsorbents could be an alternative and promising adsorbent for the removal of hazardous pollutants such as methyl violet dye from aqueous solutions.

Keyword: Spontaneous, Kinetics, Water lily, Thermodynamics, Adsorbents

1.0 Introduction

Water is the basic need of living things and is used in many ways to cater to the needs of daily life [1]. Contamination and pollution represent some major environmental problems around the world. Industries including paper and pulp, cosmetics, dyes and pigments, plastics, leather, and textiles require a large amount of water for their production and produce dye-contaminated wastewater that contains a significant number of toxic compounds [2]. The contamination of drinking water by dyes at a minute concentration (1.0 mg/L) could impact a significant colour, making it unfit for human consumption. For this reason, decolorization of dye wastewater has received considerable attention, in addition to aesthetic reasons such as a decrease in the photosynthesis activity of aquatic flora, which have a tendency to chelate metal ions, which results in the micro-toxicity of fish and other organisms [3]. However, the removal of dyes from industrial effluents is of considerable importance due to their toxicity, carcinogenicity, non-biodegradability, stability to heat and light, and their oxidizing capacity.

For such reasons, the removal of different dyes from industrial effluents and sewage using cheap and efficient methods is paramount and an important area of research [4].

Therefore, the purpose of this study is to investigate the potential of chemically treated adsorbents prepared from water lily leaves for the adsorption of methyl violet dye from an aqueous solution. Based on the literature survey carried out, these forms of adsorbents prepared would be used for the first time for the adsorption of methyl violets from aqueous solutions. It's worth mentioning that Galadima [5] has studied the adsorptive potential of various parts of waterlily, such as leaves, shoots, and roots, but their work is only limited to the adsorption of heavy metals such as Cd and Pb from aqueous solutions. In addition, this work would cover characterization, kinetic, isotherm, and thermodynamic studies of the adsorbents.

2.0 Materials and Methods

2.1 Chemicals, Reagents and Apparatus

All the chemicals, reagents, and materials used in this research were of analytical grade and were collected and used without any further purification: sodium hydroxide (NaOH), hydrochloric acid (HCl), pestle and mortar, beakers, conical flask, volumetric flask, sieve, distilled water, filter paper (Whatmann No. 1), funnels, glass rods, methyl violet (MV) dye, and a UV-visible spectrophotometer.

2.2 Sample Collections and Adsorbent Preparation

The adsorbent was prepared according to method [20]. The water lily leaves (WLL) were obtained from Gubi Dam, Bauchi State, Nigeria. The leaves were washed thoroughly with distilled water to remove dust impurities and shade-dried for 72 hours. The dried leaves were ground and sieved to a working size of 300 μ m and stored in an airtight container as a chemically treated leaf sample (AWL).

2.3 Preparation of Stock solution

A stock solution of methyl violet dye was prepared by dissolving 1 g of the dye in a 1000-ml volumetric flask at room temperature and shaking until a homogenous solution was obtained to obtain a concentration of 1000 g/L [6]. The sample at the required concentration was prepared by diluting the stock solution with distilled water to the required concentration using the dilution formula in equation (1):

$$C_1 V_1 = C_2 V_2 \dots\dots\dots (1)$$

Where C1 and C2 are the initial and final concentrations, V1 and V2 are the initial and final volumes.

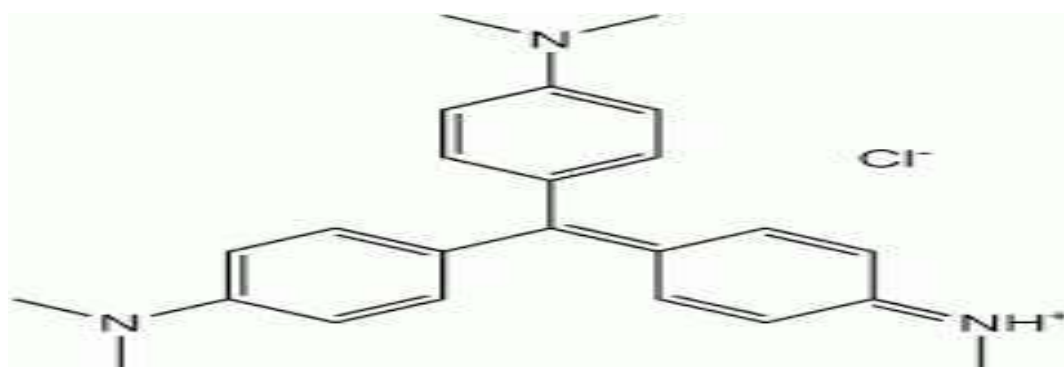


Fig 1:
Structure
of

methyl violet dye

2.4 Optimization of Experimental Parameters

2.4.1 Effect of Contact Time

The effect of contact time on the adsorption of the MV dye used in this experiment was conducted at room temperature, and the initial concentration of MV dye was 100 mg/L. An adsorbent dose of 0.1 g of raw adsorbent was introduced and shaken for the following time intervals: 15, 30, 60, 90, 120, and 150 minutes at 150 rpm [7].

2.4.2 Effect of Dosage

The effect of dosage was studied according to method [8]. The effect of adsorbent dosage was studied and carried out with an initial concentration of 100 mg/L at different adsorbent dosage amounts of 0.02 g, 0.05 g, 0.08 g, 0.1 g, and 0.2 g, respectively. The weighed samples were taken in polythene bottles with 50 mL of the stock solution. The samples were kept in an orbital shaker at room temperature at a constant speed of 150 rpm until the optimum time was determined.

2.4.3 Effect of Initial Concentration

Concentration is among the important factors influencing the rate of chemical reactions. The effect of the variation in the initial concentration of MV dye solution at room temperature using a fixed amount of the adsorbent was determined by using 30, 60, 90, 120, 150, and 180 g/L initial concentrations of methyl violet. The mixture was then shaken at the optimum time at room temperature with an adsorbent dosage of 0.02 g at a speed of 150 rpm. The solution was filtered using Whatmann filter paper, and the filtrate was then taken for UV-spectrophotometric analysis.

2.4.4 Effect of pH

The adsorption experiment was carried out at different pH values so as to determine the optimum pH for the adsorption process. The optimum initial concentration and adsorbent dosage were added into five different polythene bottles (50 mL), with each bottle conditioned at a different pH (3, 5, 7, 9, 11, and 13) and at room temperature, respectively. The pH was adjusted to a desired value with a 0.1 M HCl or 0.1 M NaOH solution, respectively. The bottles were shaken at 150 rpm and then filtered. The filtrate was analysed using a UV-spectrophotometer to determine the residual (un-adsorbed) concentration of the dye [9, 6].

2.5 Adsorption Equilibrium Experiments

For this experiment, batch adsorption was adopted because of its simplicity, as reported by [10]. The batch experiments were carried out to determine the optimum conditions for equilibrium adsorption of MV dyes onto AWL. The results obtained after optimization experiments were used to conduct the batch adsorption at ideal conditions. These systems were separately run in 60 cm³ polythene sample bottles at 30, 40, 50, and 600 °C, respectively. The samples were placed in temperature-controlled shakers for the period reported for each system. After reaching equilibrium, the content was filtrated, and the filtrate was then analyzed using a Perkin-Elmer UV-visible spectrophotometer at a maximum absorbance wavelength of 582.37 nm. The amount of the adsorbed dye was obtained using equation (2).

$$q_e = \frac{(C_o - C_e)}{m} \times V \dots\dots\dots (2)$$

While colour removal rate (% Removal) were calculated using equation (3):

$$\%R = \frac{(C_o - C_e)}{C_o} \times 100 \dots\dots\dots (3)$$

Where: q_e is the adsorption capacity (mg/g), C_o and C_e are the initial and final concentrations in mg/l) respectively for the dye in the solution, V is the volume of the dye in the solution (L), and m (g) is the mass of the adsorbent [6, 10].

2.6 FT-IR Analysis

Fourier transform infrared spectroscopy was used to study the surface functional groups present in the adsorbent before and after adsorption of MV so that an idea of the functional groups present in the adsorbent could be inferred. IR spectra were obtained with a type spectrum 100 series FTIR spectrometer (Agilent Technology Perkin Elmer Spectrum 100, USA) using the transformation of 20 scans with a spectral resolution of 4 cm⁻¹ by the attenuated total reflectance method. FTIR spectra were collected in the mid-infrared region between 4,000 and 650 cm⁻¹. All spectra were acquired using air background correction [11].

2.7 Scanning Electron Microscope (SEM) Analysis

Scanning electron microscopy (SEM) is an analysis of the surface morphology of the adsorbent and was carried out by viewing the electron micrographs of the studied adsorbent [12]. The analysis was done with a proxy scanning electron microscope (Phenom World Eindhoven). In sample preparation for the SEM analysis, a thin layer of adhesive serving as carbon glue was attached to a stub, and a very small amount of the material to be viewed was spread on the stub materials and subsequently viewed in the instrument to obtain micrographs. Scanned micrographs of AWL before and after adsorption were taken at an accelerating voltage of 15 kV and 1500X magnification.

3.0 Results and Discussion

3.1 Surface Characterization of bio-sorbents

In order to investigate the surface morphology of AWL, SEM analysis was conducted. Figs. 2 (a and b) show the surface of the biosorbent both before and after the adsorption of MV dye. The SEM micrograph in Fig. (2a) shows cavities with cracks and pores that could aid adsorption. After adsorption of MV onto AWL as presented in Fig. 2b, the figure shows the deposition of MV dye molecules onto the surface of the AWL, which results in the formation of a relatively more homogeneous surface with cracks, pores, and rough surfaces filled with dye molecules. This shows that an interaction between the MV dye molecules and the adsorbent surface apparently occurs.

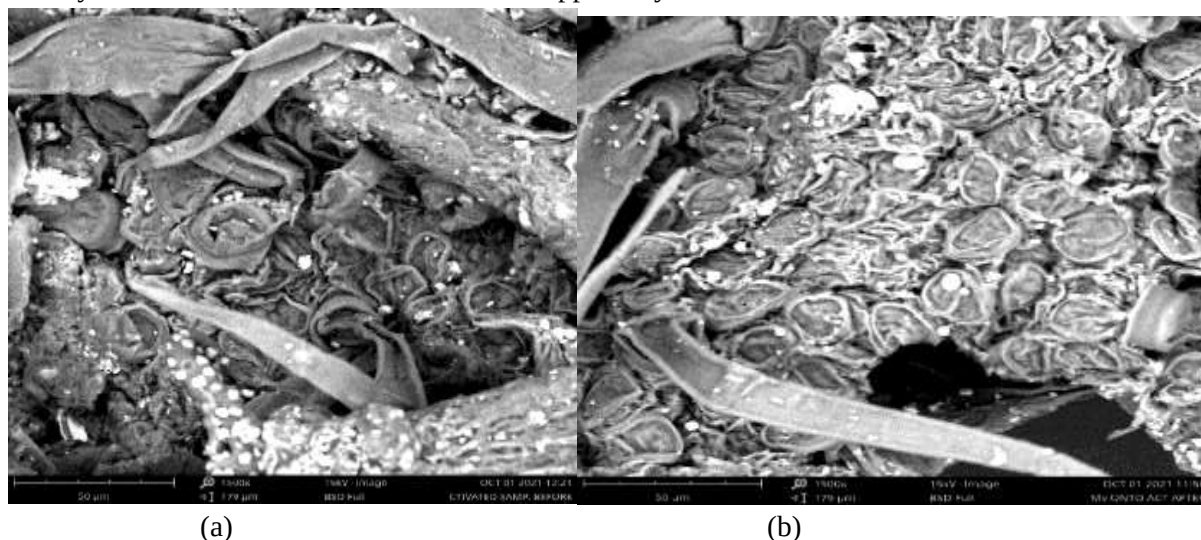
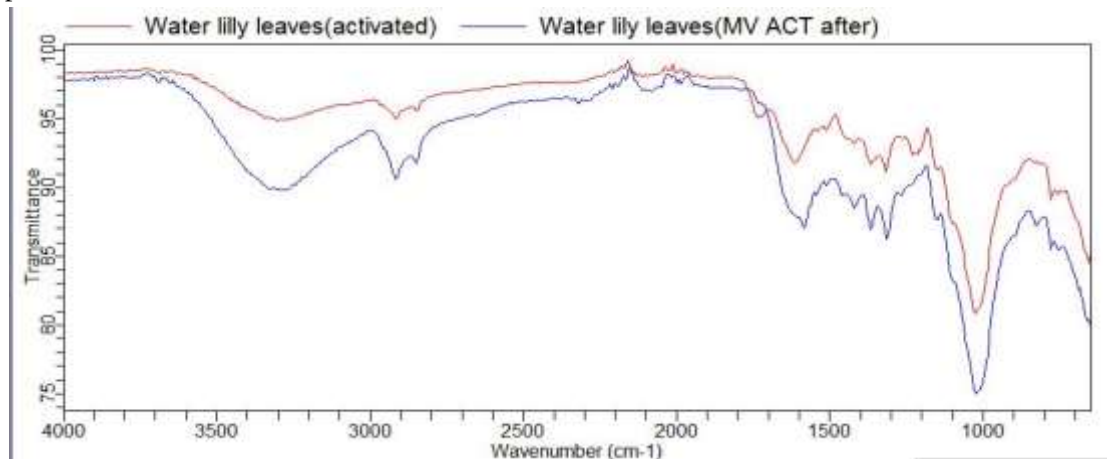


Fig 2: SEM micrograph (a) before adsorption of MV (b) after Adsorption of MV

However, the FT-IR spectroscopic analysis was used to determine the presence of functional groups present in AWL before and after the adsorption of MV dye molecules, as shown in Fig 3. The presence of O-H, C-H, C-O, carboxylic groups, alkenes, and aromatic groups was detected on the biomass

surface. It's been established by many researchers that function groups participate in the adsorption process [13, 14].



3: FT-IR Spectra of AWL adsorbent before and after adsorption of MV

3.2 Optimisation Studies

Fig. 4(a) demonstrates the effects of contact time on the adsorption of MV onto the AWL adsorbent by varying the contact time from 15 to 150 minutes at room temperature with an initial concentration of 100 mg/L. The initial MV uptake was rapid in the first 15–90 minutes and subsequently declined after 90 minutes. The higher sorption rate recorded during the initial period of the process could be partly associated with the availability of a large number of vacant sites on the adsorbent surface that are available for the rapid adsorption and accommodation of the MV molecules. After a time, lapse (90 min), the large vacant sites of AWL that were available at the beginning of the adsorption of MV from the solution had become rarely accessible or exhausted after establishing equilibrium [15, 16]. Later on, the process becomes relatively slower as the equilibrium conditions are reached, whereas the amount of MV desorbing from the adsorbent is in a state of dynamic equilibrium with the amount of MV being adsorbed onto the adsorbent surface. Similar trends were reported by [17].

Fig. 4b shows a plot for the variation of the adsorbed amount of MV with the adsorbent dosage of AWL. It was studied by varying the amount of adsorbent from 20 to 200 mg, while other parameters were kept constant. It was revealed that the amount of MV adsorbed decreased in adsorption per unit mass with increasing dosage, partly due to limited accessibility, saturation, or even possible overlapping of the adsorbent's active binding sites available for binding of MV as adsorbent dosage increased. This will equally reduce the effective adsorption process [18]. Similar trends were reported by some researchers [19, 20].

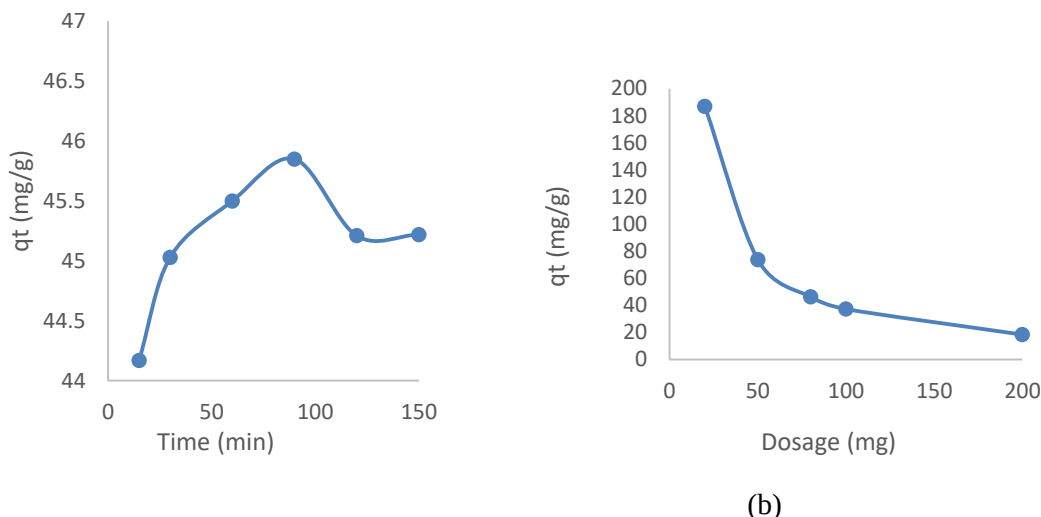


Fig 4: Effect of (a) Contact Time (b) Dosage on adsorption of MV onto AWL adsorbent

Fig. 5a shows a plot of the variation of the amount of MV adsorbed with respect to the initial concentration. From the plot, the amount of MV adsorbed by AWL increases with increasing concentration. At lower concentrations, the available driving force for the transfer of MV molecules onto RWL is low, while at higher concentrations, there was an increase in driving force, which in turn enhanced the interaction between the MV molecules in the aqueous phase and the vacant active sites of the AWL, hence the increase in the MV uptake [21]. The percent removal increases gradually at lower concentrations until it reaches a maximum before rapidly decreasing. This is due to the fact that the vacant or active sites on the AWL surface become saturated or inaccessible to MV molecules [22].

The effect of pH was studied by varying the pH from 3–13 while keeping other operating parameters constant. A plot of the variation in the amount of MV adsorbed is shown in Fig. 5b. The amount of MV adsorbed by AWL initially decreases from pH 3 to 5 and then increases significantly at the neutral pH (pH=7) of the solution as the pH is adjusted from acidic to basic. This pattern could be partly attributed to the nature of the adsorbent surface (the point of zero charge).

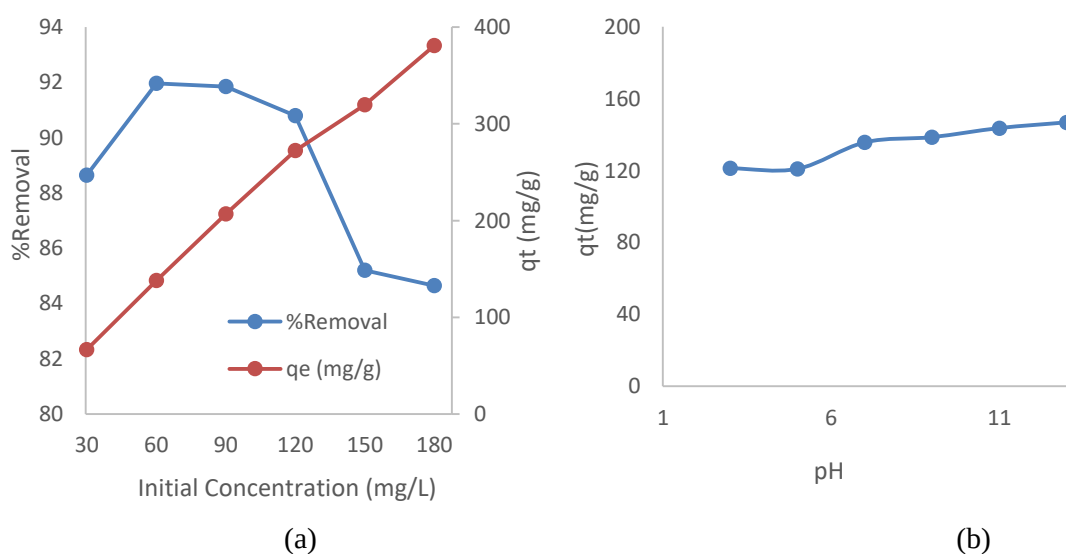


Fig 5: Effect of (a) Initial Concentration (b) pH on adsorption of MV onto AWL adsorbents

3.3 Isotherms Studies

(a) Langmuir Isotherm

According to this model, adsorption of analytes assumes or takes place on homogenous sites of the adsorbent's surface with monolayer formation [22] and can be expressed as:

$$\frac{1}{q_e} = \frac{1}{q_0} + \frac{1}{q_0 K_L C_e} \dots \dots \dots (4)$$

Where q_e is the amount of MV retained at equilibrium by the adsorbent in mg/g, q_0 is the monolayer adsorption capacity (mg/g), K_L is the Langmuir constant (L/mg), and C_e is an equilibrium concentration (mg/L) respectively. The K_L and q_0 were determined using the slope and intercept of a graph of $1/q_e$ vs $1/C_e$, and the parameters were computed as shown in Table 1.

The dimensionless separation factor R_L is defined by relation in equation (5)

$$R_L = \frac{1}{1 + K_L C_0} \dots \dots \dots (5)$$

Where C_0 is the maximum initial concentration (mg/g).

The R_L is indicating whether the adsorption process is either unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$), or irreversible ($R_L = 0$).

(b) Freundlich Isotherm

This model described the adsorption process as being irreversible, non-ideal, and resulting in multi-layer coverage on the heterogeneous surface of the adsorbents [23]; This model can be expressed using equation (6)

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \dots \dots \dots (6)$$

Where q_e is the quantity of MV adsorbed in mg/g, C_e is the equilibrium concentration of the adsorbates in mg/L, K_f is the Freundlich constant related to maximum adsorption capacity, and n is the Freundlich constant related to maximum adsorption capacity (dimensionless).

(c) Temkin Model

This model considers the interaction between adsorbent materials and the adsorbate molecules to be adsorbed, assuming that the free energy of the adsorption process is a function of the surface coverage [24]; This isotherm is expressed in equation 7.

$$q_e = \frac{RT}{bT} \ln A_T + \frac{RT}{b} \ln C_e \dots \dots \dots (7)$$

where R is the molar gas constant (Jmol⁻¹K⁻¹), T is the temperature in Kelvin, b is the variation of adsorption energy (J/Mol), and bT is the equilibrium binding constant (L/mg) corresponding to the maximum binding energy. The values of A_T and bT were obtained and tabulated in table 3 from the slope and intercept of q_e against the $\ln C_e$ plot respectively.

(d) Dubinin-Rudushkevich (D-R) isotherm

This model is used to determine the adsorption behaviour of MG towards the adsorbate using equation (8) [25].

$$\ln q_e = \log q_0 - K \epsilon^2 \dots \dots \dots (8)$$

where q_0 is the constant of D-R (mol/g) and K is the mean free energy of adsorption (kJ/mol). However, ϵ can be calculated using equation (9)

$$\epsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \dots \dots \dots (9)$$

where C_e is the adsorbate equilibrium concentration, R is the ideal gas constant (8.314 J/mol.K), and T is the temperature in Kelvin. The values of q_0 and K were obtained using the slope and intercept from the plot of $\ln C_e$ against ϵ^2 respectively.

Table 1: Calculated isotherm parameters for adsorption of Methyl violet onto AWL adsorbent

Isotherms	Parameters	Values
Langmuir	q0 (mg/g)	10000
	KL(L/mg)	0.002
	RL	0.7108
	R2	0.8928
Freundlich	1/n	0.7242
	N	1.3808
	KF	38.557
	R2	0.8712
Temkin	AT	0.5460
	bT	17.872
	B	138.63
	R2	0.9727
D-R	qs(mg/g)	343.06
	β (mol ² /kj ²)	4.0 x10-6
	ϵ (kJ/mol)	0.088
	R2	0.9852

Table 1 shows the Langmuir, Freundlich, Temkin, and D-R isotherm constants for the adsorption of MV onto AWL. The R2 values computed suggested that the D-R isotherm model provided the best conformity with the experimental data for the MV-AWL adsorption process studied. Both the equilibrium binding constant bT and the heat of adsorption (β) values were found to be 17.872 L/mg and 138.63 J/mol respectively. As a result, physical adsorption is assumed [26].

3.4 The Kinetics Studies

(a) Pseudo-first order model

The linearized form of pseudo –first order kinetic model can be express as:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} \dots \dots \dots (10)$$

where q_e and q_t (mg/g) are the amounts of dyes adsorbed at equilibrium and at time t , respectively, and k_1 (min⁻¹) is the rate constant of adsorption. The plot of $\log (q_e - q_t)$ vs. t should give a linear relationship, from which k_1 and q_e were determined from the slope and intercept of the plot presented in Table 2. The R2 values calculated were not close to unity, and Q_{cal} was not in agreement with the experimental (Q_{exp}) one at all temperatures of the experiment, indicating that the pseudo-first-order model did not fit to describe the kinetic data.

(b) Pseudo-second order model

This adsorption kinetics model can be written as;

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + t/q_e \dots \dots \dots (11)$$

Where k_2 is the rate constant of adsorption (g/mg.min), q_e and q_t are the amounts of dye adsorbed at equilibrium and at time t (mg/g) respectively. The values of k_2 and Q_{cal} were obtained from the intercepts ($1/k_2 q_e^2$) and the slope ($1/q_e$) of the plots t/q_e vs. t , respectively, and presented in Table (3). The correlation coefficient of pseudo-second order was close to unity, and Q_{cal} values computed from pseudo-second order equations showed good agreement with Q_{cal} experimental, indicating the applicability of pseudo-second order kinetic models for the AWL-MV system at all the temperatures of the experiments. Therefore, pseudo second order model fits the kinetic data of the systems generated.

(c) Elovich Model Equation

This model is described by the following relation in equation (12) [27].

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \dots\dots\dots (12)$$

The parameters α and β are the initial rate constant (mg/g.min) and desorption constant that can be calculated from the slope and intercept of the linear plot of q_t vs $\ln t$. This model gives useful information on the extent of both surface activity and activation energy for the adsorption process [28]. The R^2 values obtained for this model were all ≤ 0.4433 at all experimental temperatures. These deviations from linearity (R^2 not closed to unity) reflect or suggest that this model does not fit kinetic data of the study.

(d) Intraparticle Diffusion Equation

The possibility of using the intraparticle diffusion model as the sole mechanism was investigated according to the Weber-Moris equation (13) [18].

$$q_e = C + k \ln t^{1/2} \dots\dots\dots (13)$$

where the constant k (mg/g.min.) is the intra-particle diffusion constant ratio and C is the boundary layer thickness. If the rate limiting is only due to intra particle diffusion, then q_t Vs $t^{1/2}$ gave a linear plot which passes through the origin. Otherwise, some other mechanism or factors, along with the intraparticle diffusion mechanism, may be responsible. From the table 3, its evidently clear that intra particle diffusion model is not applicable for adsorption of MV onto AWL adsorbents since q_t vs $t^{1/2}$ does not pass through the origin. It can be concluded that intraparticle diffusion may not be the sole rate-determining step of the adsorption mechanism.

Table 2: Kinetic models parameters for adsorption of MV onto RWL

Kinetic Model		Parameters			
Pseudo-first order		$Q_{exp}(\text{mg/g})$	$Q_{cal}(\text{mg/g})$	$k_1(\text{min}^{-1})$	R^2
	300C	141.07	5.92	1.17×10^{-2}	0.0300
	400C	105.40	2.84	3.11×10^{-2}	0.4535
Pseudo-first order	500C	93.07	0.90	1.27×10^{-2}	0.0469
		$Q_{exp}(\text{mg/g})$	$Q_{cal}(\text{mg/g})$	$k_2(\text{mg/gmin})$	R^2
	300C	141.07	128.21	9.66×10^{-3}	0.9932
Pseudo-first order	400C	105.40	102.04	4.34×10^{-3}	0.9868
	500C	93.07	90.99	6.36×10^{-3}	0.9990
Elovich model			β	α	R^2
	300C		-0.526	-10.587	0.0964
	400C		0.172	1.013	0.4432
	500C		34.480	0.029	0.0003
Intraparticle diffusion			C	K_{int}	R^2
	300C		135.53	0.9045	0.1163
	400C		79.67	2.6000	0.4741
	500C		91.58	0.0160	0.0005

3.5 Thermodynamic Studies

To estimate the effect of temperature on adsorption of methyl violet dye onto the AWL adsorbent, thermodynamic parameters such as changes in Gibb's free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) were studied and evaluated using equations (14, 15 and 16)

$$K_c = \frac{C_s}{C_e} \dots \dots \dots (14)$$

$$\Delta G = -RT \ln K_c \dots \dots \dots (15)$$

$$\ln K_c = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \dots \dots \dots (16)$$

The ΔH and ΔS functions were determined from the slope and the intersection point of $\ln K_c$ versus the $1/T$ plot (figure 6). Whereas C_s is the amount of adsorbate in the adsorbed phase and C_e signifies the remaining un-adsorbed MV concentration (mg/L) in the liquid phase at equilibrium time, T and R are temperature (K) and molar gas constant (8.314 J/mol·K).

The values of the thermodynamic parameters obtained were reported in Table 3. Generally, the negative value of ΔG expresses the spontaneity and feasibility of MV adsorption onto RWL adsorbent. However, the negative values of ΔG increase with increasing temperature, indicating the adsorption of MV-AWL to be conducive at higher temperatures [29]; The negative values of ΔH (-2216 J/mol) manifest that the adsorption of MV onto AWL is an exothermic process and corresponds to physisorption ($\Delta H < 10$ kJ/mole), while the positive value of ΔS implies the randomness at the solid/liquid interface during the adsorption of AV-RWL which results in increasing MV concentration at the solid/liquid interface [30].

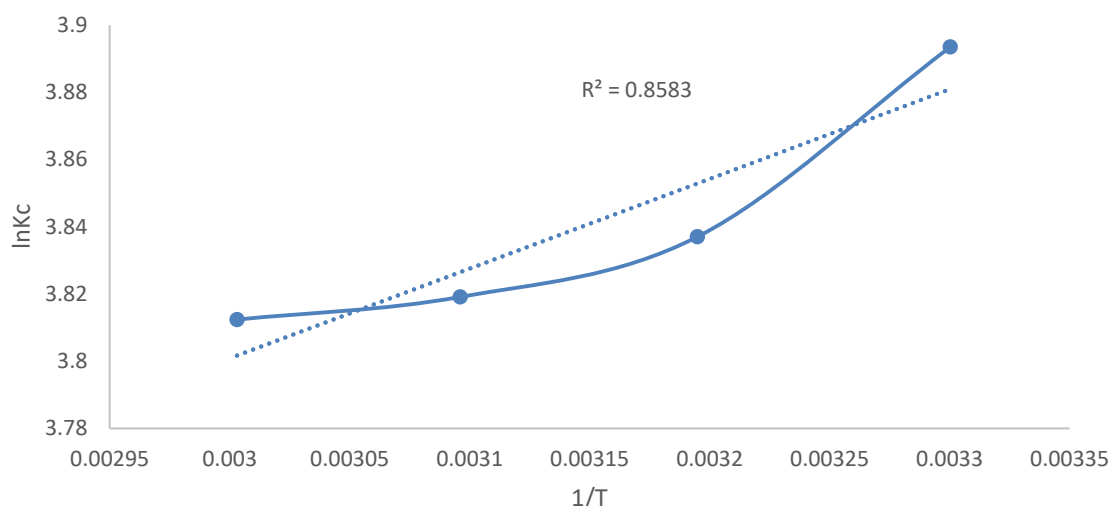


Fig 6: The Van't Hoff Plot for adsorption of MV-RWL.

Table 3: Thermodynamics parameters

T(K)	ln Kc	ΔG (kJ/mol)	ΔH (J/mol)	ΔS (J/mol.K)
303	3.894	-9.909	-2.216	24.951
313	3.837	-9.985		
323	3.819	-10.256		
333	3.812	-10.555		

4.0 Conclusion

This work shows that a water lily leaf-derived adsorbent was an effective adsorbent for the adsorption of methyl violet from an aqueous solution. The characterization of the adsorbent surface using FTIR and SEM before and after adsorption confirmed the functional groups on the adsorbent's surface responsible for the adsorption process. The adsorption of the methyl violet dye was found to be affected by changes in contact time, adsorbent dosage, initial MV concentration, and pH. Kinetically, the MV adsorption onto AWL was found to follow the pseudo-second-order kinetic model, while the D-R

adsorption isotherm model best describes the mechanism process. Thermodynamic studies confirmed that the process was spontaneous, exothermic, and increasing in randomness on the system level during the adsorbent-liquid interface interaction [31].

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Conflict of Interest

The authors declare no conflict of interest

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SN 10 EXPERIMENTAL EVALUATION OF MECHANICAL PROPERTIES OF KENAF-POLYPROPYLENE FIBRE REINFORCED CONCRETE

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Abstract

The performance of fibre-reinforced concrete (FRC) as an emerging construction material has been investigated for improved mechanical properties researchers. However, the combined performance of kenaf and polypropylene fibres as hybrid reinforcement in FRC has remained underexplored. Despite Kenaf fibre's potential to improve concrete properties; its high water absorption, low durability and subpar fibre-matrix adhesion have remained a major concern. Consequently, polypropylene fibre was incorporated into the concrete mix to supplement these shortcomings and bolster the properties. The experimental performance of the kenaf-polypropylene fibre-reinforced concrete (KPPFRC) was investigated using combined volume fractions ranging from 0.5% to 2%. The best results were achieved at a 1.5% optimal volumetric fraction consisting of 0.897kg of kenaf and 0.688kg of polypropylene fibre, with 38% and 23% increases in split tensile strength and flexural strength respectively. However, the addition of fibre does not significantly influence the compressive strength, and fibre content beyond 1.5% resulted in a decrease in the mechanical properties.

Keywords: mechanical properties, kenaf fibre, polypropylene fibre, fibre-reinforced concrete, hybrid concrete

Introduction

Background

Because of its strength, durability and versatility, concrete has dominated the construction industry as a popular construction material for centuries. However, the evolution of complex construction methodologies has revealed some of its limitations that need to be addressed to meet modern requirements. Its drawbacks include its low tensile strength which makes it prone to cracks and fractures under tension. Additionally, the production of concrete has a high environmental impact resulting from the emission of CO₂ and other environmental effects resulting from the production process. Thus, there has been a long-growing concern about the need for environmentally friendly construction materials with improved properties. In response to these concerns, research efforts have been made to explore the use of industrial, household and recyclable materials as alternative construction materials to foster environmental harmony [1]. While recycled materials are widely accepted as environmentally friendly alternative construction materials [2], they do not seem to address all the raised concerns. In this regard, the use of fibre-reinforced concrete has shown promising characteristics in addressing concerns in terms of improving tensile strength, crack resistance and durability [3-10]. This is achieved through the use of natural and synthetic fibre which is an effective way of utilising environmental waste [11].

In addition to lower tensile strength, regular concrete shows structural cracks due to dry shrinkage which may lead to the potential failure of concrete elements/structures. Conventionally, reinforcement steel has been used to produce concrete with improved tensile strength, commonly termed reinforced concrete (RC). Similarly, the application of fibre to produce fibre-reinforced concrete (FRC) has been practised for decades to achieve the same aim. Unlike in RC where reinforcing bars are specifically designed for the tensile zone of the structural element, fibres are randomly distributed throughout the concrete [12]. Fibre-reinforced concrete (FRC) is a type of concrete with enhanced structural performance resulting

from the inclusion of natural or synthetic fibres uniformly distributed and randomly oriented in the concrete matrix. The inclusion of fibrous materials offers FRC several advantages over conventional concrete, including improved tensile strength, crack resistance, impact resistance, and durability. Once in the concrete, the fibre acts as a cleavage inhibitor, develops mechanical properties, resists the impact of concrete, and reduces its brittleness [13]. These improved properties can reduce the need for conventional reinforcement in some applications, such as tunnel linings, thin overlays, and shotcrete. The FRC offers a wide range of applications in structural and non-structural applications. Furthermore, its combined behaviour with other concrete such as self-compacting concrete (SCC)[14, 15], high-performance concrete (HPC)[16, 17], ultra-high-performance concrete (UHPC)[17], hybrid fibre-reinforced concrete (HFRC)[18], and lightweight fibre reinforced concrete (LWFRC)[19], for enhanced properties and functionality have also been investigated.

Generally, randomly distributed fibres in FRC prevent the crack spread and expansion into the concrete matrix which enhances the post-cracking ductility of the concrete under static and dynamic loading. The effectiveness of fibre in improving post-cracking ductility depends on its distribution in the concrete, which is influenced by components such as quantity, aspect ratio and shape. To ensure the selection of a suitable mix design for a specific project, it is important to thoroughly and comprehensively investigate variables that affect post-fracture ductility [20].

Literature review

Several studies on modifying the mechanical properties of concrete using fibres have been reported. One study investigates the influence of varying fibre sizes on the compact capacity of FRC[21]. The study hypothesized that by increasing the amount of paste in a concrete mixture, it is possible to achieve a higher self-compressive capacity in concrete that contains an adequate dosage and fibre size while maintaining high workability. Also, investigation on the effect of length and quantity of fibres and basalt strands on the properties of concrete reveals that the length and quantity of fibres reduce concrete workability and increase the rupture coefficient with the presence of short strands in high quantities [22]. In a related study, the impact of combining shredded drink cans and steel fibres of varying volume fractions on the mechanical properties and impact resistance of concrete was presented [23]. An improvement in the performance of concrete strength was recorded, particularly in terms of compressive strength, bending strength, and indirect tensile strength. The impact resistance of the concrete reinforced with this fibre was reported to have better quality compared to the normal concrete. Albeit the use of several natural and synthetic fibres has been reported the need to explore the combined influence of natural and synthetic fibres on the properties of fibre-reinforced concrete.

Four basic fibre classifications have been identified, namely, polymers, metallic, inorganic, and carbon-based fibres [24] but have been broadly categorised as natural and synthetic fibres. In this study, Kenaf fibre (KF) and Polypropylene fibre (PPF) which are classified as natural and synthetic fibres respectively are considered[10]. Kenaf fibre is produced from a popular plant called Kenaf, which originated from Africa but with more than 70% produced in South Asia. According to a report, the Kenaf plant is currently produced in more than 20 countries to a tune of 216,200 tons in 2014 and 2015 [25]. Kenaf plant as shown in Figure 1 (a) has several advantages as a sustainable material, including rapid growth abilities which guarantee production of high volume of raw materials within a short period and at low cost. Thus, making kenaf fibre (as in Figure 1b) cheaper than glass and carbon fibres. A kilogram of kenaf fibre is reported to cost 0.53 US\$ while glass and carbon fibres cost 3.25 US\$/kg and 500 US\$/kg respectively[26]. It also produces 6-10 tons of dry fibre per acre annually which is 4 times the amount of fibre produced by pine trees, in addition to its high CO₂ absorption level and low production energy requirement[27, 28]. Due to its high stiffness and aspect ratio compared to other fibres, kenaf fibre acts as reinforcement in thermoplastic composites. The average tensile strength of

kenaf fibre ranges from 157MPa to 600MPa, with the modulus of elasticity and the average ultimate tensile strain ranging from 12800 MPa to 34200 MPa and 0.015 to 0.019, respectively.

However, its high-water absorption, low durability and poor fibre-matrix adhesion resulting from the composition of hemicellulose, lignin and pectin have been reported as serious concerns. The presence of these components results in hydrophilic properties making it less compatible to interact with hydrophobic matrices. As a result, it forms a weak bond between the fibres and matrices.



Figure 5: (a) Kenaf tree (b) Processed Kenaf fibre

On the other hand, polypropylene fibre (PPF) is a synthetic fibre derived from the thermoplastic polymer polypropylene. It is deeply crystalline with high resistance to chemical and bacterial aggressions, high stiffness and resistance, and lightweight, high strength and corrosion resistance properties. Because of its versatility, its industrial applications cover a wide spectrum including construction, textile and automotive. Figure 2 illustrates two samples of polypropylene fibres. The inclusion of PPF in the concrete mix is known to increase the concrete strength, in addition to controlling the plastic shrinkage fracture, dry shrinkage stress and increase freeze and thaw resistance. All these qualities make it a good alternative to steel fibre due to its environmentally friendly stages [29, 30]. In addition, it has a contrasting behaviour with the kenaf fibre thus, can suitably complement its shortcomings when combined in a composite matrix. The inclusion of PPF in concrete has been acknowledged to reduce water permeability by blocking small cracks within a concrete matrix and reducing the proliferation of cracks while ensuring the controlled pressure spreads to the edge of the crack. It also increases the bending strength of concrete due to its high modulus of elasticity. Although previous studies have investigated the influence of such fibres in mortar-foamed concrete, to the best knowledge of the authors none has been presented on higher-grade structural concrete.



Figure 6: Polypropylene fibre

Hence, considering the importance of expanding the scope of the inclusion of fibre in structural concrete, this paper experimentally investigates the mechanical properties of hybrid fibre-reinforced concrete incorporated with kenaf and polypropylene fibre. The aim is to leverage the outstanding properties of kenaf fibre complemented by PPF to extend the loading capacity and ductility of structural concrete and also improve the split tensile strength and flexural strength of concrete.

Materials and Experimental Methods

Material

All material and testing in this study are performed according to the provisions of the ASTM standards.

Grade 35 concrete made with Ordinary Portland Cement (OPC) type 1 as the main binder was used conforming to the specifications of ASTM C150 / C150M throughout the study, with the oxide composition determined using X-ray Fluorescence Spectroscopy (XRF) shown in Table 1.

Table 5: Chemical Composition of OPC

Oxides	Composition (%)	ASTM C150 Limits (%)
Lime (CaO)	64.54	60 - 67
Silica (SiO ₂)	21.28	17 - 25
Alumina (Al ₂ O ₃)	5.60	3.0 – 8.0
Sulphur Trioxide (SO ₃)	2.14	1.0-3.0
Magnesia (MgO)	2.06	0.1 – 4.0
Iron Oxide (Fe ₂ O ₃)	2.36	0.5 -6.0
Alkalies (K ₂ O, Na ₂ O)	0.44	0.4 – 1.3
P ₂ O ₅	0.17	-
TiO ₂	0.51	-
Loss of Ignition (LOI)	0.64	3.0 max

The aggregate used is crushed granite in the range of 4.75mm to 20mm according to ASTM C33 / C33M, with the fine aggregate making up 60% to 75% of the total volume of concrete. Clean water conformity with the provisions of ASTM C1602/C1602M-18 was used.

Two types of fibres were considered as reinforcement in the concrete, kenaf fibre (KF) and polypropylene fibre (PPF), classified as natural and synthetic fibres respectively. The KF was extracted from the kenaf bast strands having an average length of 5cm and 1400 kg/m³ density.

High moisture absorption and poor adhesion between natural fibres in a composite matrix can create void spaces and weaker joints around fibre-reinforced concrete matrix[31]. Therefore, to address these issues the kenaf fibre was first treated in 6% sodium hydroxide (NaOH) solution for 3 hours, rinsed and soaked in water for 24 hours, dried in open air for 24 hours and then in an oven for 6 hours at 80°C. This approach has been proven to be effective in improving the performance of fibre in concrete. The treated kenaf sample was tested for density and mechanical properties and then cut into the required dimensions. The measured density was used to determine the fibre volume fractions in the mix. The KF was particularly selected for its several advantages including average tensile strength ranging from 157MPa to 600MPa, modulus of elasticity and average ultimate tensile strain ranging from 12800 MPa to 34200 MPa and 0.015 to 0.019, respectively. Additional properties are presented in Table 2.

Table 6: Physical properties and Chemical composition of kenaf fibre

Property	Quantity
Fibre length (mm)	50
Density (kg/m ³)	1400
Cellulose (%)	45-57
Elongation at break (%)	1.6
Hemi-cellulose (%)	21.5
Pectin (wt.%)	3-5
Lignin (wt. %)	8-13

Similarly, Polypropylene was adopted for its exceptionally high tensile strength, high coefficient of expansion and low modulus of elasticity, and its ability to reduce cracks due to its malleability and flexural strength. Previous studies have proven its capability to increase fracture toughness, ductility and resistance to impact. Detailed properties of polypropylene are shown in Table 3.

Table 7: Characteristics of polypropylene fibre

Property	Quantity
Fibre Length (mm)	15
Density (kg/m ³)	950
Tensile strength (kN/mm ²)	0.31-0.42
Modulus of elasticity (kN/mm ²)	3.5
Flexural modulus (Gpa)	1.3 – 1.5
Elongation at break (%)	150 - 300
Strain at Yield (%)	10 -12
Specific gravity	0.9
Composition	100% PP fibre
Configuration	Fibrillated/multi-filament
Absorption	NIL
Melting point (oc)	160 -170
Thermal conductivity	low
Electrical conductivity	low

Experimental design

Preliminary analysis

The specific gravity of coarse and fine aggregate samples was determined based on the provisions of ASTM C127-15 and ASTM C128-15 respectively. The distribution of the aggregate sample was determined through sieve analysis, using a vibrating sieve shaker machine to pass a 6kg aggregate sample through a set of sieves. In each case, the set of sieves is tightly positioned and vibrated for 10 minutes on the machine.

As indicated in Figure 3(a), the coarse aggregate passing sieve 20mm, 10mm and 4.75mm was 100%, 48.8% and 4.8% respectively with a fineness modulus of 5.464. On the other hand, Figure 3(b)

illustrates a well-graded distribution with uniformity coefficient (Cu), and coefficient of gradation (Cc) of 7.5 and 2.89 respectively.

The specific gravity (SG) and water absorption of all samples were determined following ASTM C127-15. The values of the SG of the coarse and fine aggregate are 2.62 and 2.3, with corresponding water absorption of 0.33 and 2.1 respectively.

Concrete mix design

Table 3, illustrate the Fibre Reinforced Concrete (FRC) mix design with varying percentage of kenaf and polypropylene fibres. The control sample is represented by CS while FRC-#% represents fibre-reinforced concrete mix design with varying percentages of combined kenaf and polypropylene fibres. The mix design was according to the ACI 211.1-91 provisions which involve the selection of slump range and corresponding water content, followed by w/c, cement content, and total quantity of aggregate. The quantity of fibre in each mix is calculated as a percentage of the total volume of the sample. In each case, the fibres are added to the mix after achieving an adequately homogenous mix.

Cubes of 100mm dimension were prepared for the compression test, 100mm x 100mm x 500mm prism are used for flexural tests, while cylinders of 100mm diameter and 200mm depth are used for the split tensile test.

Table 8: Fibre-Reinforced Concrete mix design

Mix design per m3	Cement Content (Kg)	Water (litres)	Fine aggregate (Kg)	Coarse aggregate (Kg)	Kenaf fibre (Kg)	Polypropylene fibre (Kg)
CS	340	190	515	1385	0	0
FRC-0.5%	340	190	515	1385	0.299	0.233
FRC-1.0%	340	190	515	1385	0.598	0.459
FRC-1.5%	340	190	515	1385	0.897	0.688
FRC-2.0%	340	190	515	1385	1.196	0.981

Workability of concrete samples

The workability of each fresh concrete mix was determined to ensure adequate consistency of the sample using the slump test as highlighted in ASTM C143/C143M.

Before each slump test, the cone's inner surface was cleaned and lubricated to allow for smooth removal. The conical mould was then placed on a solid truly horizontal surface, filled with concrete in four layers. Each layer was compacted with 25 evenly distributed strokes using an iron rod before

adding the next layer. After the final layer, all excess concrete was removed and the surface was levelled. The cone was then slowly and carefully lifted vertically and placed next to the concrete sample. The iron rod was placed horizontally across the empty cone while spanning across the displaced concrete sample. The difference in height between the displaced concrete sample and the cone was measured.

Mechanical characterization of FRC samples

For each of the concrete mixes, thirty concrete samples were prepared and cured at room temperature. Three mechanical tests consisting of destructive tests, namely compressive strength test, split tensile strength test and flexural strength test were conducted on each of the hardened concrete samples at 7 and 28 days. Table 4 illustrates the sample specification and schedule of the test. All concrete cubes, prism and cylinders were adequately vibrated to expel trapped air bubbles in the concrete, after which the samples were stored to solidify in the mould under standard laboratory temperature for 24 hours. Thereafter, samples were de-moulded, weighed, labelled, and cured in a bath of pure water.

Table 9: Specimen specification and concrete tests

Tests	Sample shape and dimension (mm)	No. of samples	Curing age	Reference standard
Compressive strength test	Cube 100*100*100	15	7 days	ASTM C109 / C109M
		15	28 days	
Flexural strength test	Prism 100*100*500	15	7 days	ASTM C293 / C293M
		15	28 days	
Spilt tensile strength test	Cylinder 150R * 300	15	7 days	ASTM C496 / C496M
		15	28 days	

Compressive strength test

The compression test on the cube samples was performed following ASTM C109/C109M-02 using a universal testing machine (UTM) available at the Civil engineering laboratory of the University Tenaga Nasional (UNITEN), with experimental set-up as shown in Figure 4. The load was gradually applied at a rate of 140 kg/cm²/min. The cylindrical samples were used for split tensile test using UTM as per ASTM C496C496/C496M-17,2011.

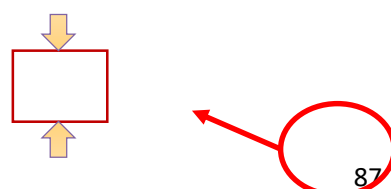


Figure 7: Compressive strength test setup

Split tensile strength test

The tensile strength of concrete is important because it greatly influences the size and extent of cracking concrete structures. Cracks emanate in concrete when the tensile strength exceeds the required limit. Thus, the use of direct tension testing of concrete tensile strength is frowned upon due to its low strength and brittle nature. The test described herein was conducted using a Universal testing machine (UTM) in accordance with ASTM C496C496/C496M-17, 2011. Upon complete curing age, each cylindrical sample is removed, air-dried, weighed and pivot

lines are drawn on the edge to ensure alignment on the same axis. With the sample drum placed inside the bearing for fixation as shown in Figure 5(a) and the bearing aligned centrally on the main board of the UTM as shown in Figure 5b, the upper crosshead was lowered until it made contact with the sample. Then, loading was gradually applied in the range of 0.7 to 1.4 Mpa/min until failure.

Figure 8: Split tensile strength test setup

Flexural strength test

The flexural test was conducted to determine the bending strength of the concrete following the guidance in ASTM C293/C293M, 2022. The test set up as shown in Figure 6 was used. Each concrete sample is positioned horizontally over the loading points, and the load is gradually applied to the centre of the sample's upper surface until failure.

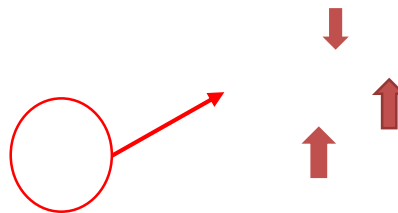


Figure 9: Flexural strength test setup

Analysis and Discussion

Workability properties

The average slump values for each concrete mix as shown in Figure 4 decreases with an increase in the fibre content. When compared with the control sample (CS), a slump reduction of 6.19%, 15.38%, 28.34% and 38.32% were observed with 0.5%, 1%, 1.5% and 2% fibre content respectively. This

indicates the influence of the water absorption property of the kenaf fibre. In addition, this can be generally attributed to the greater surface area created by the combined fibres which tend to attract more cement paste wrapped around the clump fibre thereby restricting the flow of aggregate due to reduced lubrication from the cement paste which is very high to an extent that even admixtures may not help. A similar pattern in concrete workability reduction due to the inclusion of polypropylene and glass fibres [32], Sisal and Coconut fibres [33] and polypropylene, alkali-resistant glass, and lignin fibres [34] have been reported. Abbas et al.[35], also reported a similar trend with kenaf fibre in geopolymer concrete. Nonetheless, despite the high slump reduction, it has been observed to influence the minimization of bleeding and separation of concrete constituents. However, further studies intended to explore ways of improving slump retention while ensuring adequate workability.

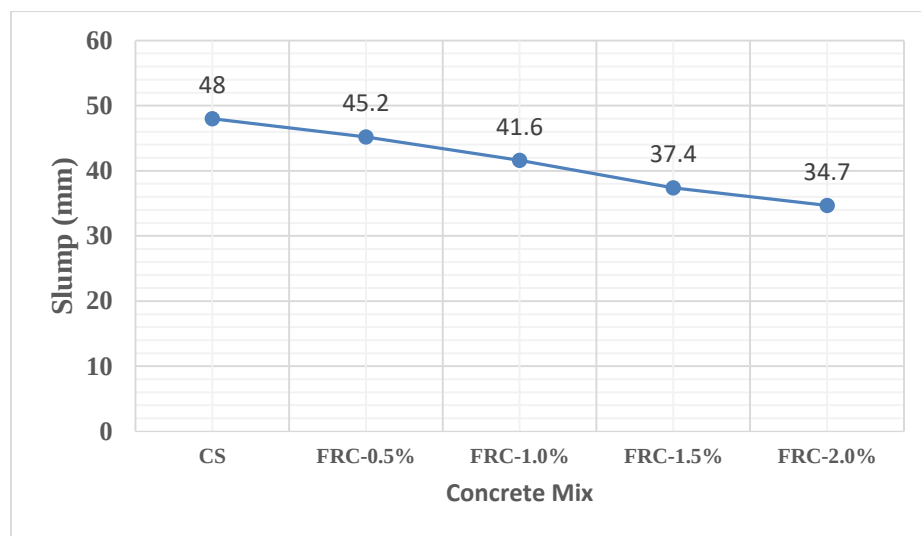


Figure 10: Slump variation withvarying fibre content

Mechanical Properties

Compressive strength

Figure 5 compares the average compressive strength of concrete reinforced with kenaf and polypropylene at 7 and 28-day curing ages.

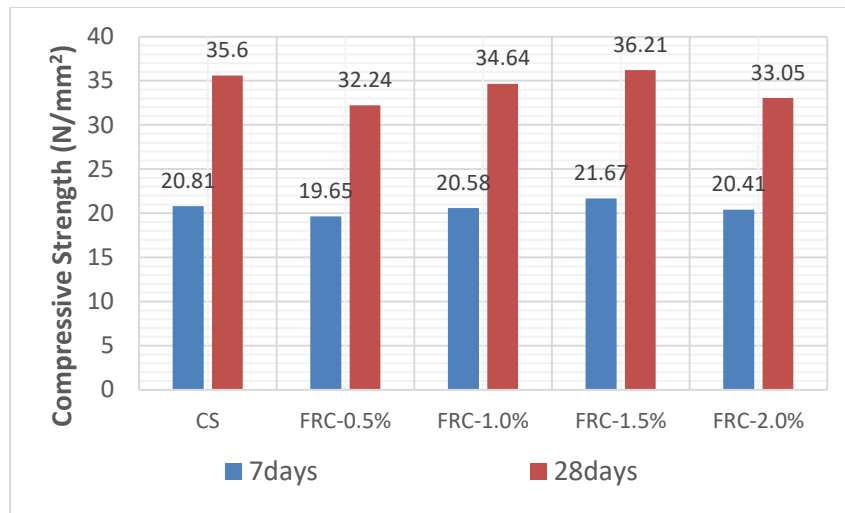


Figure 11: Compressive strength at 7 days with varying percentages of kenaf and polypropylene fibre

The experimental test results show fluctuations of compressive strength at both 7 and 28 days for fibre volume fractions investigated under the same curing condition. When compared with the normal control sample having compressive strengths of 20.81 N/mm² and 35.6 N/mm² at 7 and 28 days, all samples containing fibre gives lower compressive strengths except at 1.5% fibre content where the optimum compressive strength was recorded with an average increase of 3.97% and 1.68% (i.e., 21.67 N/mm² and 36.21 N/mm²) at 7 and 28 days respectively. Nonetheless, an increase in compressive strengths was observed in samples containing varying fibre contents (i.e., 0.5%, 1.0% and 1.5%) with values of 19.65 N/mm², 20.58 N/mm² and 21.67 N/mm² at 7 days and 32.24 N/mm², 34.64 N/mm², 36.21 N/mm² at 28 days respectively, with a decrease in compressive strength observed in samples containing 2% fibre content.

The reduction in compressive strength can be attributed to several factors, first, the dominant characteristics of kenaf fibre, which as a hydrophilic fibre has higher water content to achieve adequate workability and in turn, affect the average compressive strength [36-38]. On the hand, the hydrophobic nature of the collated polypropylene fibre used must have compensated the shortcoming of the kenaf fibre through the creation of an improved mechanical bond between the fibre matrix thereby resulting in the gradual increase in the compressive strength (i.e., from 0.5% to 1.5% fibre content). Thus, this suggests the inclusion of kenaf and polypropylene indicates no significant influence on compressive strength.

Split Tensile Strength

Thirty cylindrical concrete samples, three samples for each mix design were subjected to split tension loading according to the guidance of ASTM C496/C496M standard at 7- and 28-day curing ages. The experimental results as shown in Figure 9 show a continuous increase in the split tensile strength, unlike what was observed in the compressive strength. This was anticipated because of the combined contribution of the kenaf and polypropylene fibres. The increase is attributed to the ability of the fibres to bridge the crack in the tension zones [39, 40]. Upon splitting, the bridging effect of the fibre strands at the crack zone tends to transfer the stresses from the concrete matrix to the fibres thereby increasing the tensile strain capacity of the concrete matrix and consequently the tensile strength of the fibre-

reinforced matrix. The increase in split tensile strength is consistent with the increase in fibre content as well as the curing age.

At 7 days, the optimum split tensile strength was at 1.5% fibre content, with a 21.51% increase compared to the control sample. A continuous increase is similarly observed with increasing fibre content in the following order, 17.9%, 19.33% and 18.88% for 0.5%, 1.0% and 2.0% fibre content respectively. In each case, all samples with volume fibre content had higher split tensile strength than the control sample.

A similar trend is observed for the 28-day results as shown in Figure 9 with the highest split tensile strength obtained at 1.5% fibre as 2.51N/mm², which is 27.5% higher than the control sample. At 0.5%, 1.0% and 2.0%, an increase of 22%, 17% and 23% were recorded compared to the control sample. This contrasts with the compressive strength results, where all fibre volume fractions considered had lower compressive strength than the control sample, except at 1.5%. The improved split tensile strength is significant and impressive.

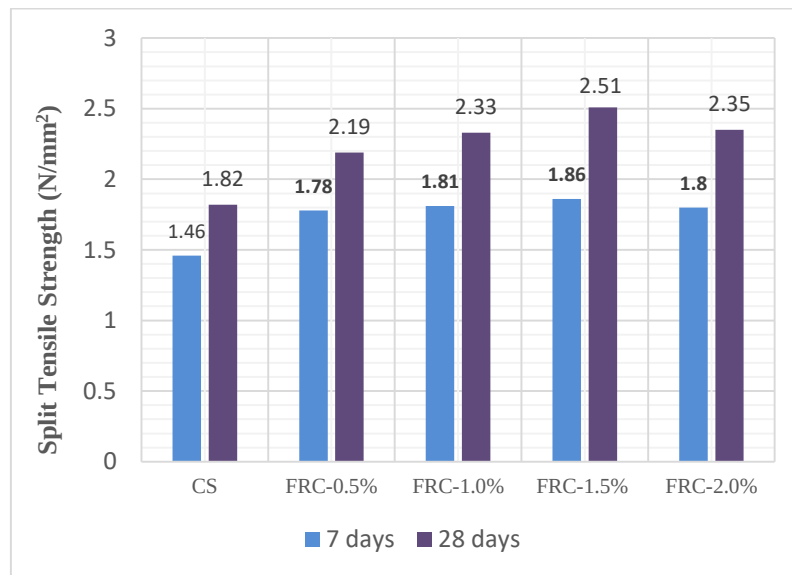


Figure 12: Split tensile strength at 7 and 28 days with varying percentages of kenaf and polypropylene fibre

Furthermore, at both curing ages, the inclusion of 2.0% fibre content caused a slight drop in split tensile strength to 1.81N/mm² and 2.35 N/mm² which is 2.7% and 6.5% at 7 days and 28days respectively when compared with split tensile strength at 1.5% fibre volume fraction. The decrease here is attributed to the fibre content exceeding the optimum content thereby distorting the fibrous matrix.

Similar fluctuations of split tensile strength of fibre-reinforced concrete with an increase in fibre volume fractions have been reported in other studies. For example, an increase in split tensile increase with increasing sisal or jute fibre has been reported followed by a decrease in the strength once the fibre content exceeds the optimum content[41]. The same trend was also observed with increasing fibre length, which can also be translated into content[42]. Under split tensile loading, the cylindrical samples fail through central diagonal cracks as shown in Figure 8.

Flexural Strength Test

The flexural strength of thirty concrete prism samples was tested using the average load-midspan deflection method according to ASTM C293/ C293M. Figure 10 compares the Flexural strength of fibre-reinforced concrete samples with varying volume fractions of kenaf and polypropylene fibre at 7 days and 28 days curing ages.

The inclusion of kenaf and polypropylene fibres in the concrete can be seen to have significantly enhanced the flexural behaviour at all volume fractions of the fibre content considered as well as the curing ages.

With increasing fibre volume fractions, the improvement of flexural strength at 7 days is significant, with the highest being 7.75 N/mm² at 1.5% fibre content which is equivalent to 17.45% higher than the control sample. Similarly, values of 6.87 N/mm², 7.23 N/mm² and 7.19 N/mm² were achieved at 0.5%, 1.0% and 2.0% respectively, corresponding to increases of 6.83%, 11.4% and 11% compared to the control sample. A similar trend was also recorded at 28 days with the highest value of 9.591 N/mm² at 1.5% fibre content which is 18.67% higher than the control sample.

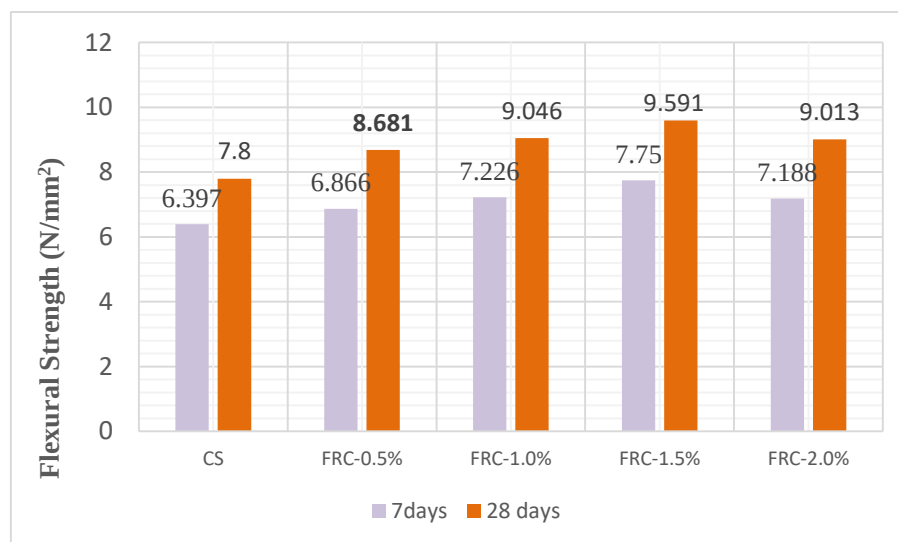


Figure 13: Flexural Strength at 7 and 28 days with varying percentages of kenaf and polypropylene fibre

The increase in flexural strength resulting from increasing fibre volume fractions is attributed to the interaction of the fibre within the crack at the tensile zone of the prism samples which significantly contributes to restricting further crack propagation thereby maintaining the concrete surface from stretching. Thereby introducing a relaxation mechanism for the microcracks zone. On the other hand, the drop in flexural strength is due to the inclusion of high porosity resulting from nonuniformity in fibre distribution which can significantly affect the concrete matrix.

Conclusion

This paper investigates the combined influence of kenaf and polypropylene fibres on the fresh and mechanical characteristics of grade 35 concrete. The experimental investigation was performed using combined fibre volume fractions of 0.5%, 1.0%, 1.5% and 2.0%.

The specific conclusions drawn from the study are:

1. The bleeding in all concrete mixes has notably decreased as the fibre content increases, which is due to the polypropylene fibre's (PPF) ability to seal the small pores within the concrete, although with a consequent decrease in the workability.
2. While the compressive strength increases with a higher fibre content, the maximum increase of 1.7% at the optimal content of 1.5% fibre is not considered significant.
3. Concrete mixes containing 1.5% combined fibre content showed an increase in split tensile and flexural strengths by 38% and 23%, respectively.
4. A general enhancement in the mechanical characteristics of concrete samples was achieved with 1.5% optimum fibre content.

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SN 11 DIETARY INTAKE OF CHROMIUM, MANGANESE, COPPER AND ZINC IN COMMONLY CONSUMED FRUIT SAMPLES IN MINNA, NIGER STATE

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ABSTRACT

Fruits are good source of essential trace elements that the human body needs for proper functionality on daily basis. Levels of chromium, manganese, copper and zinc have been analyzed and dietary intake of these fruits (orange, coconut, watermelon, banana and papaya) have also been determined for daily consumption by adults. Five commonly consumed fruit samples randomly collected from three different markets frequented by the inhabitants of Minna town in Niger state, Nigeria were analyzed using Inductively Coupled Plasma Mass Spectrometer (ICP-MS). The results from this study were used to assess the dietary intake contribution of fruits consumed. The mean values of the essential trace elements found in these fruits ranged between; Cr (0.41-1.42 mg/kg), Mn (2.69-19.87 mg/kg), Cu (2.39-12.94 mg/kg) and Zn (3.79-17.94 mg/kg). The Estimated Dietary Intake (EDI) was carried out on these fruits using a Food Frequency Questionnaire (FFQ) were 0.042, 0.510, 0.287 and 0.480 mg/person/day for chromium, manganese, copper and zinc, respectively. Values were all within the recommended daily intake requirements and thus indicate safety to consumers.

Keywords: Essential trace elements, fruits, EDI and FFQ.

1.0 INTRODUCTION

Fruits have great importance in a balanced diet due to the fact that they supply the human body system with a threshold of minerals, vitamins and other essential nutrients. Also, a rise in ascorbic acid content in these fruits play an important role in improving the bioavailability of essential elements in daily diets. Fruits contain high quality of water and organic compounds required in small quantities for a proper body function. The increase in the nutritional importance of fruits has been stimulated by an array of degenerative diseases (Wenken, 1990) prevalent in many parts of the world.

Essential trace elements include those elements the human body requires in trace amounts and their absence may result to malfunctioning of the body which may cause death in extreme cases (Willett and Stampfer, 2013). This is because these essential trace elements have direct influence in the metabolic and physiological processes of the living organisms. The determination of these trace elements in foods have been carried out by vast majority researchers because of their nutritive values (Akinyele and Shokumbi, 2015; Alzahrani *et al.*, 2016).

Trace elements such as Mn, Zn, Fe, Cu are distinguished as essential elements for human health due to their metabolic and enzymatic activities (Verma *et al.*, 2015; Santos *et al.*, 2019). Hence, the importance of optimizing the intake of essential elements to maintain good health is widely recognized. This will help to prevent health problems that could be attributed to inadequate dietary intake of essential elements which could lead to deficiency or an excess of these elements (Food and Nutrition Board, Institute of Medicine (EFSA/FAO/WHO, 2011).

Several methods exist for the assessment of a population's dietary intake pattern among them is the Estimated Dietary Intake (EDI) method which is recommended as a useful tool for the calculation of the intake levels of these essential trace elements in the human diet. Dietary intake assessments of several foods have been carried out in most parts of the world, Italy (Filippini *et al.*, 2018), Saudi Arabia (Alzahraniet *et al.*, 2017; Mohamed *et al.*, 2019) and Libya (Elbagermi *et al.*, 2012).

Also, some recent reports have been drawn for dietary intake of essential trace elements in Nigerian foods from various researchers, these include the possible effects of dietary pattern on both *adults* and children (Onianwa *et al.*, 2001; Gaya and Ikechukwu, 2016; Udousoro *et al.*, 2017; Yaradua *et al.*, 2019; Shokunbi *et al.*, 2019; Oyasowo *et al.*, 2021; Shokunbi *et al.*, 2023). This study seeks to determine the essential trace elements content and dietary intake estimate of selected fruits commonly consumed in Minna metropolis. Findings from this study would be useful in designing a dietary intake pattern for adult's population in Nigeria and thus serve as a guide to appropriate recommendations in the intake levels on consumption pattern of study fruits alongside prevent harms linked with possible deficiencies.

2.0 MATERIALS AND METHODS

2.1 Sample collection and sample preparation

Fruit samples were collected from three markets (Tunga, Bosso and Gwari markets) usually visited by the inhabitants of Minna, the capital of Niger state, north central region of Nigeria. A total of five different fruits were purchased from three locations in each market which was later homogenized into one sample. A total of 15 fruit samples from three markets (five fruits from three markets) were labelled and recorded accordingly in this study.

Fruit samples were thoroughly washed with clean tap water and sliced into smaller sizes. Petri dishes and sterilized foil papers were used to put samples for drying in oven. Samples were oven dried at a temperature of 80 ± 5 °C using Gallenkamp hot air oven to a constant temperature and pulverized for further analysis.

About 0.5g powdered portion of the dried homogenous sample was weighed directly into the Microwave digester Teflon vessels. 6 ml Ultra-pure HNO₃ and 1ml H₂O₂ was added and digested using MARS microwave digester. The resultant was dissolved in distilled water and made to mark; all the solutions prepared were then immediately assayed for essential trace elements using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS).

2.2 Dietary Intake Assessment of Essential Elements

Estimation of dietary intake (EDI) of fruit samples was carried out using a semi quantitative food frequency questionnaire (FFQ). This questionnaire was administered to about 161 adults (both male and female) and the following information were collected, age, sex and information on the fruits and mode of consumption. All samples were obtained and estimated in the raw forms as consumed and data obtained from FFQ was analyzed a coupled Microsoft Excel+Analyse-it® v. 3.0 software (Analyse-it®, 2015). Daily dietary intake of essential trace elements consumed was estimated accordingly for each food sample, this assessment was measured in mg/day. Weight equivalents of the food items consumed were used to compute individual and mean daily essential trace elemental intakes on wet weight basis. This was calculated using the equation presented below.

$$EDI = \frac{\text{Elemental level in food (mg/kg)} \times \text{food consumption (}\frac{\text{g}}{\text{person}}\text{/day)}}{1000} \dots\dots 1$$

Here, the essential trace element measured in food (mg/kg) is multiplied by intake estimated by the FFQ (g/person/day). Estimation on daily dietary intake of the essential trace elements for the diet as a whole for each food category was calculated accordingly using equation 1 above (Filippini *et al.*, 2020; Paz *et al.*, 2021).

2.3 Quality Control

The accuracy and reliability of the analytical data were ensured by using analytical grade reagents throughout the analysis. Instrument calibration was carried out by running blank standard solutions after every 10 determinations. Analytical procedures were validated by repeating samples of same identity more than once and these concentrations were calculated on dry weight basis.

3.0 RESULTS AND DISCUSSION

3.1 Essential Trace Element Content in Fruit Samples

Essential trace element (Cr, Mn, Cu and Zn) levels was analyzed in five fruits, orange, coconut, watermelon, banana and papaya collected from three markets (Tunga, Kure and Gwari markets) in Minna metropolis using ICP-MS.

The essential trace element levels in the fruit samples across all markets are given on Table 1 and the mean concentrations in all studied fruits alongside permissible limits of individual metal is shown in Table 2.

Table 1. Concentration (mg/kg) of essential trace elements in studied fruits from various Markets

Label	Fruits	Cr	Mn	Cu	Zn
mg/kg					
1	Banana GM	0.40	14.05	2.90	7.54
2	Banana KM	1.98	9.97	4.48	5.88
3	Banana TM	0.61	8.87	4.16	8.63
4	Coconut GM	0.26	23.07	10.69	21.13
5	Coconut KM	1.49	16.69	14.19	17.80
6	Coconut TM	0.42	19.85	13.95	14.89
7	Orange GM	0.32	3.27	2.46	3.90
8	Orange TM	0.40	2.10	3.33	4.08
9	Oranges KM	0.50	2.75	2.59	3.39
10	Paw-Paw GM	1.11	2.75	1.84	3.49
11	Paw-Paw KM	2.19	2.83	2.42	5.42
12	Paw-Paw TM	0.97	2.47	2.91	5.82
13	Watermelon GM	1.69	4.03	3.70	10.63
14	Watermelon KM	0.78	11.67	4.86	12.16
15	Watermelon TM	1.23	7.35	3.87	12.89

GM: Gwari market, KM: Kure market, TM: Tunga market, BDL: Below detection limit

WHO/FAO- World Health Organization/ Food and Agricultural Organization, (1996, 2021) permissible limit.

Fruits	Cr	Mn	Cu	Zn
Orange	0.41	2.71	2.79	3.79
Coconut	0.73	19.87	12.94	17.94
watermelon	1.23	7.69	4.14	11.89
Banana	1.00	10.96	3.85	7.35
Papaya	1.42	2.69	2.39	4.91
Permissible limits (WHO/FAO)	2.3	5	10	50

Chromium in the fruit samples analyzed (coconuts from Gwari market and papaya from Kure market) varied between 0.26-2.19 mg/kg in. One important factor to be considered in understanding the various concentrations of chromium in these fruits samples is the source of which it is absorbed. The sources of chromium include soil types, phosphate fertilizers, irrigation water and anthropogenic activities in air and soil (Ahmed *et al.*, 2022; Salama *et al.*, 2019). Concentrations of chromium in fruits analyzed in present study is within the permissible limit set by WHO/FAO and therefore safe for consumption. Concentrations of manganese in the fruit samples from various markets ranged between 2.10 and 23.07 mg/kg. The lowest value was determined in orange (Tunga market) and highest in coconut (Gwari market). Manganese is an essential element for human health, contributing to bone formation and as a required cofactor for enzymes responsible for amino acids, cholesterol and carbohydrate metabolism as oxidoreductase, transferase, and hydrolases (Khouzam, 2011). Manganese permissible limit in fruits is 5 mg/day (WHO/FAO, 1996). Although higher Mn contents have been found in coconut, banana and watermelon but is not beyond the tolerable limit set by EFSA (European Food Safety Authority, 2013).

Manganese deficiency is rare but can result in poor bone health, joint pain, fertility problems and an increased risk of seizures (Filippini, 2018).

Copper is obtained for body utilization from diets consumed on daily basis (Hu *et al.*, 2021) and is widely present in all fruit samples and in high concentrations compared to other elements of study. Papaya from Gwari market had the minimum concentration and coconuts from Kure market were found to have the maximum concentration. Copper levels ranged between 2.39 and 12.94 mg/kg. Copper serves as an essential micronutrient that functions as biocatalysts which is required for body pigmentation and acts as a cofactor for crucial enzyme (Linder, 1999). Deficiency of copper causes disorders and alters plant growth and development by adversely affecting vital physiological processes in plants. Permissible limit of copper in food samples is set by WHO/FAO to be 10 mg/kg and fruits have shown to be within the limit except for coconut (12.94 mg/kg).

Zinc also prevailed in high quantities with levels varying between 3.39 and 21.13 mg/kg in fruit samples across markets, the minimum concentration of zinc was found in orange, Kure market and coconut, Gwari market had the maximum concentration. Zinc is one of the most important essential trace elements that exhibit an important role in the physiological and metabolic process of living organisms, it is a component of various enzyme systems and required for protein health, immune function, and wound healing. Zinc is ubiquitous within cells in comparison to iron, which is contained in defined cellular components and has defined physiological roles (Rezaei *et al.*, 2020). Permissible limit of zinc in food samples set by FAO/WHO is 50 mg/kg (FAO/WHO, 2004) and all fruit samples are within the permissible limit of human consumption.

However, mean values obtained from this analysis is also presented in Table 2 with the following ranges Cr (0.41-1.42 mg/kg), Mn (2.69-19.87 mg/kg), Cu (2.39-12.94 mg/kg) and Zn (3.79-17.94 mg/kg).

3.2 Mean Daily Essential Trace Elements Intakes of Study Participants

Table 3: Mean daily essential trace elements intake of participants

Elements	Mean intake (mg/person/day)	Recommended intake	UL/PTDI
Chromium	0.042	57.3–83.8*a	0.3a
Manganese	0.510	1.39–5.49a	11.0a
Copper	0.287	1.20–2.07a	10.0b
Zinc	0.480	14–20b	45b

Abbreviations- EFSA: European Food Safety Authority UL: upper limit, PTDI: provisional tolerable daily intake, World Health Organization.

*: Value in µg/day, all other values are in mg/day.

a: Data of ranges of average dietary intake obtained from EFSA Scientific Opinions (EFSA, 2013, 2014).

The mean daily essential elements intakes of all the study participants based on the fruits under investigation is shown on Table 3. Participants' mean daily essential elements intakes (mg/person/day) obtained were 0.042, 0.510, 0.287 and 0.480 mg/person/day for chromium, manganese, copper and zinc, respectively. The recommended daily intakes as well as the tolerable upper intake levels (ULs)/provisional tolerable daily intakes (PTDIs) are highlighted on the table. Relative to the recommended daily intakes, the mean values of all essential elements are within range. Also, the daily intakes of the essential elements are lower than the ULs/PTDIs.

This data cannot be compared directly to the dietary intake from those reported in literature because this study is only focused on fruits. Various factors contribute to the disparity in results from other studies on dietary intake assessment (Shokumbiet *et al.*, 2019; Fillippiniet *et al.*, 2018; Rahman and Islam,

2018; Onianwaet *et al.*, 2001; Rubio *et al.*, 2009) where the quantities of foods analyzed cut across several food groups, some of which were considered as full course meals, cereals, tubers, legumes and several more food categories that were analyzed for same study of which their consumptions vary for the different populations. Other factors may include soil conditions, water for irrigation, anthropogenic activities, all may vary from different countries and locations.

Conclusion

The present study was carried out in Minna, the capital city of Niger state Nigeria. Kure, Gwari and Tunga markets are the major markets frequented by inhabitants of Minna and its environs. Although most of these fruits are not grown in Minna but brought in from various parts of the country and are commonly consumed by the metropolitans because they are cheap and sold in affordable sizes. There is therefore a need to analyze these fruits for their dietary consumption pattern so as sensitize the population on intake levels of these essential elements in specified fruits. This result reveals coconut to have the highest values in Mn, Cu and Zn. Papaya had the highest value in Cr and lowest values in Mn and Cu, whereas orange showed lowest value in Zn. Therefore, coconut and papaya are good source of Mn, Cu, Zn and Cr. The mean daily intakes essential elements in fruits by the participants were within the recommended values and hence do not pose anyharmful threat among the studied population.

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SN 12 REMOVAL OF SOME HEAVY METALS FROM TANNERY WASTEWATER USING ACTIVATED CARBON FROM *NEOCARYA MACROPHYLLA* SEEDS

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Abstract

This study presented an analysis of activated carbon derived from *Neocarya macrophylla* seeds to remove Cr^{3+} and Fe^{3+} ions from tannery wastewater. The activated carbon was prepared using an acid and a base. The base-activated carbon had a higher yield than the acid-activated carbon. The ash content increased with modification, indicating the influence of chemical interactions on ash content. X-ray diffraction (XRD) analysis revealed that the activated carbon has the miller indices of (002) and (101) for the reflection peaks at 2θ of 28.0 and 51.26°, respectively. Acid modification led to sharp and intense peaks, indicating increased crystalline size and pore development. The Fourier-transform infrared (FTIR) spectra indicated the presence of various functional groups like OH groups, carbonyl groups, C=C stretching vibrations, C-H stretching vibrations, and Si-O-Si symmetric stretching vibrations in the activated carbon. The effect of adsorbent dosage, contact time, and temperature on the adsorption process, employing the batch process techniques was investigated. The kinetic and isotherm data of the adsorption process were analyzed using the pseudo-first-order and pseudo-second-order models and the Langmuir and Freundlich isotherm models. The findings indicate that the pseudo-second-order and Freundlich models provided the best fit for the data. The results demonstrated that activated carbon was a highly efficient adsorbent for removing heavy metal ions from tannery wastewater.

Keywords: activated, adsorbent, carbon, isotherm, kinetic, *Neocarya macrophylla*

1. Introduction

Water pollution poses a significant threat to both human health and the environment. It involves the release of organic and inorganic pollutants into aquatic ecosystems, either in soluble or insoluble forms. This problem is exacerbated by the growing use of substances like dyes, volatile organic compounds, metals, and disinfectant by-products, primarily due to the rapid pace of industrialization and globalization (Gaur *et al.*, 2022). Many of these pollutants are non-biodegradable and highly toxic. For instance, heavy metals originating from wastewater in various industries, such as mining, electrical, electroplating, tannery, and smelting, are not only poisonous but also resistant to biological degradation. They pose significant threats to ecosystems and human health as they accumulate in groundwater (Saxena *et al.*, 2020). Additionally, despite being essential for living organisms and critical for enzyme function in humans, excessive concentrations of these potential toxic elements (PTEs) in the human body can lead to kidney and liver damage, as well as Alzheimer's disease. Hence, addressing the inadvertent discharge of heavy metals is a pressing environmental concern that must be resolved before contaminated water is reintroduced into the ecosystem.

Various methods, including electrochemical processes, chemical precipitation, coagulation, membrane filtration, ion exchange, bioremediation, and adsorption, have been employed to remove heavy metals from industrial wastewater. However, many of these treatment techniques have detrimental environmental impacts, limited efficiency, operational constraint, and high costs, which restrict their application (Fouda-Mbanga *et al.*, 2021). Among these methods, adsorption stands out as the most effective physicochemical approach for heavy metal removal due to its simplicity, cost-effectiveness, and the regenerative nature of the adsorbents (Abdullahi *et al.*, 2022). The adsorbents utilized for heavy metal treatment possess distinctive features like high pore volume and a large surface area, making them valuable for this purpose. Consequently, there has been a growing focus on identifying cost-

effective and unconventional sources, such as agricultural and industrial waste, for the production of efficient activated carbons. The shell of *Neocarya macrophylla* is a waste hardly biodegradable which represents an environment problem. *Neocarya macrophylla* is a tree whose height ranges from 6 m to 10 m. It belongs to the *Chrysobalanaceae* family and to the *Parinari* genus. The plant is native to West and Central Africa. This study aims to carbonize these seeds by producing activated carbons. To date, the efficiency of heavy metal removal from tannery wastewater by acid/base activated carbons in comparison has not been published in the literature. In this study, the efficiency of acid-base activated carbon produced by sequential carbonization and chemical activation techniques was evaluated. The obtained activated carbons were characterized using high-resolution transmission electron microscopy (HRTEM) and X-ray diffraction spectroscopy (XRD). The effects of different factors such as contact time, adsorbent dosage and temperature on adsorption of metal ions were investigated. Furthermore, the data obtained under different operating conditions were fit into different kinetic models and isotherms for the determination of the kinetics and sorption process.

2. Materials and Methods

2.1 Sample collection and pre-treatment

The tannery wastewater sample was collected from Majema Tannery industry, Manuri Road, Tudun Wada Area, Sokoto State and put in a fifty (50) litre galloon rinsed with diluted hydrogen trioxonitrate (V) acid. The wastewater sample was transported to the laboratory for the determination of some physicochemical parameters. The *Neocaryamacrophylla* (NM) seeds were obtained from a farm land; wash under tap water several times followed by deionized water. After thorough washing, it was cut into small pieces and dried under sun light for weeks to remove all moisture present.

2.2 Preparation of activated carbon

The dried pieces of neocarya macrophylla seeds were washed with hot water at 70 oC to remove any soluble matter present and dry in an oven at 105oC for 48 hr. The oven dried sample were powdered using conventional mixer and sieved through 100µm mesh range. The dried sample was subjected to heating in a furnace for 15 min at 550 oC and quenched in 0.1 mol/dm³ NaOH/HCl solution. The sample was washed copiously with deionized water until pH 7 was attained. The sample was dried in an oven at 105 oC for a complete dryness. The powder activated carbon was stored prior for analysis.

2.3 Characterization of activated carbon

The crystal phases and the crystallite size of the synthesized activated carbon were determined using a Bruker D8 Advance X-ray diffractometer with Cu K α radiation. The powdered sample was sprinkled on a de-greased glass slide and their diffractograms were recorded. The Fourier transform infrared spectra (FTIR) of the synthesized samples were recorded using a Perkin-Elmer 2000 FTIR spectrometer fitted with a deuterated triglycine sulphate (DTGS) detector covering the frequency range of 500-4000 cm⁻¹. The sample cell was purged with nitrogen gas throughout data collection to exclude carbon dioxide and water vapour. Ten milligrams (10 mg) of the dried samples were evenly dispersed in 200mg of spectroscopic grade KBr to record the spectra.

2.4 Batch adsorption studies

Batch adsorption experiments were conducted in order to determine the optimum equilibrium time, to generate adsorption kinetics data and adsorption thermodynamic data. The percent removal and adsorption capacity of heavy metal from digested wastewater solution using activated carbons were calculated by the following equation:

$$\% \text{ Removal} = \frac{C_o - C_f}{C_o} \times 100 \quad (1)$$

$$q_e = \frac{C_o - C_f}{M} V \quad (2)$$

where C_0 and C_f are the initial and equilibrium adsorbate concentrations in solution (mg/L), respectively, V is a known volume of synthetic wastewater (L), and M is a known mass of dry adsorbent (g).

The effect of contact time on the metal ions removal from digested solution using activated carbon were investigated by contacting 0.2 g of the samples with 40 cm³ of digested wastewater solution and agitated at speed of 150 rpm for 0, 5, 10, 15, 20 and 25 min. The effect of adsorbent dosage on the metal ion removal was investigated varying the dose at 0.4, 0.6, 0.8, 1.0 and 1.2 g. The impact of temperature was performed at temperature ranging between 30 to 70 oC. The samples were filtered at respective time and the concentrations of metal ions were analyzed using an atomic absorption spectrometer (AAS).

3. Results and Discussion

3.1 Some physicochemical characterization of activated carbon

Table 1 presents the percentage yield and bulk density of the activated carbon prepared from *Neocarya macrophylla* seeds. As can be seen, the base activated carbon (38.50 %) had a significant higher yield compared to acid activated carbon (32.03 %). The impregnation of acid and base showed an increase in percentage yield and also prevent the release of volatile mater. This corresponds to the finding of Kosheleva *et al.* (2019), who reported that the chemical incorporated into the interior of the precursor particles reacts with the products resulting from the thermal decomposition of the precursor, reducing the evolution of volatile matter and inhibiting the shrinking of the particle; in this way, the conversion of the precursor to carbon is high, and once the chemical is eliminated after heat treatment, a large amount of porosity is formed.

The moisture content of acid modified and base modified carbon were 4.62 % and 4.30 %, respectively as presented in Table 1. As seen in Table 1, there is significant effect of impregnation toward the content of moisture in the sample, suggesting that there would correlation between adsorption capacity of activated carbon and moisture content. The reduction in moisture content leads to better activation carbon in adsorption process due to less competition of water vapour within the pores of the sample. Ash is a non-carbon substance which is attached to the surface of the carbon. The values of the ash content increased on the impregnated carbon as represented in Table 1. The base and acid modified carbon contain 4.2 % and 5.8 %, respectively. The chemical modification of activated carbon brings about the significant changes in the ash content of the produced activated carbon. This could be as a result of interaction of chemical with the ash content in the activated carbon. The bulk densities of the samples are presented in Table 1. The bulk density of modified activated carbon recorded low value and this property can be explained by low ash contents of the modified activated carbon.

Table 1: Some characteristics of activated carbon

Sample	% Yield	Bulk density (g/cm ³)	Moisture (%)	Ash (%)
Acid-AC	32.03	0.412	4.62	5.8
Base-AC	38.50	0.508	4.30	4.2

3.2 Characterization of activated carbons

3.2.1 XRD of activated carbon

The phase analysis of modified activated carbon and their XRD patterns are presented in Fig. 1. The diffraction peaks of the samples at 28°, 51.26°, 54.40° and 68.5° show the amorphous structure of activated carbon due to the reflection of (002), (100), (101) and (010) planes, respectively. The existence of other peaks is attributed to modifiers added to the surface of the carbon. The sharp and intense peak in the acid modified sample was as a result of enlargement of crystalline size and development of pores. Based on the JCPDS file, the structure of the activated carbon has the miller indices of (002) and (101) for the reflection peaks at 28° and 51.26°, respectively. Winata *et al.* (2021) observed that two main peaks at 26°, which are attributed to the (002) and 40° correspond to the (101). The XRD patterns also show that samples exhibited the uniform pattern changes, with the presence of some peaks are associated to the chemical agents in the samples. This might be as a result of incomplete removal of the chemical agent (binding interaction on the surface) during washing for the neutralization of the yielded activated carbon.

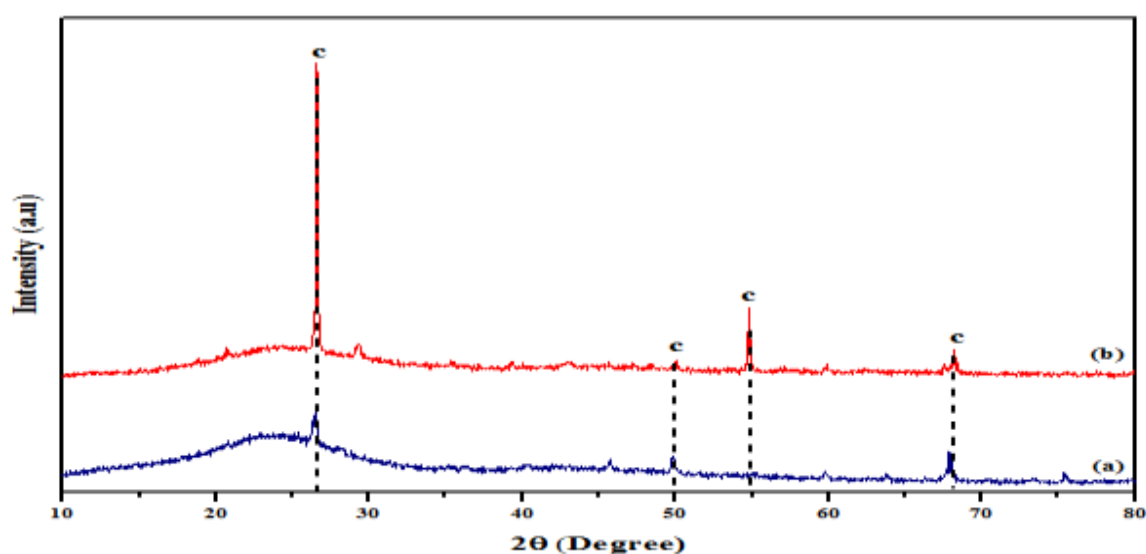


Figure 1: XRD results of (A) acid modified carbon and (B) base modified carbon

3.2.2 FTIR

Fig. 3 shows the FTIR spectra of acid and base activated carbon. The presence of OH group stretching vibration at absorption band of 3430 cm⁻¹ correspond to hemicellulose, lignin, and absorbed water molecules. The existence of carbonyl groups was responsible for absorption band at 1693 cm⁻¹ and the stretching vibrations of C=C at absorption band of 1590 cm⁻¹ could be attributed to the existence of aromatic ring in the lignin. The results of the characterization demonstrate that a functional group on a sample surface was relatively near to the finding of Sujiono *et al.* (2022). The presence of C-H stretching vibrations at 2915 and 2850 cm⁻¹, which might be due to the existence of hemicellulose and cellulose. The presence of absorption band at 790 cm⁻¹ is responsible for the presence of Si-O-Si symmetric stretching vibration.

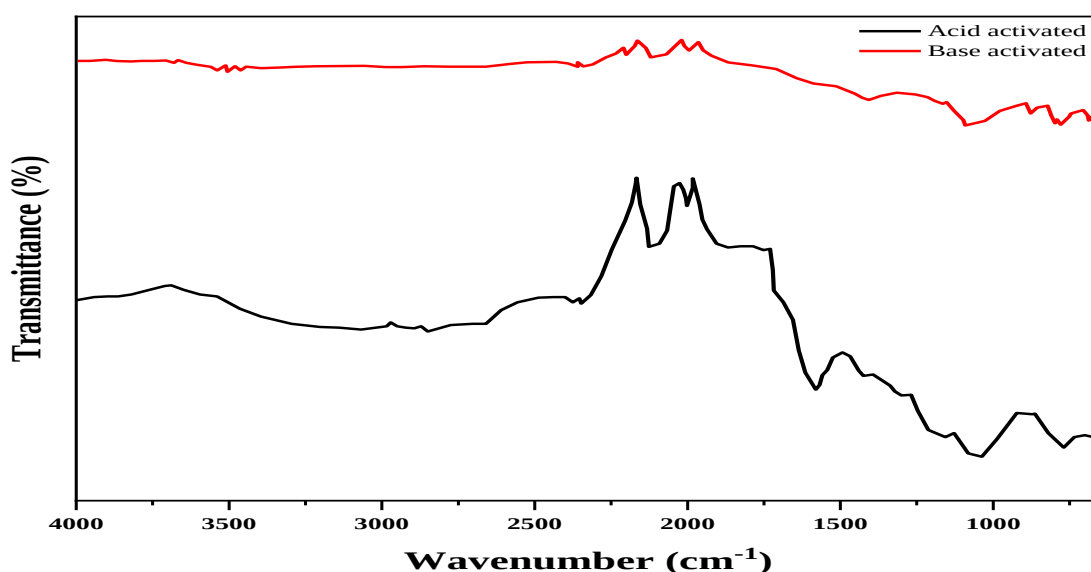


Figure 2: FTIR of acid and base-activated carbon

3.3 Batch adsorption studies

3.3.1 Effect of contact time

The effect of contact time on metal ions removal using acid and base activated carbon was investigated by changing contact time from 0 to 25 min (Fig. 4 a and b). The figure shows that the percentage removal of metal ion sorbed increased along with time until equilibrium was reached. At first stage, the metal ion removal was fast due to the large number of active sites existing on the adsorbent which saturated with the passage of time until equilibrium was reached. The high percentage removal achieved using acid activated carbon was 52.23 % for Fe^{3+} and 65.75 % for Cr^{6+} while base activated carbon had 59.82 % for Fe^{3+} and 69.20 % for Cr^{6+} .

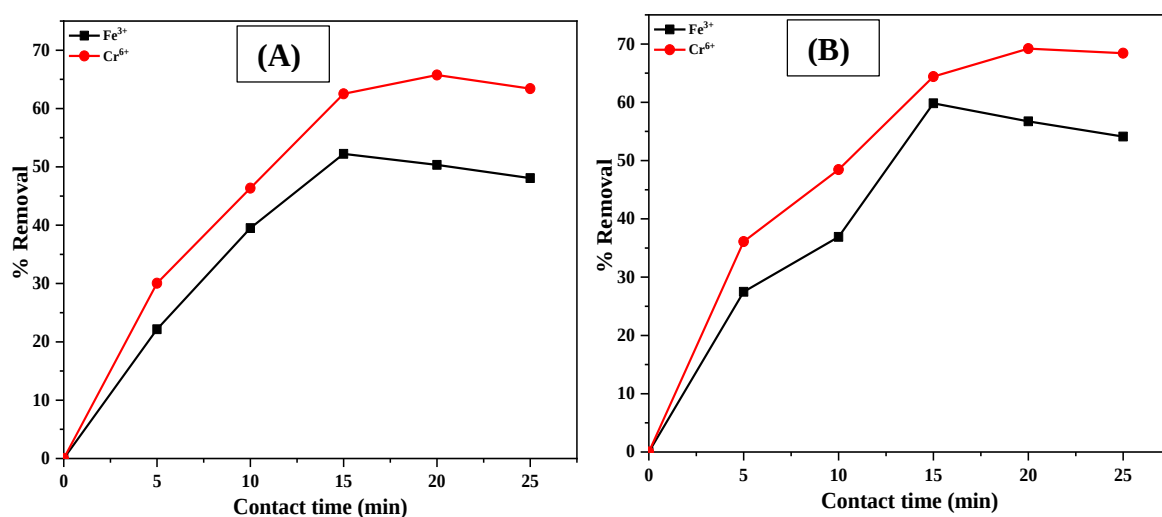


Figure 3: Effect of contact time in the removal of Cr^{6+} and Fe^{3+} from tannery wastewater using (A) acid activated carbon (B) base activated carbon

3.3.2 Effect of dosage

The adsorbent dosage showed a significant effect on the removal of metal ions from tannery wastewater as observed by varying the dosage from 0.4 to 1.2 g of acid and base activated carbon (see Fig. 5). The results as presented in Fig. 5(a) indicated that acid activated carbon exhibited percentage removal of 36.64 to 91.23 % for Fe(III) ion and 42.05 to 96.01 % for Cr(VI) ions. The base activated carbon showed the percentage removal of Fe(III) ion from 40.15 to 99.03 % and 51.47 to 100 of Cr(VI) ions removal from tannery wastewater. The migration of heavy metal ions on the adsorbent depends on the ionic/atomic radius of the heavy metals with Cr and Fe ions having ionic radii of 0.052 and 0.0645 nm, respectively. The percentage removal of other heavy metals increases with increasing dosage of the adsorbents dosage. This increment may be attributed to the availability of the adsorption sites which is in agreement with the findings of Lui *et al.* (2020).

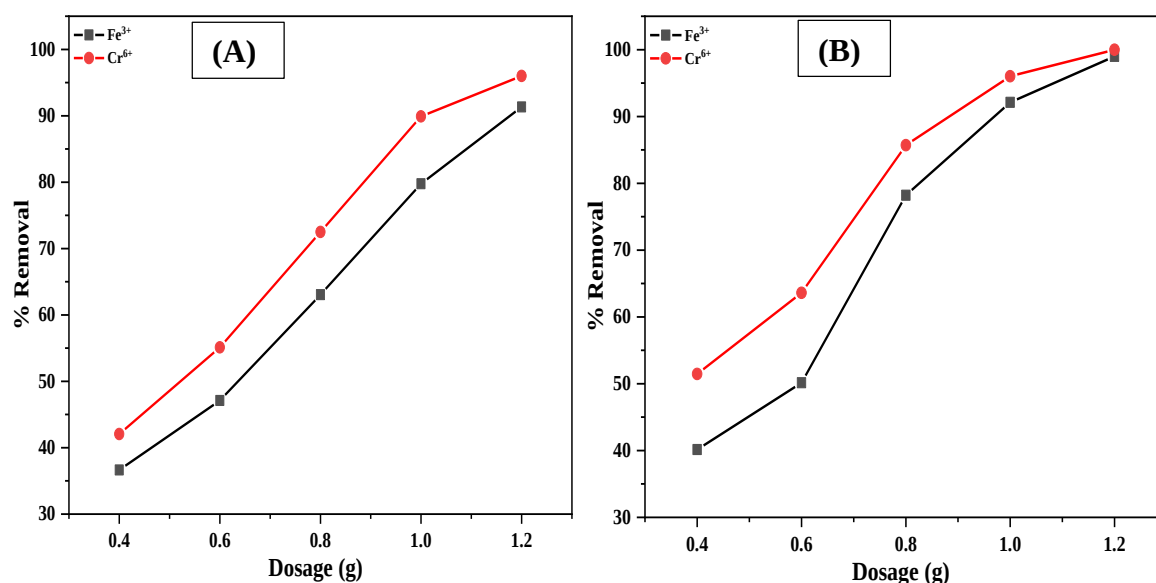


Figure 4: Effect of adsorbent dosage in the removal of Cr⁺⁶ and Fe³⁺ from tannery wastewater using (A) acid activated carbon (B) base activated carbon

3.3.3 Effect of temperature

The removal efficiency Cr(VI) and Fe(III) ions from tannery wastewater with respect to the applied temperature using acid and base activated carbon are shown in Fig. 6(a-b). It was noticed that the removal rate of metal ions increases with increasing solution temperature, indicating that the interaction between metal and biosorption is an endothermic process. The variation in the removal of metal ions appears to be linked to the increased tendency of these ions to escape from the aqueous phase into the bulk solution, resulting in a subsequent increase in the thickness of the boundary layer (Masoumi *et al.*, 2022). The rise in removal at higher temperatures can also be attributed to the reduced solubility of metals at relatively elevated temperatures.

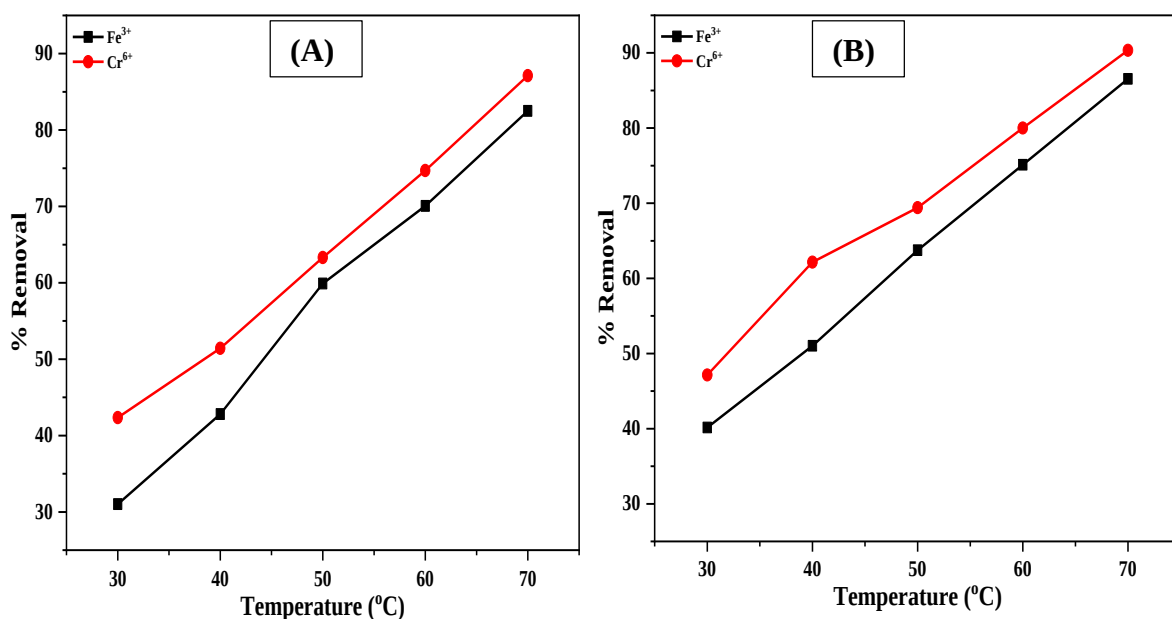


Figure 6: Effect of temperature in the removal of Cr⁶⁺ and Fe³⁺ from tannery wastewater using (A) acid activated carbon (B) base activated carbon

3.4 Adsorption isotherm

The linear Langmuir and Freundlich adsorption isotherm equations (3 and 4) are used to calculate the isotherms parameter of the metal ions removal from wastewater as presented in Table 2.

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m} \quad (3)$$

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (4)$$

where C_e is the equilibrium concentration of solution (mg/dm³), q_e is the adsorption capacity (mg/g), q_m is the maximum adsorption capacity (mg/g) and b is the adsorption equilibrium constant (L/mg). K_f and n are known as Freundlich constants. The sequence of adsorption was determined to be Cr>Fe using acid and base activated carbon. The results from the isotherm study indicate the Langmuir model have higher correlation coefficients (R^2) as displayed in Table 2. This attributes that the adsorbent sites were uniformly distributed across the surface, and metal ions formed mono layers on the sorbent surface. The values of the nf constant for the Freundlich model were found between 0.2 to 1, suggesting that the adsorption of metal ions on the surface of the adsorbent is favourable.

Table 2: Isotherm models of metal ions removal in wastewater

Adsorbent			Metal ion		Langmuir				Freundlich			
					K_L	Q_m	R^2		K_f	n	R^2	
Acid activated carbon		Fe			0.0231	40.23	0.9894		2.18	0.226	0.8853	
					0.0261	68.51	0.9936		2.49	0.248	0.9139	
Base activated carbon		Fe			0.0613	67.84	0.9971		2.86	0.312	0.9213	
					0.0783	89.71	0.9982		3.14	0.405	0.9404	

3.5 Adsorption kinetic study

The adsorption experimental data were fitted for pseudo-first-order and pseudo-second-order using equ. 5 and 6.

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (5)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (6)$$

where q_e and q_t are the amount of metal ion (mg/g) at equilibrium time and time t , respectively, k_1 is the pseudo-first-order rate constant and k_2 is the pseudo-second-order rate constant. Table 3 shows the kinetic parameters of the adsorbents for the removal of Cr and Fe ions from wastewater. The results indicated that the adsorption process fitted well for pseudo-second-order kinetics for the Cr and Fe ions. The results are also satisfactory to the higher correlation coefficients (R^2) of pseudo-second-order compared to pseudo-first-order model. This indicates that the adsorption mechanism involves chemical sorption interactions between the adsorbent and the metal ions.

Table3: Kinetic models of metal ions removal in wastewater

Adsorbent	Metal ion	Pseudo-first-order				Pseudo-second-order		
			k_1	q_e	R^2	k_2	q_e	R^2
Acid activated carbon	Fe		0.0505	26.75	0.8952	0.708	36.66	0.9893
	Cr		0.102	36.72	0.9232	1.382	60.33	0.9910
Base activated carbon	Fe		0.092	45.06	0.9650	1.645	65.74	0.9989
	Cr		0.138	51.09	0.9217	2.936	83.65	0.9992

4. Conclusion

The study focused on removal of Cr and Fe ions from tannery wastewater using activated carbon from *Neocarya macrophylla* seeds. The XRD phase analysis of modified activated carbon showed the diffraction peaks of the samples at 28.0, 51.26, 54.40 and 68.50 with the reflection of (002), (100), (101) and (010) planes, respectively. The HRTEM structures of activated carbon samples are porous microstructure consisting of curled carbon layer. The FTIR spectra of acid and base activated carbon indicated the presence of OH group stretching vibration at absorption band of 3430 cm⁻¹ related to hemicellulose, lignin, and absorbed water molecules. The batch adsorption process of the removal of metal ions is influenced by contact time, dosage and temperature. The adsorption isotherm and kinetic data followed Langmuir isotherm and pseudo-second-order model. The thermodynamic parameters confirmed the spontaneous nature of adsorption process. These results show that acid and base activated carbon are potential candidates for the removal of Cr(VI) and Fe(III) ions from tannery wastewater.

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SN 13 MICROSTRUCTURE OF CB/SiO₂ HYBRID REINFORCED SOLID TYRE TREAD COMPOUND CONTAINING GROUND TYRE RUBBER AND THEIR EFFECT ON FATIGUE RESISTANCE

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Abstract

The study investigates the microstructure of carbon black filled tyre tread compound containing 20 phr ground tyre rubber (GTR) and compares the microstructure with those of similar compounds filled with hybrid carbon black/precipitated silica (CB/SiO₂) reinforcement. In the compounds filled with hybrid filler reinforcement, amount of the GTR was maintained at 20 phr, while the amount of the hybrid filler (CB/SiO₂) were in the ratios 55/5, 50/10 and 45/15 respectively. The formulations were prepared and the ingredients weighed. The compounds were mixed by two-step mixing method. The first step of the mixing was carried out in a laboratory internal mixer at 60°C and 100°C respectively; while the second step was carried out on a two-roll mill. The vulcanisation of each rubber compound was carried out on a compression moulding machine at 150°C using the cure time obtained from rheometric measurement. 2 mm rubber sheets were produced. Samples were also produced for flex and fatigue experiment. Samples for scanning electron microscopy were cut out from the 2 mm vulcanized rubber sheets, cryogenically fractured in liquid nitrogen, sputter coated with platinum before they were observed under the scanning electron microscope. Fatigue tests were performed on the prepared samples on the testing machine. Results obtained from SEM analysis of the fractured surfaces show good dispersion and distribution of ingredients in the control samples that was not filled with GTR. The images obtained from the SEM analysis of the control sample show rough fractured surfaces. The micrograph of the sample containing GTR and mixed at 60°C shows that GTR was not very compatible with the matrix as detachment of GTR was observed. Improved mixing was achieved with increased mixing temperature. The addition of precipitated silica at 5 phr in the hybrid filler reinforcement resulted to poor dispersion. The dispersion improved as the amount of silica increased to 10 phr and 15 phr respectively as observed from the SEM images. The results obtained from flex and fatigue test show that the compounds filled with hybrid CB/SiO₂ in the ratio of 50/10 and 45/15 phr exhibited no crack after 1000 cycles due to good dispersion resulting from the synergistic effect of the hybrid filler reinforcement at the optimal amount of silica.

Keywords: Tyre, ground tyre rubber, recycling, scanning electron microscopy

1. Introduction

The use of tyres is indispensable in the automobile industry. The number of new automobile tyres for passenger cars, trucks and other machines produced globally exceed 1.6 billion per year (Goldstein Market Intelligence, 2020). China is the world largest producer of automobile tyre. In 2019, it global

production of tyres was estimated to be 16.86 million tons (Bijinaet *al.*, 2023). The production of tyres requires the use of so many materials, but rubber is the major component of tyres. The rubber in tyres are in vulcanized state. The chains are highly cross-linked and therefore very stable to the environment. As a result of their cross-linked nature, they do not degrade when disposed after the service of the tyre. The rubber in tyre takes about 800-1000 years to degrade in the soil (Chenet *al.*, 2021). End-of-life tyres (ELTs) constitute environmental problems. According to report (Chenet *al.*, 2021), about 14.6 million ton of waste tyres were generated in 2018. ELTs add to solid waste. The combustion of waste tyres contributes to atmospheric pollutants such as SO₂, NO_x, dioxins, dibenzofurans, etc. Even the heavy metals in the ash such as Mn, Cr and Pb can lead to soil and water pollution. Researchers and industries are therefore exploring the various options such as tyre retreading, rubber reclaiming, the use of waste tyres as fuels, waste tyre pyrolysis and the grinding of waste tyres and subsequent utilisation as fillers in composites in order to reduce the amount of end-of-life tyres in the environment. Our current research effort is towards the incorporation of ground tyre rubber (GTR) in tyre tread compounds as part replacement of the rubber (Umunakweet *al.*, 2021; Umunakweet *al.*, 2021). It has been reported in literature that the addition in rubber compounds reduces the tensile strength, tear strength and elongation of the vulcanisates while increasing the heat build-up, hardness and stiffness (Rajan *et al.*, 2006; Mangili *et al.*, 2015; Simon and Bárány, 2023). Our work is focused on improving the properties of tyre tread compound containing GTR through hybrid filler reinforcement and this work reports the microstructure and flex and fatigue resistance of solid tyre tread compound containing 20 phr GTR.

2. Materials and Method

2.1 Materials

60 mesh size ground tyre rubber (GTR) was provided by the Rubber Technology Research Centre, Thailand. The base elastomers are natural rubber (NR) grade STR 20 (L. C. E. H Bangkok (Thailand) Co. Ltd). And butadiene rubber (BR) (BR 01) (BST Elastomers Co., Ltd.). The compounding ingredients include zinc oxide (ZnO) (Thai-Lysaght Co., Ltd.) stearic acid (Asia Chem Co., Ltd.), poly(1,2-dihydro-2,2,4-trimethyl-quinoline) (TMQ) (Monflex PTE Ltd.), N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine (6PPD) (Eastman Chemical Switzerland LLC), aromatic oil (P. S. P. Specialties Public Company Limited) carbon black (N330) Birla Carbon (Thailand) Public Company Limited), precipitated silica (Tokusil 255) (OSC Siam Silica Co. Ltd.), bis(3-triethoxysilylpropyl)-tetrasulfide (TESPT or Si69 coupling agent) (Briture Co. Ltd.), sulphur (The Siam Chemical Public Company Limited) and N-tert-butyl-2-benzothiazylsulphenamide (TBBS) (Ningbo Actmix Rubber Chemicals Co., Ltd.). The recipe used to produce the various vulcanisate samples are presented in Table 1.

Table 1: Recipe of the tyre tread vulcanisate

	Chemical/Sample code	Amount (phr)						
		Control	F1	F2	F3	F4	F5	
of the The were weighed recipe Table 1. The carried out by	NR(STR20)	80	64	64	64	64	64	2.2 Mixing rubber compounds ingredients based on the presented in mixing was two-step
	BR (01)	20	16	16	16	16	16	
	60 mesh size GTR	-	20	20	20	20	20	
	ZnO	4	4	4	4	4	4	
	Stearic acid	2	2	2	2	2	2	
	6PPD	1.5	1.5	1.5	1.5	1.5	1.5	
	TMQ	1	1	1	1	1	1	
	Aromatic oil	10	10	10	10	10	10	
	CB (N330)	60	60	60	55	50	45	
	Silica	-	-	-	5	10	15	
	Si69	-	-	-	0.5	1	1.5	
	S	2	2	2	2	2	2	
	TBBS	1.2	1.2	1.2	1.2	1.2	1.2	

mixing as described in literature (Umunakweet *al.*, 2023). The “control” and sample “F1” were mixed in the order of mixing presented in Table 2 (Umunakweet *al.*, 2023). The mixing step 1 was carried out in a 500 ml laboratory internal mixer (Brabender plasticoder lab station, Germany) at a starting temperature of 60°C, fill factor of 0.78 and rotor speed of 40 rpm. The rubber compound dumped from the internal mixer was allowed to cool to room temperature. Thereafter, the mixing step 2 of the rubber compound was carried out on a two-roll at 30°C for 5 minutes for homogenization. The step 1 mixing for each of samples “F2”, “F3”, “F4”, and “F5” was also carried out using the same internal mixer at the same rotor speed and fill factor, but starting mixing temperature of 100°C to ensure silanization reaction (Sattayanuraket *al.*, 2020), in the order of mixing shown in Table 3 (Umunakweet *al.*, 2023). The step 2 mixing for the samples were carried out on a two-roll mill at 30°C for 6 minutes after the samples dumped from the internal mixer had cooled to room temperature. TBBS and S which served as the curatives were added during mixing on two-roll mill at the 3rd and homogenized mixing was ensured. All the rubber compounds were kept at room temperature for 24 hours before further processing was carried out.

Table 2: Sequence of addition of materials during mixing in the step 1 for samples “control”, and “F1” (Umunakweet *al.*, 2023)

Time (minute)	Operation
0	Loading STR 20, BR150 and GTR (for F1)
1st	ZnO, stearic acid, 6PPD, TMQ, ¼ of carbon black

3rd	$\frac{3}{4}$ of the carbon black, aromatic oil
6th	Sulfur + TBBS
8th	Dumping

Table 3. Mixing sequence in the step 1 for samples “F2 to F5” (Umunakweet *al.*, 2023)

Time (minute)	Operation
0	Loading STR 20, BR150 and GTR
1st	ZnO, stearic acid, 6PPD, TMQ, $\frac{1}{4}$ of carbon black, silica and Si69 (Si69 only added in “F3 – F5”)
3rd	$\frac{3}{4}$ of the carbon black, aromatic oil
6th	Dumping

2.3 Production of the rubber vulcanisates

2 mm sheet rubber vulcanisates through compression moulding using hydraulic press (Wabash MPI, USA) under applied moulding pressure of 20 tons-force at 150°C using the cure time (tc90) determined from rheometer (Umunakweet *al.*, 2023). The samples for flex and fatigue test having thickness of 4.5 mm were moulded with their moulds using tc90 + 3 minutes as the cure time.

2.4 Characterisations of the moulded sample

2.4.1 Scanning electron microscopy (SEM) on the samples

Specimens for SEM analysis were cut from the 2 mm vulcanisates sheets using the cutting machine. The cut specimens were then cryogenically fractured using liquid nitrogen. The fractured specimens were mounted on the stub and sputter coated with platinum. The images of the fractured were obtained with the Hitachi field emission scanning electron microscope at applied voltage of 10 kv and magnification of 30,000.

2.4.2 Measurement of flex and fatigue resistance

The resistance to cracking under repeated flexing strain was studied using flex and fatigue testing tester (GT-7011-D) according to ASTM D430-06 (2018) standard. The specimens were installed on the machine and flexed at frequency of 5 Hz (300 cycles per minute) at room temperature (23°C). The presence and grade of crack based on ASTM D430-06 (2018) standard were initially checked after 500 cycles. Subsequently, at intervals of 1000 cycle until 10,000 cycles, the specimens were checked for presence and grade of cracks.

3. Results and Discussion

3.1 Microstructure of the rubber vulcanisates

The SEM micrographs of the cryogenically fractured surface topography of the control sample and those filled with 20 phrGTR (F1 to F5) are shown in Figure 1(a-f). The SEM micrograph of the

fractured surface of the control (without GTR) sample (Figure 1a) shows good dispersion and distribution of the additives. The fractured surface shows rough surfaces indicating high energy requirement to cause failure. This correlates with the good physic-mechanical properties of the control sample earlier reported (Umunakwe *et al.*, 2023). The SEM micrograph of the fractured surface of sample F1 containing 20 phrGTR and mixed at initial temperature of 60°C is shown in Figure 1b. The micrographs show detachment of the GTR from the rubber matrix and this resulted to the poor mechanical properties exhibited by sample. In the SEM micrograph of sample F2 (Figure 1c) containing 20 phrGTR and mixed at initial temperature of 100°C, microstructure appear more homogenous compared with sample F1. The mixing of the GTR and the rubber matrix was improved. However, the fractured surface appear smooth, an indication of poor resistance to fracture. The properties of sample F2 are therefore better than those of sample F1 but generally not improved. The micrograph of sample F3 containing 20 phrGTR and 5 phr silica in a hybrid carbon black/silica (55/5) reinforcement system is shown in Figure 1d. Silica was trapped as agglomerates in the matrix due to their small amount and lack of shear force for better dispersion and distribution. Hence, sample F3 exhibited poor physic-mechanical properties. The best improvement in the properties were achieved in the samples containing 10 phr silica in hybrid carbon black/silica (50/10) filler reinforcement of the tyre tread compound containing GTR. The SEM micrograph of sample F4 (Figure 1e) shows improved dispersion and distribution of the materials in the matrix and rough fractured surface, hence, the properties of the rubber vulcanisates containing GTR were improved through hybrid carbon black/silica (50/10) reinforcement with the help of silane coupling agent. As the amount of silica increased in the carbon black/silica (45/15) hybrid reinforcement (Figure 1f), the dispersion were still good as no agglomerations were observed in the SEM micrograph. All the results show that in a tyre tread compound containing GTR, the optimal amount of silica in the hybrid carbon black/silica reinforcement is 10 phr in a 60 phr filler loading.

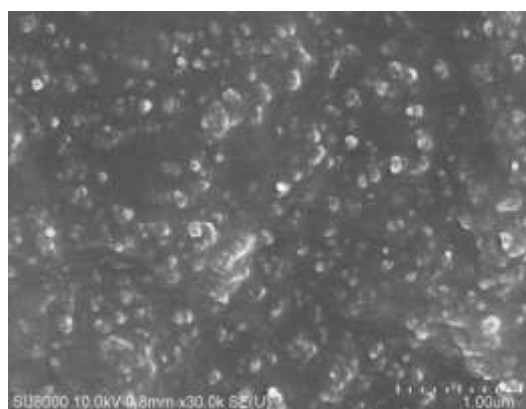


Figure 1a: SEM image of the control sample

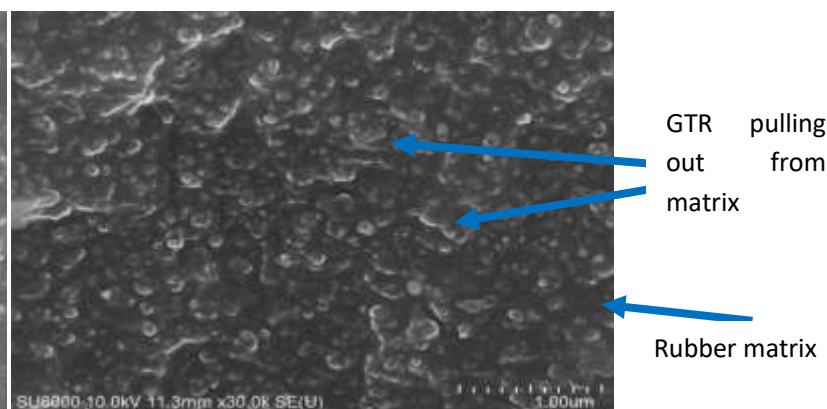


Figure 1b: SEM image of sample F1

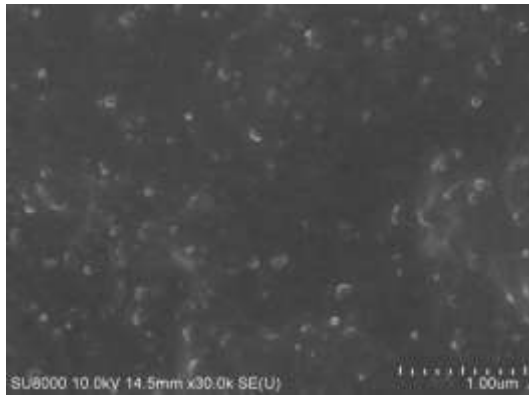
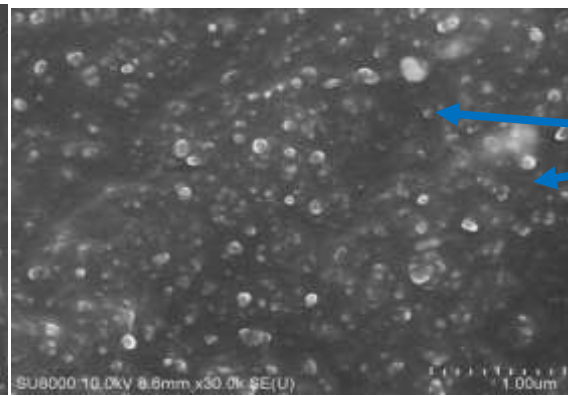


Figure 1c: SEM image of sample F2



Some of the agglomerated silica in the matrix

Figure 1d: SEM image of sample F3

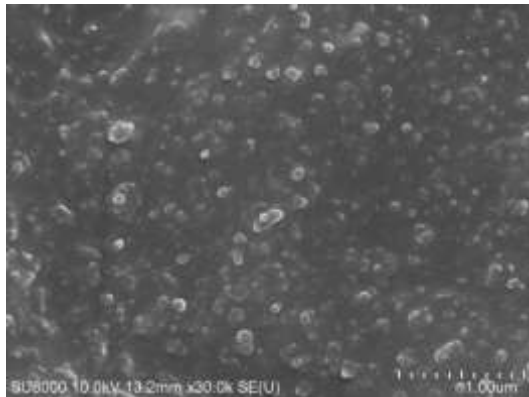


Figure 1e: SEM image of sample F4

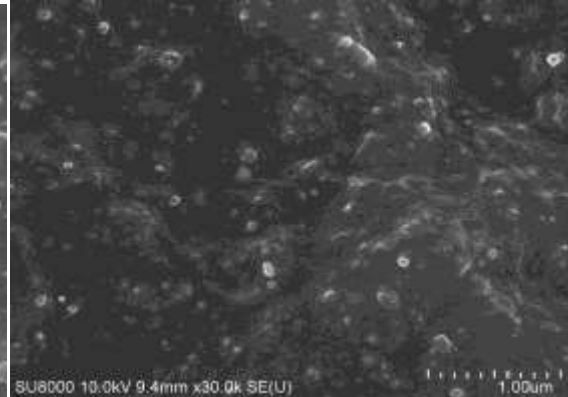


Figure 1f: SEM image of sample F5

3.2 Flex and fatigue properties of the rubber vulcanisates

The flex and fatigue resistance of the rubber vulcanisates are shown in Table 4. The control sample did not exhibit any crack. Also, the samples containing hybrid carbon black/silica reinforcement from 10-15 phr (samples F4 and F5) exhibited no crack after 10,000 cycles due to good dispersion resulting from the synergistic effect of hybrid filler reinforcement in the tyre tread compound containing GTR.

Table 4: Flex and fatigue resistance of the vulcanisate samples

Sample	Control	F1	F2	F3	F4	F5
Number of cycle	Grade of Crack					
500	0	0	0	0	0	0
1000	0	0	0	1	0	0
2000	0	0	0	2	0	0
3000	0	1	0	3	0	0
4000	0	1	0	3	0	0
5000	0	1	0	3	0	0
6000	0	1	0	3	0	0
7000	0	1	1	3	0	0
8000	0	1	1	3	0	0
9000	0	1	1	3	0	0
10000	0	1	1	3	0	0

4. Conclusions

This work has presented the results of SEM analysis of the microstructure of tyre tread compound containing GTR filled with carbon black/silica hybrid reinforcement. The SEM images show that GTR is not very compatible when incorporated in rubber matrix. The images of the fractured surfaces of the rubber vulcanisates obtained from SEM show that the incorporation of silica at optimal amount in carbon black reinforced solid tire compound containing GTR resulted to improved dispersion and distribution of materials in the rubber matrix leading to resistance to fracture and improved flex and fatigue resistance of the vulcanisates.

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SN 14 EFFECTS OF SESAME STRAW ASH ON COMPRESSIVE STRENGTH AND DURABILITY OF MORTAR

Sulaiman, T. A., Yau, Y., Abdurrahman, A. A., Aliyu, I., Abdullah, M., Mohammed A.

ABSTRACT

Large quantities of agricultural waste are generated annually, and most of them are disposed to landfills littering the environment. The use of agricultural waste ashes as a partial replacement of cement, helps to reduce the use of cement in the production of mortar and concrete. This study aimed at assessing the effect of sesame straw ash as a partial replacement of cement on the compressive strength and durability of SSA mortar. Effects of sesame straw ash (SSA) on cement paste were investigated for addition of 0, 5, 10, 15, 20 and 25 % SSA by weight of cement. The compressive strength and durability of mortar made with different percentages of SSA (i.e. 0 – 25 %) were investigated. 70 mm cubes of SSA-mortar were tested for compressive at 3, 7, 28, 56 and 90 days of curing according to BS 1881-116: (1983) and water absorption was investigated. The outcomes of the study show that the consistency, setting times, and soundness of SSA-cement paste increase as the percentage of SSA content increases. The compressive strength of SSA-mortar increase as the curing age increases, and decreases as the percentage of SSA content increases. Additionally, addition of SSA content increases the water absorption of mortar. It was concluded that SSA is low reactive pozzolana and the maximum amount of SSA to be used should be around 5 % to 10 % replacement in mortar production.

Keywords: Cement, Compressive Strength, Mortar, Sesame Straw Ash (SSA), and Water Absorption,

1. INTRODUCTION

The need to produce concrete or mortar from agricultural wastes cannot be over-emphasized. The use of supplementary cementitious materials (i.e. agricultural wastes) in the production of green concrete or mortar is highly imperative in many conditions where there is a need to modify the characteristics of concrete (Sulaiman *et al.*, 2022). The utilization of waste materials in the construction industries will reduce the usage of natural resources. Many researchers have investigated the use of various agricultural wastes as supplementary for cement with individual agricultural waste materials showing unique performance with respect to percentage replacement (Aliu *et al.*, 2023). Researchers intensified their search for local materials that could be used as a partial replacement for cement in the construction industries in order to lower the cost of the production of concrete and mortar (Ettuet *et al.*, 2013). The usage of agricultural waste ash as a partial replacement for cement can contribute to reducing the overall cost of concrete (Hakeem *et al.*, 2022). Agwa *et al.*, (2020) justified that the utilization of waste ashes from agricultural sector in the concrete industry can produce more environmentally friendly and sustainable concrete as greener concrete.

Sesame crops produce a large amount of agricultural waste, which can be used as fuel and finally converted into ash. This waste forms an environmental burden that must be disposed (Hakeem *et al.*, 2022). The global production of sesame is about 5,532,000 metric tons per annum and has escalated to 6,016,000 metric tons in 2018 with the cultivated area estimated at 11,743,000 ha (Myint *et al.*, 2020). According to Orame *et al.*, (2020) the addition of Sesame Plant Mucilage (SPM) content in concrete increased flexural strength and tensile strength and their values are higher than that of control mix at all curing age. Hakeem *et al.*, (2022) reported that the addition of Nano-sized sesame

stalk ash (NSSA) blended with rice straw ash (RSA) increased the splitting tensile strength by 2 % and 5 % respectively. According to Hakeem *et al.*, (2022), the mixtures containing (20% RSA and 2.5 % NSSA) achieved the highest splitting tensile and flexural strength of 7.3 N/mm² and 10.7 N/mm². Sulaiman *et al.*, (2020) reported that the flow of fresh mortar decreased while consistency, setting times and soundness of SSA-cement paste increased as the percentage of sesame straw ash (SSA) content increased. However, the compressive strength of SSA-mortar increased as the SSA content increased up to 10 % at 28 days and then decreased. . According to study carried out on the effect of adding Sesame stalks fibre SSF to the concrete mixture by Elmardi *et al.*, (2021) indicated that the strengths of concrete made with SSF content decreased as the percentage of sesame stalks fibre SSF increased. They concluded that the addition of SSF increases the concrete resistance against crack growth.

The objective of this study is to evaluate the effects of sesame straw ash as a partial replacement of cement in mortar.

2. Materials and Methods

2.1 Materials

The cement used was Portland limestone cement (PLC), having a moisture content of 1.81 % and specific gravity of 3.16. Its chemical oxides are presented in Table 1. The fine aggregate used was sourced from Zaria Local Government Area, Kaduna State, Nigeria, with a silt content of 2 %, a specific gravity of 2.68 and bulk density of 1737 kg/m³. The sesame straw ash (SSA) used was obtained by burning the sesame straw (SS) sourced from Jigawa State, Nigeria. It has a moisture content of 1.95 %, and a specific gravity of 2.69. Finally, the water used was potable, sourced from the Department of Civil Engineering Laboratory of ABU, Zaria, Kaduna State, Nigeria.

2.2 Methods

2.2.1 Physical Properties Tests on Cement and Sesame Straw Ash (SSA)

The specific gravity and moisture content tests of cement and SSA were carried out according to BS 812, Part 2, (1975) and BS EN 196-6:1995 respectively.

2.2.2 Sieve Analysis of Fine Aggregate

The sieve analysis tests were carried out according to BS 812-103.1 (1985) in order to know the particle size distribution fine aggregate.

2.2.3 Consistency, Setting Times, Soundness of Test of SSA-Cement Paste

The consistency, setting times, and soundness tests conducted on SSA-cement paste were in accordance with BS EN 196-3 (1995).

2.2.4 Compressive Strength of SSA-Mortar

The compressive strength test conducted in accordance with BS EN 12390, Part 3, (2009). Mortar samples were cast and cured in potable water, and a total of 3 cubes were considered for an average for each curing age 3, 7, 28, 56 and 90 days.

2.2.5 Water Absorption test of SSA-Mortar

The water absorption test was performed on SSA-mortar specimens in accordance with BS 812, Part 2, (1995). A total of fifteen (15) samples were cured for 28 days, and then after 28 days of curing, three (3) samples were tested for a mean.

2.2.6 Mix Design

The mix ratio adopted for this study is 1:3 and absolute volume method was used to calculate the mix proportions.

3. Results and Discussions

3.1 Chemical Properties of cement and SSA

The results of the XRF test performed on cement, SSA are presented in Table 1. The oxide composition of SSA indicates that the sum of aluminium oxide (Al_2O_3), iron oxide (Fe_2O_3) and silicon oxide (SiO_2) is 31.76 % which is less than the lower limit of 70 % specified by ASTM C 618 for class F and N pozzolana, and 50 % for class C pozzolana. It is a low-reactive pozzolana.

Table 1: Oxide Composition of Cement, SSA and RHA

Oxide	Na_2O	MgO	Al_2O_3	SiO_2	SO_3	BaO	K_2O	CaO	Fe_2O_3
Cement (%)	0.18	1.05	2.83	21.43	1.42	0.01	0.62	68.02	2.77
SSA (%)	1.01	0.45	8.21	23.32	0.84	20.53	5.32	6.27	

3.2 Sieve Analysis of Fine and Coarse Aggregate

The particle size distributions of fine aggregate are shown in Figure 1. It was observed that the fine aggregate used belongs to zone 1 in line with BS 882, part 2(1992) for grading limits for fine aggregate. Moreover, the fine aggregate has a silt content of 2 which is less than the maximum of 6.0 and specific gravity of 2.72.

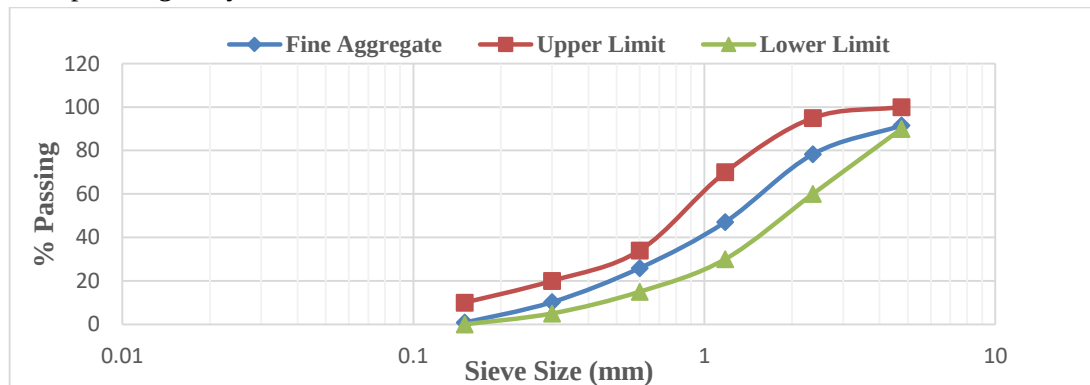


Figure 1: Particle Size Distribution of Fine Aggregate

3.3 Consistency of SSA-Cement Paste

The results of the consistency test carried out on SSA-cement paste are shown in Figure 2. It was observed that as the quantity of SSA content increased the value of consistency increased. This trend shows that SSA-cement paste required more water to get the desired consistency as the additional amount of SSA was added. The increase in water requirement may be due to the high porosity of SSA when compared to cement, the findings are consistent with the work of Sulaiman and Aliyu 2020, and Sulaiman *et al.*, 2020.

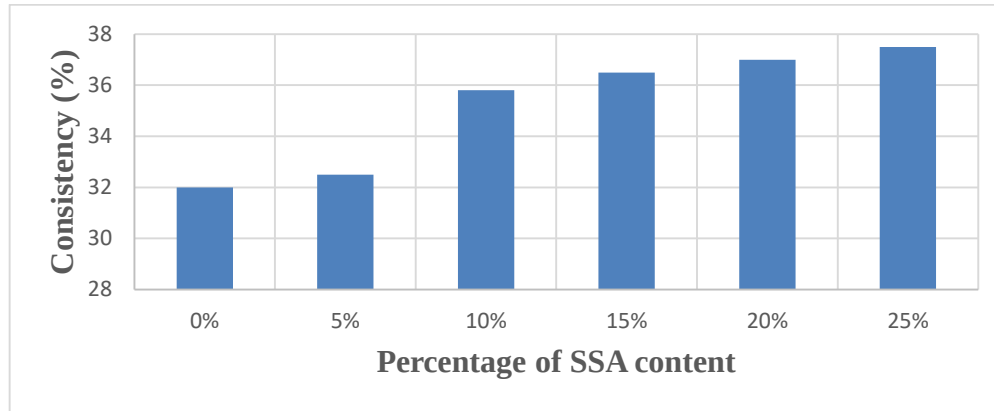


Figure 2: Relationship between Consistency and percentage of SSA Content

3.4 Setting Times of SSA-Cement Paste

The results of initial setting time and final setting time test of SSA-cement paste are presented in Figure 3. It was discovered that the initial setting time and final setting time increased as the percentage of SSA content increased. The increase might be due to the presence of potassium oxide that impedes the complete combination of lime and causes setting negative influence on the setting, this is consistent with Sulaiman *et al.*, 2020.

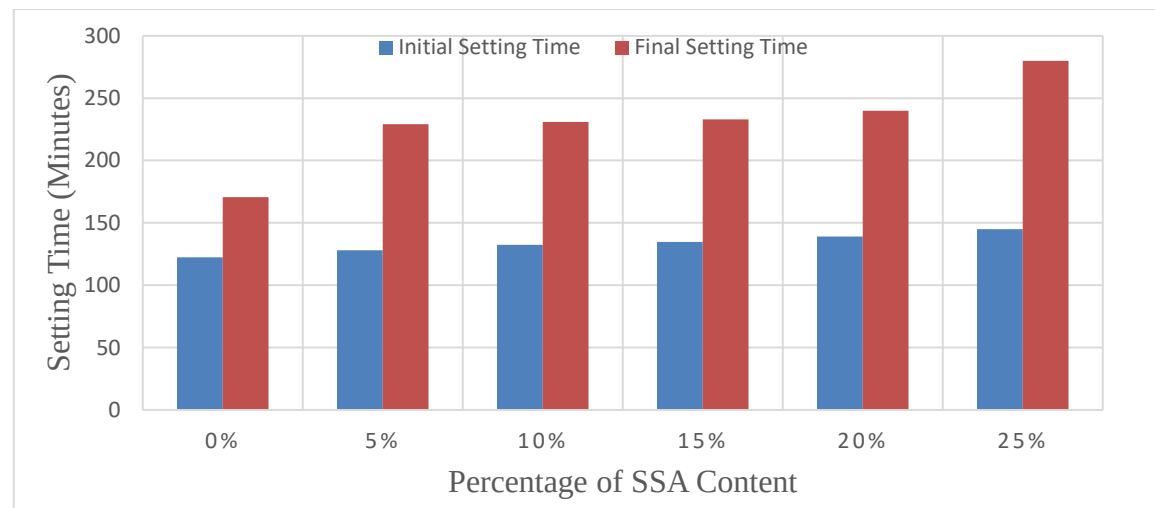


Figure 3: Relationship between Setting Times and percentage of SSA Content

3.5 Soundness of SSA-Cement Paste

The results of the soundness test conducted on cement paste blended with SSA were presented in Figure 4. It was observed that the soundness of SSA-cement pastes increased as the percentage of SSA content increased. The same pattern was observed by (Sulaiman and Aliyu, 2020). Moreover, the values found at each level of replacement (i.e. from 0.1 mm to 3.4 mm) were within the acceptable limits as specified by BS EN 196-3 (1995).

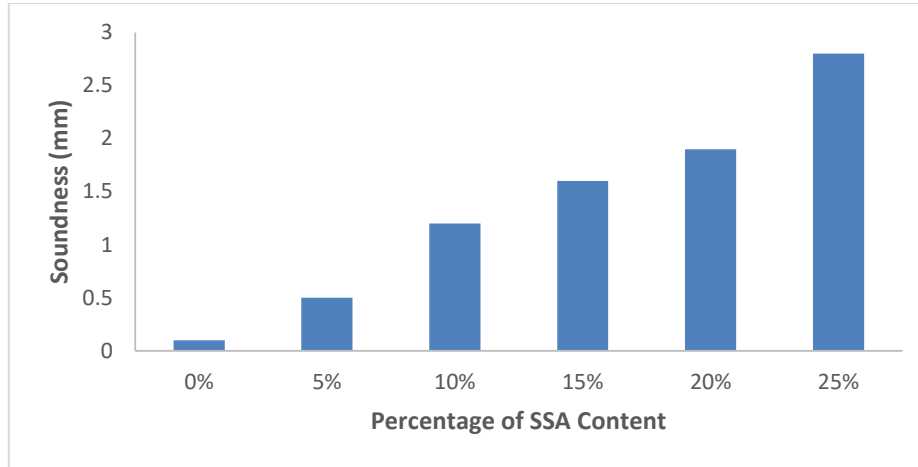


Figure 4: Relationship between Setting Times and percentage of SSA Content

3.6 Compressive Strength of SSA-Mortar

It was observed from Figure 5 that the compressive strength of SSA mortar decreased as the percentage of SSA content increased. On the other hand, there is an increase in compressive strength as the curing age of SSA mortar increased. So, the reduction in the compressive strength of mortar containing SSA of 5 % and above, may be due to the dilution effect of cement and the formation of weaker C-S-H gel as a result of pozzolanic reaction of SSA, this is consistent with Ogork and Abdulkarim (2017); Sulaiman *et al.*, 2020 and Ogork *et al.*, (2014).

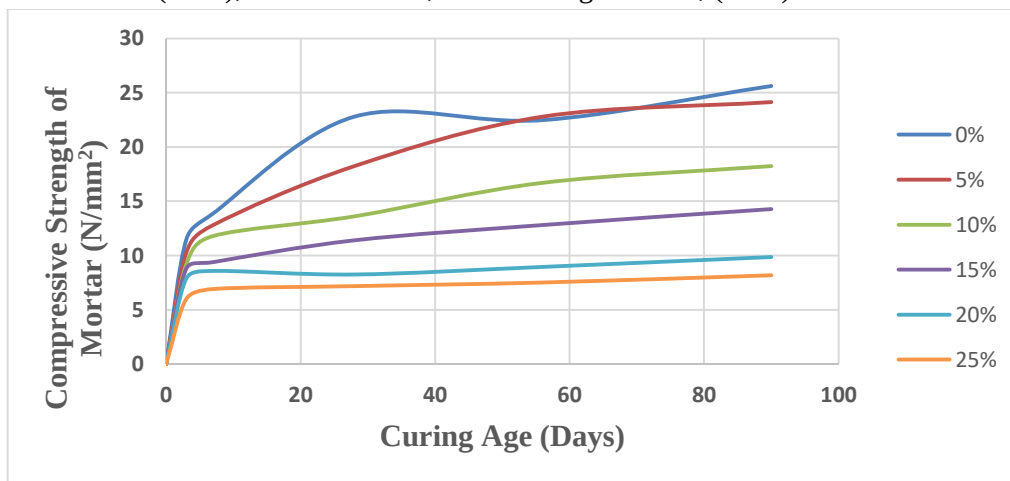


Figure 5: Compressive Strength against Curing Age

3.7 Water Absorption of SSA-Mortar

The results of the water absorption test carried out on SSA-mortar are presented in Figure 5. It was observed that as the quantity of SSA content increased amount of water absorbed increased. It shows that SSA-mortar absorbed more water than the control. The increase in water absorption may be the result of adding SSA content. It may be as a result of the increase in consistency in a mix containing SSA, in which the water occupies the space in SSA mortar and as it evaporates, it leaves voids that led to increase in the absorption of water, this is consistent with Ogork and Abdulkarim (2017).

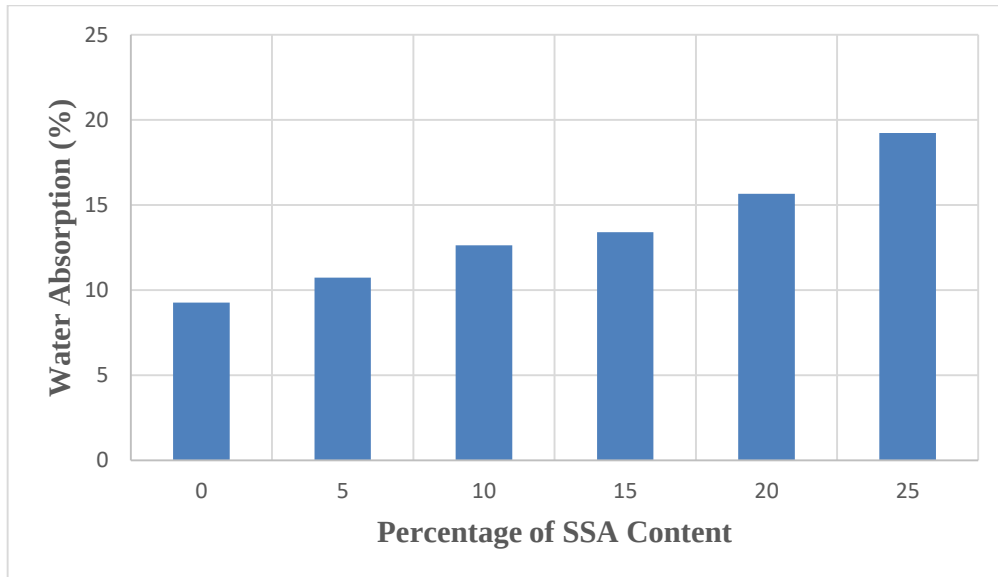


Figure 6: Water Absorption against Percentage of SSA Content

Conclusions

Based on the tests carried out, the following conclusions were outlined;

- i. Sesame straw ash (SSA) is a low reactive pozzolana.
- ii. Addition of SSA content increased the consistency, initial and final setting times and soundness of SSA-cement paste.
- iii. Addition of SSA content increased the compressive strength of SSA-mortar.
- iv. The water absorption of SSA mortar increased with an increase in addition of SSA content.
- v. Up to 5 % to 15 % SSA content is recommended for the production of mortar

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SN 15 TRACE METAL CONTENTS OF SOME COMMONLY CONSUMED TUBERS FROM THREE NORTH-CENTRAL STATES OF NIGERIA

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ABSTRACT

Trace elements could however be deleterious to human health when present at either excessive, deficient, or imbalanced concentrations within the body. This study determined the concentrations of six trace metals (Zn, Mn, Fe, Cu, Co, Cr) in yam, cassava, sweet potatoes, and Irish potatoes from three North-central states of Nigeria (Niger, Nasarawa, Benue). A total of 60 tuber samples were bought from which 12 composite samples were made and analysed using Microwave Plasma Atomic Emission Spectrometry (MP-AES) after digestion with Aqua regia solution. The results showed a wide variation in concentrations of the analysed trace metals in the samples with Co not being detected in 6 of the 12 analysed samples. The overall individual mean metal concentrations were in the order: Fe > Zn > Mn > Cu > Cr > Co. Yam ranged (mg/kg): Zn 34.50-45.25, Mn 14.50-19.75, Fe 31.50-182.75, Cu 20.75-30.25, Co 0.25-0.25, Cr 4.00-17.75. Cassava ranged (mg/kg): Zn 29.75-53.00, Mn 31.25-44.00, Fe 17.25-172.00, Cu 9.75-12.50, Co 1.00-1.00, Cr 4.00-17.25. Sweet potatoes ranged (mg/kg): Zn 28.25-32.25, Mn 27.25-50.25, Fe 25.25-176.00, Cu 18.50-26.50, Co 1.25-1.25, Cr 4.25-17.50. Irish potatoes ranged (mg/kg): Zn 49.75-55.50, Mn 36.00-50.50, Fe 37.00-156.50, Cu 17.50-19.50, Co 0.25-1.75, Cr 4.00-20.00. The Pearson's correlation analysis showed high positive correlations between Fe and Cr (0.975); and Mn/Co (0.818). Except for Cr, all the other analysed metals were below the acceptable limits of FAO/WHO in foods. Further study is recommended to ascertain the geochemical information of the soils where the tubers are grown.

KEY WORDS: Trace Metals, Tubers, Yam, Cassava, Sweet Potatoes, Irish Potatoes, MP-AES.

1. INTRODUCTION

The consumption of balanced diets is one of the most important determinants of human health. Tubers are underground food-storing stems or root that serves as a storage organ for energy and nutrients, and are important food source for both humans and animals. They are a major source of energy, starch, essential vitamins, minerals, and other nutrients for many people around the world especially in less developed countries in African countries like Nigeria; and serve as a source of income and diversity in diet (Bioseet *et al.*, 2020a; Bioseet *et al.*, 2020b; Wilberforce, 2015; Aregahegn *et al.*, 2013; Asha and Nair, 2002). Tubers are second to cereals as global sources of carbohydrates, with a lot more industrial applications (Chandrasekara and Josheph, 2016).

Irish Potatoes (*Solanumtuberosum*) are currently the fourth most important food crop in the world after maize, wheat, and rice, with a production of 368 million tonnes. It is a crop of highland origin and has been domesticated as a major food crop in the cool highland areas of South America, Asia, and Central and Eastern Africa (Chandrasekara and Josheph, 2016). Sweet Potatoes

(*Ipomoea batatas* L.) originated from Central America but is currently the seventh most widely grown in many tropical, subtropical, and warm temperate regions in the world. Sweet potato can be grown all around the year under suitable climates and is considered a typical food security crop for poor populations (Chandrasekara and Josheph, 2016). Cassava (*Manihot esculenta*) originated in South America and is distributed to tropical and subtropical regions of Africa and Asia. It is a perennial shrub that is the most widely cultivated root crop in the tropics serving as an important staple for more than 500 million people in the world due to its high carbohydrate content (Chandrasekara and Josheph, 2016; Nassar *et al.*, 2008; Blagbrough *et al.*, 2010). Yams (*Dioscorea* spp) is a member of the monocotyledon with over 600 species that is a staple food across Africa, Southeast Asia, Latin America, and the Caribbean regions (Scarcelli *et al.*, 2017; Liu *et al.*, 2007). Yam tubers have various bioactive components, like mucin, dioscin, dioscorin, allantoin, choline, polyphenols, diosgenin, and vitamins such as carotenoids and tocopherols (Iwuet *et al.*, 1990; Bhandari *et al.*, 2003). Several studies have also shown yam extracts' hypoglycemic, antimicrobial, and antioxidant activities (Kelmanson *et al.*, 2000; Chan *et al.*, 2004). Yam is a major source of starch and plays a significant role in food security, medicine, and economy in the developing countries (Obidiegwu *et al.*, 2020).

Food consumption is identified as the major path for human exposure to certain environmental contaminants, including heavy metals and excess trace elements (Akinyele and Shokunbi, 2015a). Trace elements are micro nutrients that are needed by the humans or animals in very small quantities (Akinyele and Shokunbi, 2015a; Fraga, 2005). Trace elements are critical components in our foods providing optimal nutrition and health (Ole, 2012). They are essential components of enzymes and molecules that play important roles in maintaining several physiological and biochemical processes (Joseph *et al.*, 2016). These micronutrients could however pose potential health challenges and be deleterious to health when present at imbalanced (excessive or deficient) concentrations within the body (Filipiak-Szoket *et al.*, 2015). Hence, the need for the introduction of consumption safe limits and continuous monitoring. Data on trace element composition in foods are of utmost importance to consumers, educationists and health professionals. Also, the measurement of trace elements (in foods and body) is increasingly attracting interest from physicians because deviations in trace elements uptake and/or metabolism are known to be related to certain dysfunctions (Awad and Lilly, 2010). This research work aims at determining the concentration of six trace elements (Zn, Mn, Fe, Cu, Co, Cr) in four commonly consumed tuber foodstuffs (yam, cassava, sweet potatoes, Irish potatoes) from three North-central states of Nigeria.

2. MATERIAL AND METHODS

Study Area

Nigeria is the most populous Black Nation in the world with a population of 140,431,790 million (2006 census) or 188,462,640 (2015 estimate). Situated between latitudes 4° and 14°N and longitude 2° and 15°E on the Gulf of Guinea, West of the African continent, comprising of 36 states and the Federal Capital Territory, Abuja. Niger, Nasarawa, and Benue are 3 of the 6 states that form the North-central geo-political zones of Nigeria (Fig. 1). Niger State with a total land area of 76,363 km² (29,484 sq mi), and an estimated population of about 3,954,772 (2006 Census), has its capital at Minna. It has twenty-five Local Government Areas with farming as its dominant occupation, producing Rice, Maize, Sorghum, Yam, Cassava, Millet, Mango, Sheanut, Wood, Sugarcane, Livestock, (Meat, Hides & Skin), Fisheries, Groundnut, Cotton, Soya Beans, Melon, and Forestry.

Nasarawa State with Capital at Lafia has a total land area of 27,137.8 sq km. **It has thirteen Local Government Areas** with agriculture as the mainstay of its economy with the production of varieties of cash crops which include yam, cassava and melon throughout the year. While Benue State with twenty-three Local Government Areas has capital in Makurdi, and a population of 4,780,389 (2006 census), whose main occupation is farming, with yam, rice, beans, cassava, potatoes, maize, soya beans, sorghum, millet and cocoyam as their major produce, while the inhabitants of the riverine areas engage in fishing as their primary occupation.

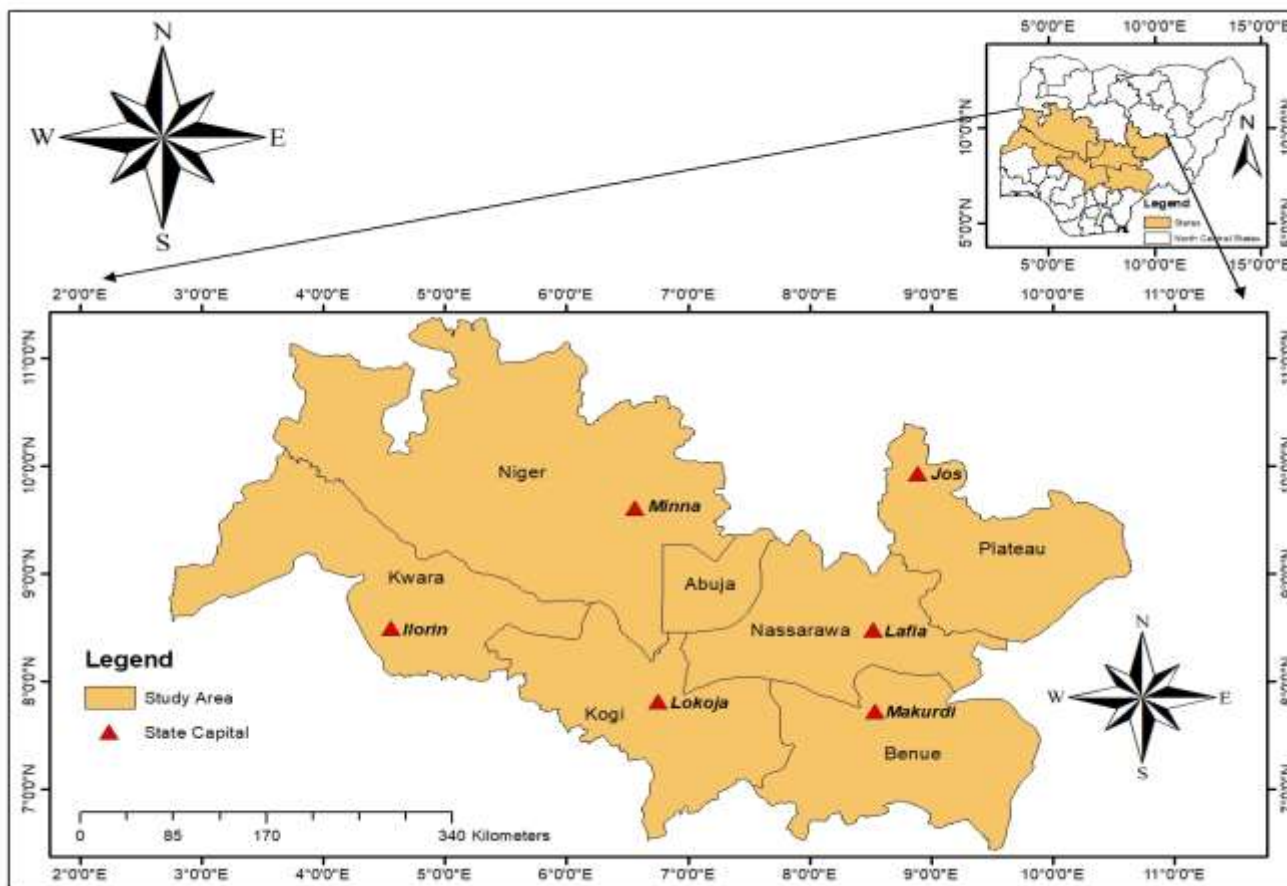


Fig.1: Location of the Study Sampling States on North central Map of Nigeria

Sample Collection and Pre-treatment

The tuber samples were acquired by market-basket survey based on the general guidelines provided by the World Health Organisation in which composite samples were made by mixing equal quantities of samples and used for analyses (WHO, 1985; Akinyele and Shokunbi, 2015a; Nasreddine *et al.*, 2010; Leblanc *et al.*, 2005). Five varieties of each of the four commonly consumed tuber samples in North central states (Fig. 2) were purchased from the major markets in each of the three states (Niger, Nasarawa and Benue states) by systematic random sampling and packed in well labelled polyethylene bags and safely transported to the laboratory. The samples were carefully cleaned to remove sand and other physical impurities, then sliced and air-dried before being oven-dried at 80 – 105 °C for approximately 16 h (to constant weight). Equal quantities of the five dried varieties of each sample were then mixed to form composite of the sample. The composite samples were then pulverized with a mill and the resulting fine powder stored in well labelled clean, dry and air-tight polyethylene containers ready for digestion (Akinyele and Shokunbi, 2015a; Ihedioha and Okoye, 2013). The mill was washed with distilled water and air-dried each time a fresh sample was grinded to avoid contamination of subsequent samples. In all, a total of 60 tuber samples were bought for this research from which 12 composite samples were made and used for the analysis.

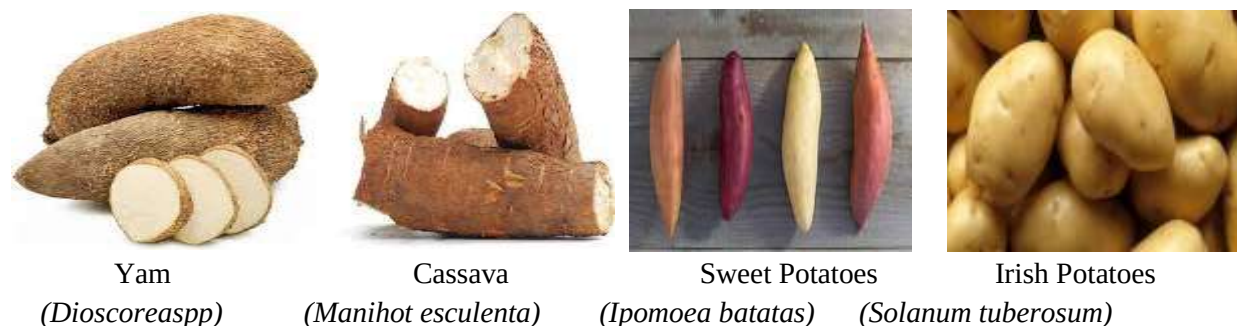


Fig 2: Tuber Samples

Sample Digestion

The ground composite tuber samples were wet digested with freshly prepared Aqua Regia mixture. Exactly 1.00 g of each of the sample was weighed into 125 cm³ Erlenmeyer flask to which 20.0 cm³ of the acid mixture was added in a fume hood. The mixture was tightly covered with a glass slit (to enable refluxing) and heated on a hot plate to 150 °C for about for 2½ h (until when clear yellow solution was obtained). The digest was allowed to cool and filtered into a 25.0 cm³ volumetric flask, using Whatman® filter paper No. 42. The conical flask was then carefully rinsed with distilled deionized water and filtered into the content in the volumetric flask and up to mark with distilled deionized water. This was then transferred to a well cleaned and labeled polystyrene sample bottles and kept for trace metal analyses (Akinyele and Shokunbi, 2015b, Demirel *et al.*, 2008).

Quality Control

Standard routine laboratory procedures were adequately adhered to. All materials (plastic and glass wares) were thoroughly washed with detergent and soaked in 10 % (v/v) HNO₃ for at least 24 h and then carefully but thoroughly rinsed with distilled deionized water before use. All reagents used were of analytical grade and all solutions prepared using distilled deionized water.

Sample Blanks and Sample Duplicates were included in each digestion batch and analyzed together with the foodstuff samples for method validation (i.e. to ensure the precision and repeatability of the digestion procedure and the instrumental analyses). The Sample blanks were prepared by taking a known volume of the digestion acid mixture through the same digestion procedure and analyzed for all the metals (Akinyele and Shokunbi, 2015a; Asegbeloyinet *al.*, 2015; Ihedioha and Okoye, 2013; Nasreddineet *al.*, 2010; Cabrera *et al.*, 2003).

Instrumentation

The concentrations of trace metals in the food samples – zinc, manganese, iron, copper, cobalt, chromium (Zn, Mn, Fe, Cu, Co, Cr) were determined by Microwave Plasma Atomic Emission Spectrometry (MP-AES) Model 4210 at Central Research Chemistry Laboratory, UsmanuDanfodio University, Sokoto, Nigeria.

3. RESULT AND DISCUSSION

The results of the content of the 6 trace metals in the studied tuber samples from 3 of the North-central states, Nigeria are presented in Table 1, while Table 2 shows the respective descriptive statistical analysis for the trace metal contents in the studied tubers from the 3 North-central states.

Table 1: Concentrations (mg/kg) of Trace Metals in the Tuber FoodSamples from the 3 North-central States

STATE	FOOD SAMPLES	Zn	Mn	Fe	Cu	Co	Cr
Niger	Yam	45.25	14.50	182.75	20.75	ND	17.25
	Cassava	32.50	36.00	172.00	12.50	ND	17.25
	Sweet Potatoes	32.25	28.75	176.00	26.50	ND	17.25
	Irish Potatoes	51.00	36.00	148.50	18.00	0.25	17.00
	Yam	40.00	19.00	144.75	30.25	ND	17.75
Nasarawa	Cassava	53.00	44.00	19.00	11.75	1.00	4.50
	Sweet Potatoes	28.25	50.25	25.25	18.50	1.25	4.25
	Irish Potatoes	55.50	50.50	37.00	19.50	1.50	4.00
	Yam	34.50	19.75	31.50	23.00	0.25	4.00
	Cassava	29.75	31.25	17.25	9.75	ND	4.00
Benue	Sweet Potatoes	30.75	27.25	151.75	21.00	ND	17.50
	Irish Potatoes	49.75	45.25	156.50	17.50	1.75	20.00

Tabulated values are means of 3 determinations ND = Not detected

Zn Zinc, Mn Manganese, Fe Iron, Cu Copper, Co Cobalt, Cr Chromium

Table 2: Descriptive Statistics for Trace Metal Content of Tubers from the 3 North-central States

FOOD SAMPLES	N		Zn	Mn	Fe	Cu	Co	Cr
Yam	3	Range	34.50 -	14.50 -	31.50 -	20.75 -	0.25 - 0.25	4.00 -
		Mean $\pm$	45.25	19.75	182.75	30.25	0.25 $\pm$ 0.00	17.75
		SD	39.92 $\pm$ 5.38	17.75 $\pm$ 2.84	119.67 $\pm$ 78.69	24.67 $\pm$ 4.96		13.00 $\pm$ 7.80
Cassava	3	Range	29.75 -	31.25 -	17.25 -	9.75 -	1.00 - 1.00	4.00 -
		Mean $\pm$	53.00	44.00	172.00	12.50	1.00 $\pm$ 0.00	17.25
		SD	38.42 $\pm$ 12.70	37.08 $\pm$ 6.44	69.42 $\pm$ 88.84	11.33 $\pm$ 1.42		8.58 $\pm$ 7.51
Sweet Potatoes	3	Range	28.25 -	27.25 -	25.25 -	18.50 -	1.25 - 1.25	4.25 -
		Mean $\pm$	32.25	50.25	176.00	26.50	1.25 $\pm$ 0.00	17.50
		SD	30.42 $\pm$ 2.02	35.42 $\pm$ 12.87	117.67 $\pm$ 80.95	22.00 $\pm$ 4.09		13.00 $\pm$ 7.58
Irish Potatoes	3	Range	49.75 -	36.00 -	37.00 -	17.50 -	0.25 - 1.75	4.00 -
		Mean $\pm$	55.50	50.50	156.50	19.50	1.17 $\pm$ 0.80	20.00
		SD	52.08 $\pm$ 3.02	43.92 $\pm$ 7.34	114.00 $\pm$ 66.80	18.33 $\pm$ 1.04		13.67 $\pm$ 8.50
All Tubers	12	Range	28.25 -	14.50 -	17.25 -	9.75 -	0.25 - 1.75	4.00 -
		Mean $\pm$	55.50	50.50	182.75	30.25	1.00 $\pm$ 0.63	20.00
		SD	40.21 $\pm$ 10.12	33.54 $\pm$ 12.27	105.19 $\pm$ 70.95	19.08 $\pm$ 5.95		12.06 $\pm$ 7.03

Zn Zinc, Mn Manganese, Fe Iron, Cu Copper, Co Cobalt, Cr Chromium

Table 3: Correlation Matrix of the Trace Metals Content among the 3 North-central States Tuber Samples

	Zn	Mn	Fe	Cu	Co	Cr
Zn	1.000					
Mn	0.307	1.000				
Fe	-0.004	-0.416	1.000			
Cu	-0.079	-0.487	0.387	1.000		
Co	0.516	0.818	-0.392	-0.215	1.000	
Cr	0.032	-0.358	0.975	0.368	-0.313	1.000

DISCUSSION

The result of the trace metal concentrations in the 4 analysed tubers from the three North-central states of Nigeria (Table 1) showed a wide variation in concentrations of the analysed trace metals in the samples with Co not being detected in 6 of the 12 analysed tuber samples. From the statistical analysis of the result (Table 2), Fe in Yam had the highest mean concentration (119.67 ± 78.69 mg/kg) while Co (0.25 ± 0.00 mg/kg) in Yam had the lowest mean concentration. Across the 12 analysed tuber samples (from 3 North-central States), Fe (105.19 ± 70.95 mg/kg) had the overall maximum mean concentration while Co had the lowest mean concentration (1.00 ± 0.63 mg/kg), with the overall individual mean metal concentrations in the order: Fe > Zn > Mn > Cu > Cr > Co.

Zn Concentration in the Tubers Samples: Zn is an essential trace element that functions as a component and cofactor of about 300 enzymes involved in cell and normal growth, and in the metabolism of proteins, carbohydrates, lipids, and energy; It is particularly important for healthy skin, essential for a healthy immune system and plays a crucial role in growth, and in insulin activity. (Falah and Saja, 2017; Burjonrappa and Miller, 2012; Das and Das, 2012; Osredkar and Sustar, 2011; Plum *et al.*, 2010;). The overall Zn concentration in the studied tubers ranged between 28.25 mg/kg in Sweet Potatoes and 55.50 mg/kg in Irish Potatoes. The highest mean concentration of Zn in the 4 analysed tubers was found in Irish Potatoes (52.08 ± 3.02 mg/kg), while the lowest was in Sweet Potatoes (30.42 ± 2.02 mg/kg). The mean Zn concentrations in the studied tubers are in descending order: Irish Potatoes > Yam > Cassava > Sweet Potatoes.

Yam recorded a mean Zn concentration of 39.92 ± 5.38 mg/kg. This was lower than the 40.00 ± 3.54 and 57.00 ± 1.40 mg/kg mean Zn values respectively recorded for native peeled yam from Benin City, Nigeria (Bioseet *et al.*, 2020b) and yam from West Bengal, India (Chaudhury *et al.*, 2018). Cassava recorded a Zn mean concentration of 38.42 ± 12.70 mg/kg. This was higher than the 0.287, and 16.85 ± 0.04 mg/kg mean Zn values respectively recorded for Cassava in Rukpoku, Rivers State, Nigeria (Ndukwe *et al.*, 2020), and in Ebocha, Rivers State, Nigeria (Kalagboret *et al.*, 2017). It was however, lower than the 77.75 and 108.32 mg/kg mean Zn values respectively recorded for cassava from Enyigba Mining Site in South Eastern Nigeria by Nworuet *et al.* (2018), and Wilberforce (2015). Sweet Potatoes recorded a Zn mean concentration of 30.42 ± 2.02 mg/kg, which was higher than the 18.25, and 6.65 ± 0.26 mg/kg mean Zn obtained in Native potatoes from Junín, Peru (Orellana *et al.*, 2020), and in potatoes from Abeokuta, South-West Nigeria (Akinyele and Shokunbi, 2015a). It is however, lower than the 74.60 mean Zn concentration recorded for Sweet potatoes from Enyigba Mining Site in South Eastern Nigeria (Wilberforce, 2015). Irish potatoes had a Zn mean concentration of 52.08 ± 3.02 mg/kg. This was higher than the 24.65 ± 5.87 mg/kg mean Zn obtained in Irish potatoes from Benin City, Nigeria (Bioseet *et al.*, 2020a). In general, all the 12 analysed composite tubers from the 3 North-central states in this study were below the acceptable 99.40 mg/kg Zn limits of FAO/WHO in foods (FAO/WHO, 2002).

Mn Concentration in the Tubers Samples: Manganese is an essential element required for various biochemical processes in the body and helps to form connective tissues, bones, blood-clotting factors, and sex hormones. It also aids in the normal functioning of the central nervous system, and its deficiency causes reproductive failure in both males and females (Saraf and Samant, 2013; Palacios, 2006; Fraga, 2005). The overall Mn concentration in

the studied tubers ranged between 14.50 mg/kg in Yam and 50.50 mg/kg in Irish Potatoes. The highest mean concentration of Mn in the 4 analysed tubers was found in Irish Potatoes (43.92 ± 7.34 mg/kg), while the lowest was in Yam (17.75 ± 2.84 mg/kg). The mean Mn concentrations in the studied tubers are in descending order: Irish Potatoes > Cassava > Sweet Potatoes > Yam.

Yam recorded a mean Mn concentration of 17.75 ± 2.84 mg/kg. This was higher than the 4.42 ± 0.38 and 13.30 ± 0.60 mg/kg mean Mn values respectively recorded for yam from Abeokuta, South-West Nigeria by Akinyele and Shokunbi, (2015a) and yam from West Bengal, India (Chaudhury *et al.*, 2018); but lower than the 22.00 and 82.62 mg/kg mean Mn values respectively obtained in yam from Enyigba Mining Site in South Eastern Nigeria by Nworuet *al.* (2018), and Wilberforce (2015). Cassava recorded a Mn mean concentration of 37.08 ± 6.44 mg/kg. This was higher than the 0.080, and 6.00 ± 0.02 mg/kg mean Mn values respectively recorded for Cassava in Rukpoku, Rivers State, Nigeria (Ndukwe *et al.*, 2020), and in Ebocha, Rivers State, Nigeria (Kalagboret *al.*, 2017). It was however, lower than the 40.00 and 624.26 mg/kg mean Mn values respectively recorded for cassava from Enyigba Mining Site in South Eastern Nigeria by Nworuet *al.* (2018), and Wilberforce (2015). Sweet Potatoes recorded a mean Mn concentration of 35.42 ± 12.87 mg/kg, which was higher than the 0.17 ± 0.05 and 9.25 ± 0.25 mg/kg mean Mn respectively obtained in white sweet potatoes from Benin City, Nigeria (Bioseet *al.*, 2020a), and in potatoes from Abeokuta, South-West Nigeria (Akinyele and Shokunbi, 2015a). It is, however, lower than the 84.90 mean Mn concentration recorded for Sweet potatoes from Enyigba Mining Site in South Eastern Nigeria (Wilberforce, 2015). Irish potatoes had a Mn mean concentration of 43.92 ± 7.34 mg/kg. This was higher than the 0.23 ± 0.07 and 1.75 mg/kg mean Mn obtained in Irish potatoes from Benin City, Nigeria (Bioseet *al.*, 2020a) and from Yaoundé, Cameroon (Gimouet *al.*, 2014). In general, all the 12 analysed composite tubers from the 3 North-central states in this study were below the acceptable 500.00 mg/kg Mn limits of FAO/WHO in foods (FAO/WHO, 2002).

Fe Concentration in the Tubers Samples: Iron (Fe) is an essential element in man and plays a vital role in the formation of red blood cells (haemoglobin), oxygen and electron transport in the human body, and in respiration, energy metabolism, destruction of hydrogen peroxides, and DNA synthesis (Kalagbor and Diri, 2014; Melaku, 2009). The overall Fe concentration in the studied tubers ranged between 17.25 mg/kg in Cassava and 182.75 mg/kg in Yam. The highest mean concentration of Fe in the 4 analysed tubers was found in Yam (119.67 ± 78.69 mg/kg), while the lowest was in Cassava (69.42 ± 88.84 mg/kg). The mean Fe concentrations in the studied tubers are in descending order: Yam > Sweet Potatoes > Irish Potatoes > Cassava.

Yam recorded a mean Fe concentration of 119.67 ± 78.69 mg/kg. This was higher than the 12.00, and 7.25 ± 0.43 mg/kg mean Fe values respectively recorded in yam from Enyigba Mining Site in South Eastern Nigeria by Nworuet *al.* (2018), and yam from Koraput, India (Padhan *et al.*, 2018); but lower than the 206.80 ± 122.90 and 1242.50 ± 4.00 mg/kg mean Fe values respectively obtained in yam from Benin City, Nigeria (Bioseet *al.*, 2020a), and yam from West Bengal, India (Chaudhury *et al.*, 2018). Cassava recorded a Fe mean concentration of 69.42 ± 88.84 mg/kg. This was higher than the 0.665, and 42.31 ± 0.01 mg/kg mean Fe values respectively recorded for Cassava in Rukpoku, Rivers State, Nigeria (Ndukwe *et al.*, 2020), and in Ebocha, Rivers State, Nigeria (Kalagboret *al.*, 2017). It was however, lower than the 96.60 ± 7.14 mg/kg mean Fe value recorded for cassava from Gokana, Rivers State, Nigeria (Nwineewii, 2020). Sweet Potatoes recorded a Fe mean concentration of 117.67 ± 80.95 mg/kg, which was higher than the 94.53, 45.87 ± 8.31 , and 7.25 ± 0.25 mg/kg mean Fe values respectively obtained in native potatoes from Junín, Peru

(Orellana *et al.*, 2020), for sweet potatoes in Kumasi, Ghana (Apauet *et al.*, 2014), and for sweet potatoes in Abeokuta, South-West Nigeria by Akinyele and Shokunbi, (2015a); but lower than the 129.75 ± 0.91 mg/kg mean Fe obtained in red sweet potatoes from Benin City, Nigeria (Bioseet *et al.*, 2020a). Irish potatoes had Fe mean concentration of 114.00 ± 66.80 mg/kg. This was slightly higher than the 113.70 ± 38.47 mg/kg mean Fe value obtained in Irish potatoes from Benin City, Nigeria (Bioseet *et al.*, 2020a), and much higher than the 38.90 ± 0.40 mg/kg mean Fe obtained in Irish potatoes from Amhara Region, Ethiopia (Tadesse *et al.*, 2015). Similarly, all the 12 analysed composite tubers from the 3 North-central states in this study were below the acceptable 425.50 mg/kg Fe limits of FAO/WHO in foods (FAO/WHO, 2002).

Cu Concentration in the Tubers Samples: Cu is an essential micronutrient necessary for the hematologic and neurologic systems. It is necessary for the growth and formation of bone, the formation of myelin sheaths in the nervous systems helps in the incorporation of Fe in haemoglobin, assists in the absorption of Fe from the gastrointestinal tract, and in the transfer of Fe from tissues to the plasma (Falah and Saja, 2017; Jeremias *et al.*, 2006). The overall Cu concentration in the studied tubers ranged between 9.75 mg/kg in Cassava and 30.25 mg/kg in Yam. The highest mean concentration of Cu in the 4 analysed tubers was found in Yam (24.67 ± 4.96 mg/kg), while the lowest was in Cassava (11.33 ± 1.42 mg/kg). The mean Cu concentrations in the studied tubers are in descending order: Yam > Sweet Potatoes > Irish Potatoes > Cassava.

Yam recorded a mean Cu concentration of 24.67 ± 4.96 mg/kg. This was higher than the 0.50, 6.03 ± 0.19 and 12.75 mg/kg mean Cu values respectively recorded in yam from Mangu, Plateau State, Nigeria (Haladu *et al.*, 2018), in yam from Abeokuta, South-West Nigeria by Akinyele and Shokunbi, (2015a) and yam from Enyigba Mining Site in South Eastern Nigeria by Nworuet *et al.* (2018); but lower than the 40.12 mg/kg mean Cu value obtained in yam from Enyigba Mining Site in South Eastern Nigeria by Wilberforce (2015). Cassava recorded a Cu mean concentration of 11.33 ± 1.42 mg/kg. This was higher than the 0.139, and 2.44 ± 0.17 mg/kg mean Cu values respectively recorded for Cassava in Rukpoku, Rivers State, Nigeria (Ndukwe *et al.*, 2020), and in Kogi State, North-central Nigeria (Emurotu and Onianwa, 2017). It was however, lower than the 16.50 mg/kg mean Cu value recorded for cassava from Enyigba Mining Site in South Eastern Nigeria by Nworuet *et al.* (2018). Sweet Potatoes recorded a Cu mean concentration of 22.00 ± 4.09 mg/kg, which was lower than the 42.24 mg/kg mean Cu value obtained in Sweet potatoes from Enyigba Mining Site in South Eastern Nigeria by Wilberforce (2015); but higher than the 0.31 ± 0.00 , and 8.20 ± 0.50 mg/kg mean Cu respectively obtained in red sweet potatoes from Benin City, Nigeria (Bioseet *et al.*, 2020a), and Varaždin, Croatia (Stančić *et al.*, 2016). Irish potatoes had a Cu mean concentration of 18.33 ± 1.04 mg/kg. This was similar to the 18.57 ± 0.08 mg/kg highest Cu concentration recorded in Nevsehir, Turkey (Leblebiciet *et al.*, 2017); but higher than the 0.36 ± 0.23 , 4.20 and 8.80 mg/kg mean Cu values obtained in Irish potatoes from Benin City, Nigeria (Bioseet *et al.*, 2020a), from Bokos, Plateau State, Nigeria (Haladu *et al.*, 2018), and from Kerala, India (Divya *et al.*, 2015). In general, all the 12 analysed composite tubers from the 3 North-central states in this study were below the acceptable 73.30 mg/kg Cu limits of FAO/WHO in foods (FAO/WHO, 2002).

Co Concentration in the Tubers Samples: Cobalt is an integral component of the vitamin B-12 molecule (cobalamin) that is required in the manufacture of red blood cells, and in the formation of amino acids and neurotransmitters. Excessive intake of it may cause the overproduction of red blood cells, fibrosis in the lungs and asthma; while its deficiency is associated with disturbances in vitamin B-12 synthesis leading to anaemia and hypothyroidism (Kalagboret *et al.*, 2014; Battaglia *et al.*, 2009; Housecroft and Sharpe, 2008;

Lombaert *et al.*, 2008). The overall Co concentration in the studied tubers ranged between 0.25 mg/kg in Yam and Irish Potatoes, and 1.75 mg/kg in Irish Potatoes. The highest mean concentration of Co in the 4 analysed tubers was found in Sweet Potatoes (1.25 ± 0.00 mg/kg), while the lowest was in Yam (0.25 ± 0.00 mg/kg). The mean Co concentrations in the studied tubers are in descending order: Sweet Potatoes > Irish Potatoes > Cassava > Yam.

Yam recorded a mean Co concentration of 0.25 ± 0.00 mg/kg. This was lower than the 1.42 mg/kg mean Co value recorded in yam from Koraput, India (Padhan *et al.*, 2018), but higher than the 0.013 mg/kg mean Co value obtained in yam in Yaoundé, Cameroon (Gimouet *et al.*, 2014). Cassava recorded a Co mean concentration of 1.00 ± 0.00 mg/kg. This was comparable to the 0.92 ± 0.01 mg/kg mean Co value obtained in Cassava in Ebocha, Rivers State, Nigeria (Kalagboret *et al.*, 2017), but higher than the 0.20 ± 0.05 and 0.008 mg/kg mean Co values respectively recorded for Cassava in Kogi State, North-central Nigeria (Emurotu and Onianwa, 2017), and in Yaoundé, Cameroon (Gimouet *et al.*, 2014). Sweet Potatoes recorded a Co mean concentration of 1.25 ± 0.00 mg/kg, which was higher than the 0.02 mg/kg mean Co value obtained in Sweet potatoes from Yaoundé, Cameroon (Gimouet *et al.*, 2014). Irish potatoes had a Co mean concentration of 1.17 ± 0.80 mg/kg. This was higher than the 0.016 mg/kg mean Co value obtained in Irish potatoes from Yaoundé, Cameroon (Gimouet *et al.*, 2014). In general, Co was detected in only 6 of the 12 analysed composite tuber samples, and all of them were below the acceptable 50.0 mg/kg safe Co limits of FAO/WHO in foods (FAO/WHO, 2002).

Cr Concentration in the Tubers Samples: Chromium is needed for the biosynthesis of glucose tolerance factor and maintenance of normal blood glucose levels (Prashanth *et al.*, 2015; Berdanier and Zemleni, 2009). Chromium exist in two forms: A biologically active trivalent Cr(III) which is found in foods, and a toxic hexavalent Cr(VI) that results from industrial pollution. Cr (III) and its compounds are not considered a health hazard, but the toxicity and carcinogenic properties of Cr (VI) have long been known. Cr (III) is effective in the management of diabetes and is a cofactor with insulin (Falah and Saja, 2017; Kalagboret *et al.*, 2014). The overall Cr concentration in the studied tubers ranged between 4.00 mg/kg in Yam, Cassava and Irish Potatoes and 20.00 mg/kg in Irish Potatoes. The highest mean concentration of Cr in the 4 analysed tubers was found in Irish Potatoes (13.67 ± 8.50 mg/kg), while the lowest was in Cassava (8.58 ± 7.51 mg/kg). The mean Cr concentrations in the studied tubers are in descending order: Irish Potatoes > Yam > Sweet Potatoes > Cassava.

Yam recorded a mean Cr concentration of 13.00 ± 7.80 mg/kg. This was higher than the 0.043, and 0.08 ± 0.06 mg/kg mean Fe values respectively recorded in yam from Enyigba Mining Site in South Eastern Nigeria by Nworuet *et al.* (2018), and in yam from Benin City, Nigeria (Bioseet *et al.*, 2020a). It is also higher than the 2.00 and 3.74 mg/kg mean Cu values respectively recorded in yam from Mangu, Plateau State, Nigeria (Haladu *et al.*, 2018), and yam from Koraput, India (Padhan *et al.*, 2018). Cassava recorded a Cr mean concentration of 8.58 ± 7.51 mg/kg. This was higher than the 0.06, and 1.69 ± 0.18 mg/kg mean Cr values respectively recorded for Cassava from Enyigba Mining Site in South Eastern Nigeria by Nworuet *et al.* (2018), and from cassava tubers planted along the east-west road of Rivers State, Nigeria (Ogah and Ekpete, 2021). Sweet Potatoes recorded a Cr mean concentration of 13.00 ± 7.58 mg/kg, which was higher than the 0.04 ± 0.03 and 0.07 ± 0.00 mg/kg mean Cr values respectively obtained in white and red sweet potatoes from Benin City, Nigeria (Bioseet *et al.*, 2020a). Similarly, the value was higher than the 0.19 ± 0.02 and 1.50 mg/kg obtained in sweet potatoes from Abeokuta, South-West Nigeria by Akinyele and Shokunbi, (2015a), and Mangu, Plateau State, Nigeria (Haladu *et al.*, 2018). Irish potatoes had a Cr mean concentration of

13.67±8.50 mg/kg. This was higher than the 0.05±0.02, 0.08, and 0.50 mg/kg mean Cr values respectively obtained in Irish potatoes from Benin City, Nigeria (Bioseet *et al.*, 2020a), from Yaoundé, Cameroon (Gimouet *et al.*, 2014), and from Mangu, Plateau State, Nigeria (Haladu *et al.*, 2018). In general, except for about 5 samples with moderately high Cr values, all the remaining 7 analysed composite tubers in this study, representing 58.3 % had too high Cr values over the acceptable 2.30 mg/kg Cr limits of FAO/WHO in foods (FAO/WHO, 2002). These high values of Cr are of concern since Cr at elevated concentrations (especially Cr (VI) is toxic and harmful to health (Egedigwe-Ekelemeet *et al.*, 2023).

Correlation Analyses:

The interdependent association between studied metals was measured using **Pearson's correlation** analysis. **Correlation coefficient** with positive and negative signs indicate positive and negative correlations respectively. The positive correlation indicates a direct relationship between the variables such that both variables increase or decrease together, while a negative correlation implies an inverse relationship between the variables such that as one increases the other decreases, and vice versa. A correlation coefficient value of 1 indicates a perfect correlation while zero (0) indicates no correlation or no relationship between the two variables (Salau *et al.*, 2020; Oral *et al.*, 2018; Salau, 2015; Karadas and Kara, 2012; Sola-Larrañaga and Navarro-Blasco, 2009).

Table 3 showed the correlation matrix / coefficient of the 6 elements in the studied tuber samples. High positive correlations are observed between Fe and Cr (0.975); and Mn and Co (0.818). Moderate positive correlations are observed for Zn/Co (0.516). Low (weak) positive correlations are observed for Fe/Cu (0.387), Cu/Cr (0.368), and Zn/Mn (0.307). A weak negative correlation was observed for Mn/Cu (-0.487), Mn/Fe (-0.416), Fe/Co (-0.392), Mn/Cr (-0.358), and Co/Cr (-0.313); and a negatively very weak correlation was observed for Cu/Co (-0.215); while very negligible weak negative correlations were observed for Zn/Cu (-0.079), and Zn/Fe (-0.004).

As for elements with positive correlations, it implies that if increasing the consumption of the food samples will favour the increase of one element, the second correlated element will as well be favourably gained along; similarly, a decrease in the element goes along with the decrease in the other correlated element. On the other hand, negatively correlated elements indicates that, as one element increases the other decreases, and vice versa. While those that tends toward zero (0) implies very little or no correlation. This information could help to know if consumption for certain desirable mineral element might carry along the undesirable element. It also helps in identifying the signature or characterization of the general profile of the samples, as elements with strong correlations in food quality control study, often represent the signature of the food samples (Salau *et al.*, 2020; Hassan *et al.*, 2019; Salau and Hasan, 2019; Salau and Hasan, 2018; Salau, 2015; Sola-Larrañaga and Navarro-Blasco, 2009). Except for Co and Cr, Zn has high positive correlation with all elements in the studied cereal and legume samples.

4. CONCLUSIONS

The results showed a wide variation in concentrations of the analysed trace metals in the samples with Co not being detected in 6 of the 12 analysed tuber samples. Across the 12 analysed tuber samples (from 3 North-central States), Fe (105.19±70.95 mg/kg) had the overall maximum mean concentration while Co had the lowest mean concentration (1.00±0.63 mg/kg), with the overall individual mean metal concentrations in the order: Fe > Zn > Mn > Cu > Cr > Co. The **Pearson's correlation** analysis showed

high positive correlations for Fe/Cr (0.975), and Mn/Co (0.818). Except for Cr with higher values above recommended standards, all the other analysed metals in the 12 composite tubers from the 3 North-central states (in this study) were below the acceptable limits of FAO/WHO in foods, suggesting the relative safety for the consumption of the studied tubers. However, the high Cr values are of concern since Cr at elevated concentrations (particularly Cr (VI) is toxic and harmful to health especially with prolonged consumption of the tubers.

Recommendations: The high Cr values may possibly be due to the local soil characteristics or contamination from atmospheric depositions and other farming practices where these tubers were grown, transported and sold (Biose et al., 2020a; Melnikov *et al.*, 2016). Hence, there is the need for further study to ascertain geochemical information of the soils where the tubers are grown; and government regulations on sanitary measures on how and where these tubers are transported and sold. There is also the need for adequate periodic monitoring and implementing of necessary measures to regulate and curb excessive intake of trace metals by consumers who take them as food.

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SN 16 THE NEED AND IMPACT OF STRUCTURAL MODIFICATION OF BIOCHAR FOR IMPROVED PROPERTIES: A MINI REVIEW

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Abstract

Structural modification of biochar involves stretching or splitting its layers in order to improve its surface area and reactivity. The mini review on the need and impact of biochar modification are considered in this study. Highlights on biochar applications and limitation were presented, along with various activation and exfoliation methods. Impacts of modified biochar in different applications are also elucidated. In conclusion, biochar modification is required in order to increase its surface area, reactivity, and functionality in a variety of applications. It can increase biochar's efficiency in fields like agriculture, environmental cleanup, and other areas where its special qualities are used to solve particular problems or produce better results.

1 Introduction

In the quest for a sustainable solution, biochar has emerged as a promising candidate. This carbon-rich substance represents a beacon of hope and a potent weapon in the ongoing battle against environmental degradation and the decline of our agricultural systems. Biochar's emergence as a game-changing tool underscores the scientific community's unwavering commitment to harnessing nature's wisdom to mend the wounds inflicted upon our planet. It stands as a testament to our capacity to adapt and innovate, offering a ray of optimism as we strive to forge a more sustainable and harmonious coexistence with the Earth. Biochar can be produced through various thermochemical conversion processes [1].

Biochar can be significantly enhanced through exfoliation or activation processes [2] to achieve a more enhanced carbon based material status. Carbon is an electronically conductive substance that has good stability, low density, and satisfactory corrosion resistance. In addition, applying oxidizing chemicals in thermal procedures, also known as activation, makes it easy to design and control the porosity and morphology of carbons [3]. Activated carbon is a variety of carbonized material with a high degree of porosity and large surfaces. The preparation of activated carbon can be achieved in two major ways: physical and chemical [4]. The physical activation method of preparing activated carbon is a two-step process involving the process of carbonization (pyrolysis) in a neutral atmosphere followed by activation in atmospheric oxidizing gases such as steam, carbon dioxide, carbon dioxide, and nitrogen, or air mixtures with rising temperature in the range of 800-1100 °C [5]. Chemical activation involves treating the material with chemicals, such as phosphoric acid or zinc chloride, to promote the formation of pores [6]. The combination of these two activation methods is also possible.

Also, thermal exfoliation and oxidation exfoliation method are essential processes in modifying the properties of biochar to enhance its performance in various applications. The thermal exfoliation of biochar

is an attractive method for creating nano-carbon due to its simplicity and efficiency [7]. Thermal exfoliation involves subjecting biochar to elevated temperatures in an inert or controlled atmosphere. Oxidation of biochar involves the introduction of oxygen or oxidative agents to the material. The different chemical processes that occur during the carbonization phase and the subsequent oxidation of the biochar could potentially change the original structure and chemical makeup of the final carbon-derived substance. The chemical makeup of the biomass precursors as well as the composition of the elements have a significant impact on the high yield of carbon from biochar, doping, and heteroatoms [8].

These methods aim to modify its physical and chemical properties, increasing its surface area and reactivity for various applications. Different routes and their effects on the properties and applications of the improved carbon based materials are elucidated in this review.

2 Thermochemical conversion processes

It is a great technique to recover energy and carbon by using biomass precursors to create biochar that has exceptional qualities. One of several methods for utilizing the energy content of these renewable and waste materials is through thermochemical processes [9]. Because it may be used to produce clean energy as well as renewable energy compounds. Thermochemical processing of biomass has drawn a lot of attention for mitigation reasons [10]. Thermochemical conversion processes play a pivotal role in the production of biochar, a carbon-rich material with diverse applications in agriculture, environmental remediation, and carbon sequestration. Various thermochemical conversion methods have been employed over the years to transform the original biomass into solid fuel. The thermochemical processes that can be employed for the production of biochar are pyrolysis [11], hydrothermal carbonization or wet carbonization[12], torrefaction or dry carbonization [13], and gasification [14]. Biochar can also be gotten from biomass via pyrolysis (slow pyrolysis, fast pyrolysis, gasification), torrefaction, or hydrothermal carbonization, depending on the designation [15].

The updraft top-lit retort gasification method of carbonization is a type of biochar production process that is commonly used (Figure 2.1).

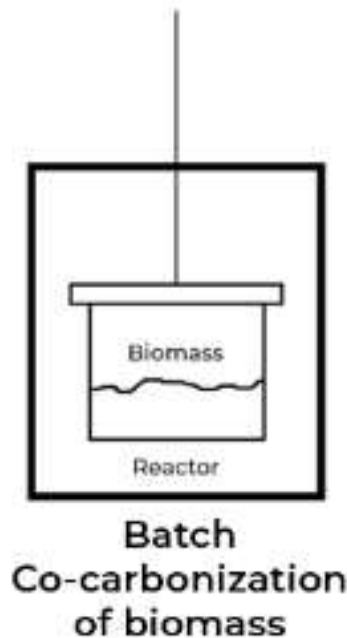


Figure 2.1 Carbonization chamber reactor

2.1 Properties and uses of biochar

Biochar is an available porous carbonaceous substance created when biomass feedstock undergoes thermochemical degradation in the absence or presence of oxygen [16]. Biochar is a form of charcoal created by heating organic matter in a low-oxygen environment. When produced from sustainable and renewable sources, such as agricultural and forestry waste, biochar has the potential to store carbon in a stable form for hundreds or even thousands of years. The process of making biochar involves heating biomass at high temperatures (between 300 and 600 °C) in a closed reactor with little to no air. In these circumstances, biomass is thermochemically transformed into biochar[17]. The major elemental composition in biochar is carbon, oxygen, nitrogen, and a non-combustible inorganic substance known as ash [18]. The feedstock used can affect the properties of the resulting biochar. For example, biochar made from wood chips tends to have high carbon content and relatively low ash content, while biochar made from sewage sludge may contain higher levels of heavy metals.

In general, biochar has several desirable properties that make it useful for a variety of applications. Figure 2.2 provides a diagrammatic representation of the diverse uses and applications of biochar, highlighting its versatility and potential contributions to various fields. The several desirable properties of biochar include:

- High surface area: Biochar's high surface area, a key feature illustrated in Figure 2.2, allows it to adsorb and retain substantial quantities of water and nutrients, making it a valuable soil amendment.
- Porosity: Biochar's remarkable porosity, as visually depicted in the figure 2.1, provides an ideal habitat for beneficial soil microbes. This symbiotic relationship between biochar and soil microorganisms contributes to improved soil health and nutrient cycling.
- Stability: Biochar is resistant to decomposition and can persist in the soil for hundreds or even thousands of years.

- Carbon sequestration: Biochar can sequester carbon, which can help to mitigate climate change.
- Heavy metal adsorption: Biochar can adsorb heavy metals, which can help to remediate contaminated soils.
- Water filtration: Biochar can be used as a filter medium to remove impurities from water.
- Energy production: Biochar can be used as a fuel for energy production, either through direct combustion or gasification.

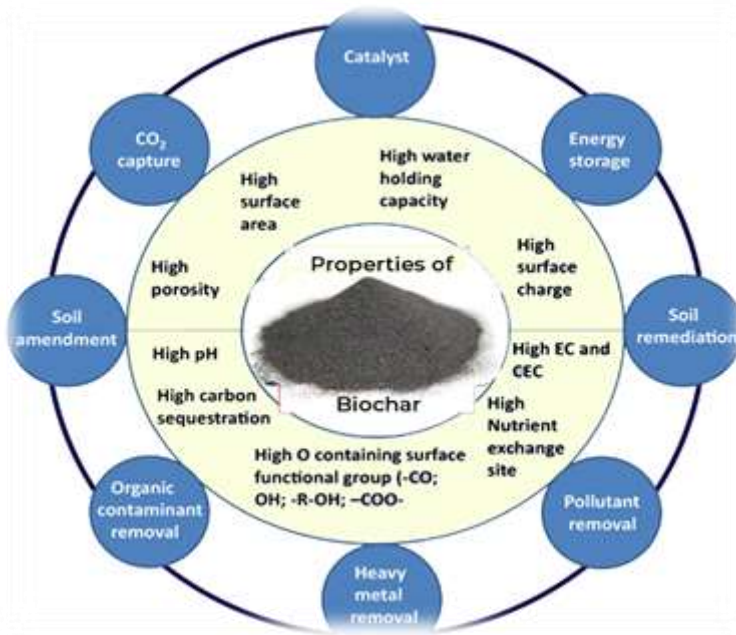


Figure 2.2 Uses and various applications of biochar

Figure 2.2 serves as a visual representation of the multifaceted applications of biochar, reinforcing the importance of its properties in various domains, as discussed earlier in this study.

The exceptional qualities of biochar make it widely applicable in a lot of areas. Biochar is also used strategically for the capture and sequestration of CO₂ [19]. It can also be used in soil for remediation [20], animal feeding [21], the treatment of wastewater [16], and many more. Biomass made from agricultural waste has become more popular as a precursor material for carbon-based energy storage systems, due to its availability and low cost. As an alternative to conventional carbon electrodes, biomass-derived carbon is a viable contender for energy storage applications due to its large specific surface area and strong electrical conductivity [22]. Numerous uses for biochar exist, including the production of energy, agriculture, carbon sequestration, wastewater treatment, and bio-refinery [17].

Notwithstanding, biochar exfoliation is required in order to increase its surface area, reactivity, and functionality in a variety of applications. Activation and exfoliation approaches have great effects on biochar structure modifications. They are known to increase biochar's efficiency in fields like agriculture, environmental cleanup, and others where its special qualities are used to solve particular problems or produce better results.

3 **Activation of Carbon**

The activation of carbon represents a transformative process that plays a pivotal role in enhancing the properties and versatility of carbonaceous materials. Carbon activation is instrumental in augmenting the surface area, porosity, and reactivity of carbon, thereby making it a versatile and valuable material for an extensive array of applications [23]. Carbon, in its various forms, is an elemental building block of life and a ubiquitous material in our environment. From natural sources like wood and coal to engineered structures such as activated carbon, carbon materials serve as the backbone for numerous industrial, scientific, and environmental applications. However, it is the process of activation that unlocks the hidden potential within these carbon materials [24], transforming them into highly effective tools for addressing diverse challenges.

At the heart of carbon activation lies the remarkable ability to substantially increase the material's surface area and porosity. This transformation occurs through a controlled alteration of the carbon structure. The result is a porous framework characterized by an extensive surface area that far surpasses the original carbon material [25]. This augmented surface area is riddled with intricate pores and voids, creating an expansive platform for chemical interactions, adsorption, and storage. The enhanced surface area, porosity, and reactivity of activated carbon make it a versatile workhorse across multiple domains. One of the foremost applications of activated carbon is in the field of adsorption, where it excels at capturing and removing various molecules and contaminants from gases, liquids, and solutions. Whether it's purifying drinking water, eliminating volatile organic compounds in industrial processes, or adsorbing pollutants in air and wastewater, activated carbon stands as a stalwart ally in environmental remediation [26].

Furthermore, activated carbon's capacity for energy storage is paramount in the context of the global energy challenge [27]. Activated carbon is a crucial component in energy storage devices like supercapacitors and batteries[28]. Its high surface area and electrical conductivity enable the efficient storage and release of energy, making it essential in the quest for sustainable and high-performance energy storage solutions.

3.1 *Oxidation method of Activation*

The oxidation method of carbon activation involves the controlled reaction of carbonaceous materials with oxidizing agents, such as nitric acid (HNO_3) or potassium permanganate (KMnO_4), leading to the introduction of oxygen-containing functional groups and the creation of a highly porous structure. This process enhances the carbon's surface area and adsorption capacity, rendering it effective in the removal of contaminants from various media, including air and water.

Numerous studies have explored the oxidation method as an effective means of activating carbon materials. For instance, Gupta and Nandi (2022) investigated the activation of coconut shell carbon using nitric acid and reported a substantial increase in its surface area and porosity [29]. The introduction of oxygen groups, such as carboxyl ($-\text{COOH}$) and hydroxyl ($-\text{OH}$) moieties, enhanced its adsorption capacity for organic compounds. As the oxidizing agent interacts with the carbonaceous material, it breaks down carbon bonds and replaces them with oxygen-based groups. This chemical transformation is akin to giving the carbon a set of chemical handles, which vastly increase its reactivity and interactions with other molecules.

Simultaneously, the oxidation process drives the creation of a highly porous structure within the carbon material. These pores and voids, intricately carved into the carbon's framework, amplify its surface area manifold. This augmented surface area is a key characteristic that sets activated carbon apart. It provides an expansive playground for chemical interactions, making it exceptionally effective in capturing, immobilizing, and removing a diverse array of molecules and contaminants from different environments.

Moreover, the oxidation method has found notable application in the field of water and wastewater treatment. Activated carbon produced through this method has been widely employed for the removal of pollutants, such as heavy metals, dyes, and organic contaminants, from aqueous solutions (Yang et al., 2019; Xiong et al., 2021). Additionally, its modified surface chemistry makes it suitable for catalytic applications, such as the degradation of organic pollutants (Molina-Sabio and Rodríguez-Reinoso, 2016).

The utility of activated carbon produced through the oxidation method is multifaceted. One of its most prominent applications is in environmental remediation. In the realm of air and water purification, activated carbon stands as an indomitable force against a wide spectrum of contaminants. It readily adsorbs volatile organic compounds (VOCs), noxious odors, heavy metals, and organic pollutants from air and water sources, leaving them purified and safe for consumption or discharge.

3.2 Thermal Exfoliation method of Activation

The thermal exfoliation method of carbon activation represents a fascinating and highly innovative approach to enhancing the properties of carbonaceous materials. In this process, carbonaceous substances are carefully exposed to elevated temperatures within an inert or meticulously controlled atmosphere. This controlled thermal treatment serves as the crucible in which the carbon's transformation unfolds, leading to remarkable changes that have far-reaching implications in various scientific and industrial domains [30]. At the heart of the thermal exfoliation method lies the controlled application of heat to carbonaceous materials. This precise heating process is executed within an inert environment or under strict control, creating an environment that encourages the carbon structure to expand and exfoliate. This controlled expansion causes the layers of carbon to peel away from each other, resulting in the creation of an intricate and highly porous network. The hallmark of the thermal exfoliation method is the remarkable enhancement of surface area and porosity within the carbon material. This unique structural modification translates into an expansive surface area that is punctuated by a labyrinthine network of pores and voids. The increase in surface area and porosity is of paramount importance, as it amplifies the carbon's capacity for interactions with other molecules, adsorption of contaminants, and storage of energy.

Studies exploring the thermal exfoliation method have unveiled its vast potential for generating nano-carbon materials with exceptional properties. For instance, in the realm of graphene production, Zhang et al. (2017) embarked on the thermal exfoliation of graphite oxide, heralding the formation of graphene nanosheets. These graphene nanosheets possess an expansive surface area, rendering them eminently suitable for a range of cutting-edge applications. From supercapacitors that store energy efficiently to gas storage materials that can revolutionize clean energy solutions, the impact of thermal exfoliation on carbon materials cannot be overstated. In the context of biochar, thermal exfoliation has emerged as a focal point of exploration, offering promising prospects for enhancing the material's properties. Exfoliated biochar, because of this process, exhibits an astonishing improvement in its adsorption capacity. This property renders exfoliated biochar exceptionally effective in critical domains such as soil improvement, pollutant remediation, and renewable energy production.

Recent studies by Saikia, Benoy [8] and Qian et al. (2018) have accentuated the potential of exfoliated biochar in the realm of agriculture and environmental management. Its heightened adsorption capacity equips it with the power to rejuvenate soil health by efficiently retaining essential nutrients and mitigating soil degradation. Moreover, exfoliated biochar acts as a stalwart guardian against environmental pollutants, offering a sustainable solution for the removal of contaminants from soil and water. Additionally, its

newfound properties make it a candidate for renewable energy production, aligning with global initiatives to harness sustainable resources for clean energy generation.

4 Impacts: Applications of Exfoliated/Activated Carbons

The activation and exfoliation of carbon materials through oxidation and thermal processes have paved the way for the creation of novel carbonaceous materials with a wide range of applications.

Environmental Remediation

One of the most prominent applications of exfoliated/activated carbons is in environmental remediation. These materials excel in capturing and immobilizing contaminants from air, water, and soil. The introduction of oxygen-containing functional groups during the oxidation process enhances their adsorption capacity. Activated carbons obtained via thermal exfoliation, with their increased surface area and porosity, exhibit remarkable adsorption properties. They are utilized to remove a wide range of pollutants, including heavy metals, organic compounds, and volatile organic compounds (VOCs). These applications extend to air and water purification, soil remediation, and the treatment of industrial effluents [31].

Energy Storage

Exfoliated/activated carbons play a pivotal role in energy storage solutions. In the realm of supercapacitors, their high specific surface area and electrical conductivity make them exceptional candidates for electrode materials. The thermal exfoliation method, in particular, has led to the creation of graphene-based carbons with extraordinary capacitive properties. These materials enable the development of high-performance supercapacitors with rapid charge-discharge rates and long cycle lifespans. Additionally, activated carbons derived from oxidation processes have found application in lithium-sulfur batteries, where they enhance the overall performance and stability of the energy storage devices (Chen et al., 2019; Wang et al., 2020).

Catalysis

Exfoliated/activated carbons serve as effective catalyst supports in various catalytic reactions. The functional groups introduced through oxidation impart catalytic activity to these materials. They are employed in diverse catalytic processes, including the synthesis of chemicals, degradation of pollutants, and conversion of biomass into valuable products. Furthermore, carbons obtained via thermal exfoliation, such as graphene nanosheets, exhibit excellent catalytic properties due to their high surface area and structural integrity. They find application in the fields of heterogeneous catalysis, photocatalysis, and electrocatalysis (Wang et al., 2017; Li et al., 2021).

Gas Separation and Storage

Exfoliated/activated carbons are invaluable in gas separation and storage applications. Their tunable porosity and adsorption properties enable efficient capture and storage of gases, including hydrogen, methane, and carbon dioxide. These materials are integral in carbon capture and storage (CCS) technologies, where they mitigate greenhouse gas emissions. Additionally, activated carbons obtained through thermal exfoliation are utilized in gas adsorption systems, such as natural gas storage, hydrogen storage for fuel cells, and gas purification processes (Feng et al., 2020; Kim et al., 2019).

Agriculture and Soil Improvement

In the realm of agriculture, exfoliated/activated carbons derived from biomass sources offer sustainable solutions. Exfoliated biochar, with its increased adsorption capacity and enhanced nutrient retention, serves as an effective soil amendment. It improves soil fertility, water retention, and the availability of essential

nutrients to plants. These materials also aid in carbon sequestration, mitigating the impacts of climate change. The thermal exfoliation method enhances the effectiveness of biochar in soil improvement, making it a valuable resource in sustainable agriculture (Saikia et al., 2020; Novak et al., 2016).

Conclusion

In conclusion, biochar exfoliation or any other structural modification is required in order to increase its surface area, reactivity, and functionality in a variety of applications. Exfoliation can increase biochar's efficiency in fields like agriculture, environmental cleanup, and others where its special qualities are used to solve particular problems or produce better results. The individual application and desired features determine the method of structural upgrade to use. The adsorption capability, nutrient retention, and overall efficiency of biochar in achieving soil health, environmental remediation, and carbon sequestration objectives can all be improved through structural alteration.

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SN 17 PLANTAIN FIBRE REINFORCED POLYSTYRENE COMPOSITE: A MINI REVIEW

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Abstract

The need for sustainable combination of agricultural and plastic wastes in composite development has been recently explored. This mini review explored the fibre extraction and solvation-to-resin methods involved in the valorisation of plantain fibre and polystyrene waste for composite development, respectively. Effects of fibre treatment, content and fibre length on microstructural, thermal and mechanical properties of fibrillated polystyrene composite were elucidated. The need for improved cross composites are versatile and environmentally benign, but careful processing and consideration of their inherent material properties are required for successful development linking effects between fibre and solvated polystyrene could be improved by introduction of co-filler particulates. In conclusion fibrillated polystyrene composites are versatile and environmentally benign, but careful processing and consideration of their inherent material properties are required for successful development.

1 Introduction

The alarming rate at which waste materials are improperly disposed has been of great concern globally. Major categories of these contaminants are agricultural, industrial, and commercial wastes[1]. Continuous accumulation of these waste materials cause significant and sometimes, lasting damage to the environment as well as to living organisms. It is estimated that as many as 9-23 million tonnes of packaging plastics globally used end up as pollutants in the ocean [2]. The presence and accumulation of polystyrene, a micro plastic commonly used in packaging and manufacturing of household items is known to be harmful to the health of living things and also to the environment.

Plantain stalk, an agricultural waste though majorly biodegradable can constitute nuisance to the environment especially when improperly disposed. Therefore, the need arises for the use of these waste materials for other impactful and environmental-friendly purposes. In the continued struggle of getting rid of non-biodegradable waste materials, whose accumulation in the environment pose serious threats and hazards to life, different methods and approaches have been developed and used[3]. One of the widely adopted methods in existence to offset and contain these threats is reusing and recycling these so called waste materials into other useful products.

Engineered composites are materials that are made by fusing two or more different materials, each of which has a variety of distinct features to produce a new material with improved characteristics. Engineered materials possess laudable properties such as strength, stiffness, toughness, durability, resistance to heat, chemicals and other environmental factors as a result of the combination of different compatible materials[4]. The high cost and adverse environmental effects of extracting and mining conventional materials such as steel and aluminium, coupled with their high density has favoured the development and adoption of light and low cost materials like engineered composites, especially for large-scale applications where weight reduction is important such as in aerospace, automotive and sports equipment[5]. Composites are also perfect for complex designs that call for unique material attributes, since they may be manufactured to have precise characteristics and shapes.

In an attempt to also improve the mechanical properties of polystyrene for use as sound-proof, dampening and insulating materials, the usage of plantain fibre has been employed as fillers in the development of a polystyrene composite by the incorporation of these waste materials[6]. This mini review therefore focuses on the recent development in the solvated polystyrene based approach of valorising polystyrene waste as the matrix in the development of an economical, mechanically-sound and environmental-friendly plantain fibre reinforced polystyrene composite.

2 Fibre Extraction from Plantain Waste

A natural fibre obtained from the pseudo stems, stalks, or leaves of the plantain plant (*Musa paradisiaca* or *Musa sapientum*). These plants are cultivated mostly for their fruits, but their fibres can also be used for a number of different applications[3, 7].

Any of the existent retting processes such as biological retting [8] and mechanical retting [6, 9, 10] may be used in the extraction of fibres from the pseudo-stem of plantain. The fibre extracted from the pseudo-stem of plantain is a bast lignocellulosic fibre, containing lignin, hemicellulose and cellulose in different proportions. Other compounds present such as wax, minerals, pectin and some water soluble compounds binds the fibres together into a bundle which upon retting are decomposed, easing the extraction of the fibres [8]. Some methods that have been used by various researchers in extracting the fibre include biological/water retting process [11-13], mechanical retting [9, 10], among others. Due to certain drawbacks of the extracted plantain fibre in its natural state, it is most often modified before it is used. As observed by [11], treated plantain fibre possessed better strength compared to the untreated fibre. Common methods that have been employed in modifying and enhancing the properties of plantain fibre are alkaline treatment [8] and saline and alkaline treatment combined [10, 11]. The elemental analysis of the extracted plantain fibre is given in Table 1, with elements Indium, Pottasium and Silicon found above 10%. Although below 10% in percentage distribution, elements like Calcium, Aluminium and Chlorine are also found in significant proportion

Table 2.1 Characterization of plantain fibre (Adeniyi, Onifade et al. 2020)

Element	Symbol	Percentage (%)	Composition
Indium	In	35.01	

Potassium	K	25.05
Silicon	Si	13.87
Calcium	Ca	7.76
Aluminium	Al	4.00
Chlorine	Cl	3.74
Sulphur	S	2.06
Iron	Fe	1.04
Titanium	Ti	0.19
Copper	Cu	0.18
Manganese	Mn	0.09
Arsenic	As	0.009
Lead	Pb	0.008
Barium	Ba	0.004

3 Polystyrene

Polystyrene (PS) is a micro plastic made up of styrene monomers obtained from petrochemicals. It is made up of long hydrocarbon chains with phenyl groups linked to alternating carbon atoms [14]. It is a widely used plastic known for its hardness, heat resistance, light weight, strength, durability and low cost. Polystyrene is transparent but can be coloured by introducing colourants. The aforementioned properties are responsible for this polymer's wide area of application, which includes its use as a packaging material and in household items [14].

Polystyrene is usually available in two usable and recyclable forms: solid and expanded form. The expanded polystyrene foam however loses its foam characteristics after recycling. Currently, majority of the polystyrene waste generated is disposed to landfills which is a great threat to the environment and living organisms as well [14].

3.1 Recycling of waste polystyrene through solvation

In an effort to curb the detrimental impacts of waste polystyrene on the environment, the expanded and solid polystyrene wastes have been recycled to extruded plastic lumber which has in turn been used in window construction and flooring of buildings [14]. Expanded polystyrene has also been used as a substrate in the production of poly-electrolytes with good flocculating properties [15]. It is also being used in development of materials with considerable strength and structural properties use in construction and furniture. [16] investigated the use of expanded polystyrene as a component of the aggregates in concrete manufacturing.

As reported by various authors, polystyrene based composites can be produced through techniques such as melt blending, solution blending and in-situ polymerization[4, 17, 18]. Manual mixing and hand lay-up method includes preparation of polystyrene based resin by solvating in a suitable solvent, mixing a specified concentration of filler with the resin, moulding and curing. Popular solvents known for their ability to

dissolve expanded polystyrene are chloroform, dichloromethane and other petroleum-based solvents[19]. The choice of a solvent for dissolving polystyrene will rely on a number of variables, including the intended application and the characteristics of the polystyrene being employed. It is crucial to take into account both the solvent's safety and impact on the environment. Moulded composite can be cured either at room temperature or thermally at higher temperatures. Thermal curing is mostly preferred as it involves shorter curing time and serves as a more efficient means of curing composites.

4 Plantain Fibre-reinforced Polystyrene-Based Composites

A special kind of composite material called plantain fiber-reinforced polystyrene composite uses plantain fibres as a reinforcing agent within a polystyrene matrix (Figure 4.1. In order to generate a material with distinct features and prospective applications, this composite blends the qualities of polystyrene and plantain fibres[20-22]. The pseudostems or leaves of the plantain plant are where plantain fibres are generated. For reinforcement in composite materials, these natural fibres are frequently employed as a sustainable and environmentally beneficial substitute for synthetic fibres [21, 23].

Due to its lightweight and insulating qualities, polystyrene is a thermoplastic polymer that is frequently utilised in a variety of sectors. The matrix substance holding the plantain fibres together in this composite is polystyrene. The plantain fibres are impregnated with polystyrene resin during the production process, and then the resin is cured or solidified. Depending on the intended use, common processing methods include compression moulding, extrusion, and injection moulding[24]. Composites made of plantain fibre and reinforced polystyrene can combine the qualities of the two materials. The polystyrene matrix contributes to the composite's lightweight and heat insulating qualities, while the natural fibres can improve its strength, stiffness, and impact resistance[25].

Many studies have been conducted on fibre-reinforced polystyrene composites over the years. In a recent usage of solvated polystyrene resin as the matrix, Adeniyi, Onifade [26] showed that plantain fibres and solvated polystyrene resin can be used to create composite materials. Plantain Fibre Polystyrene Composites were made utilising the hand lay-up method., Three levels of fibre content (five weight percent, ten weight percent, and fifteen weight percent), and three levels of fibre length (two millimetres, four millimetres, and six millimetres) were employed. The composite sample with a 4 mm fibre length, 10% fibre content, and 0% treatment concentration had the highest tensile strength of 401.84 MPa, according to the results of the tensile examination of the composites. The SEM study and FTIR data also demonstrated improved adhesion between the matrix and the untreated fibre in comparison to the treated fibre. Also, Onifade, Ighalo [27], developed fibrillated polystyrene composites using biochar made from plantain stalk fibre as the filler. Differential Scanning Calorimetry (DSC) and Fourier Transform Infra-Red Spectroscopy (FTIR) were used to assess the composites' thermal and functional characteristics, respectively. Estimated heat capacities of the composites from the thermal test findings also demonstrated that a percentage range of biochar should be kept at 10–30% to provide a composite with a heat capacity range between 2000–4000 J/kg.K. Additionally, the thermal characteristics of the composite are improved by the addition of thermally stable biochar.

In a similar development, four sets of polystyrene/plantain fibre composites were made, and they were tested for their tensile properties (Young's modulus and elongation at peak), impact, and water absorption behaviours in accordance with ASTM standards[28]. It was found that the composites' young modulus, impact strength, and percentage water absorption increased while their elongation at peak decreased as

plantain fibre content increased. These findings suggest that additional modifications must be made in order to produce a composite with strong interfacial adhesion as well as high tensile strength. Future research is also required in order to determine the activities of solvated polystyrene over untreated fibre during composite curing.

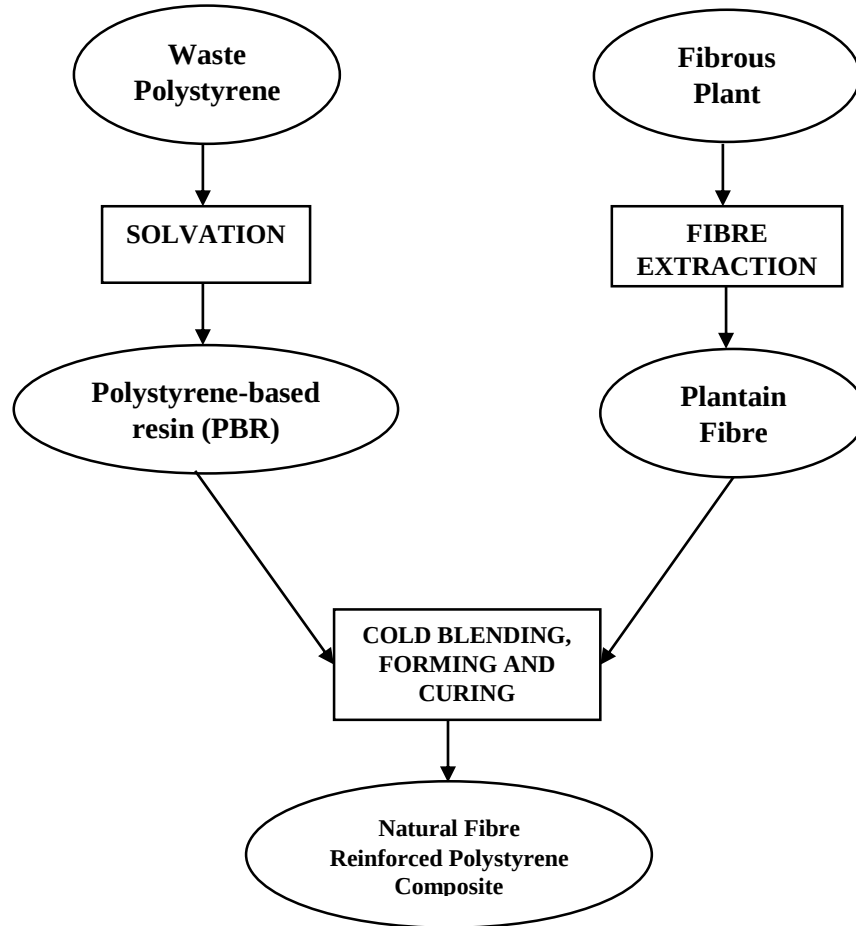


Figure 4.1 Development of natural fibre reinforced polystyrene composite development. Adapted from (Adeniyi, Abdulkareem et al. 2021)

5.1 Applications and Environmental Benefits

These composites can be used in a variety of sectors, including packaging, transportation, and construction. For instance, they can be utilised to produce strong, lightweight car interior parts, as well as packaging materials with enhanced mechanical performance. Utilising plantain fibres instead of synthetic fibres made from non-renewable resources helps to enhance sustainability. The successful conversion of solid polystyrene into solvated polystyrene for use in composite manufacturing is a step towards reducing the environmental issue brought on by waste polystyrene's inability to biodegrade. Polystyrene composites can also be recycled, which lessens their impact on the environment even further.

6 Challenges and Conclusions

Consistent fibre dispersion and adherence inside the solvated polystyrene matrix has been identified as a major limitation in the development of fibrillated polystyrene composite [28]. It is an important factor to take into account while developing composites include attaining uniform mechanical characteristics and resolving potential problems like moisture absorption and deterioration over time. Hence the need for the introduction of suitable cofillers as crosslinker.

Briefly stated, plantain fiber-reinforced polystyrene composites are a type of composite material that combines the lightweight and insulating qualities of polystyrene with the natural reinforcing properties of plantain fibres. These composites have a variety of possible uses and are environmentally friendly, but they need to be processed carefully and their material qualities must be taken into account for their development to be effective.

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**SN 18 PREPARATION AND IN VITRO PHASE CHARACTERIZATION OF BAG – S53P4
GLASS-CERAMICS USING MICROWAVE ENERGY IRRADIATION APPROACH**

Seun S. Owwoye*, Esther O. Isinkaye, Ayobami O. Ayorinde, Erica I. Jubril

ABSTRACT

In this work, S53P4 bioglass (BG) and bioglass-ceramics (BGCs) were prepared by melt-quenching followed by sintering approach using microwave assisted energy irradiation. The batch material composed of 53% SiO₂, 23% Na₂O, and 20% CaO and 4% P₂O₅ (all in weight percent) was mixed thoroughly and charged inside alumina crucible. The crucible was then placed inside microwave kiln box and put inside microwave oven for melting. The oven was powered and timer set. The melt required 40 minutes for completed melting at a temperature of about 1300°C when read with thermocouple. The melt was then quenched rapidly in water to produce BG frits. The obtained BG frits were later powdered using pulverizer and pelletized by addition of binder (1% PVA solution) followed by sintering at temperature 800 – 1050°C to obtain BGCs. The samples were then immersed in biological fluids (Na-PBS and Tris-HCl) for 6 hours to determine their in-vitro bioactivity and hydroxyapatite (HAP) formation and afterward characterized. The hardness result showed significant improvement as temperature increase while the bulk density increase with decrease in porosity for the BGCs. All the samples showed good HAP formation in the biological fluids as indicated by the XRD after immersion in biological fluids. However, BG showed better HAP peaks compared with BGCs. The results showed sintering temperature have good impact on the BGCs tested properties while not impairing their in-vitro bioactivity.

Keywords: S53P4 bioglass; in vitro bioactivity; phase analysis; melt-quenching; microwave.

1. Introduction

As of today, several artificial biomaterials targeted for bone regeneration and repair have been developed. These artificial biomaterials include calcium orthophosphate, bioactive glasses and glass-ceramics, human demineralized bone matrix, variety of polymers and composites among others [1].

Among these biomaterials, bioglasses and glass-ceramics are materials of interest and well investigated considering their excellent biocompatibility and bone bonding ability [2]. Bioglasses are amorphous silicates based materials which are biologically compatible, bond to bone and stimulate new bone growth whilst dissolving overtime. They possess the ability to restore diseased or damaged bone to its original state and function. Since its first discovery in the late 1969 by Hench et al. [3], several bioglasses have now been developed [4] among which S53P4 is prominent for its good bioactivity, osteointegration and antimicrobial properties [5].

BAG – S53P4 has been widely used for several clinical applications like chronic osteomyelitis therapy, filling of bone cavity and cranio-maxillofacial surgery among others [6, 7].

Despite their excellent bioactivity and biocompatibility, bioactive glasses are limited to very low load-bearing applications due to their poor mechanical properties resulting from their brittleness, and low fracture toughness [8]. As a result, bioactive glass-ceramics (BGCs) containing precipitation of various crystalline phases was developed with good combination of improved mechanical strength and bioactivity [9]. The two major methods that have been practised to produce bioglasses are traditional melting approach using furnace [10] and sol-gel method [11].

Recently, the search for low-cost synthesis route ushers in the era of microwave assisted synthesis with advantage of achieving glass preparation in few minutes and also modify the reaction environment to obtain

nano-phase powders [12]. In this regard, the present work aimed to develop S53P4 BGCs by microwave energy irradiation melt-quenching followed by sintering approach.

2. Materials and method

2.1. Materials

The starting materials used in this work are pure silica (SiO_2 , 99% purity), anhydrous sodium carbonate (Na_2CO_3 , 99.8% purity), calcium carbonate (CaCO_3 , 99.8%), ammonium di-hydrogen orthophosphate ($\text{NH}_4\text{H}_2\text{PO}_4$, 99.9 % purity) as precursor for P_2O_5 , and Polyvinyl Alcohol (1% PVA solution) as binder. These materials are of pure chemical grade and used in their as-received state.

2.2. Glass melting

A 100 g batch material were composed comprising of 53 SiO_2 – 23 Na_2O – 20 CaO – 4 P_2O_5 (wt. %) and accurately weighed by electronic digital weighing balance (± 0.01 accuracy). The weighed materials were thoroughly mixed to avoid batch inhomogeneity. The mixed batch was then poured inside alumina crucible prior to melting. The crucible containing the batch material was then enclosed inside a microwave kiln and placed inside microwave oven (Model: P90N30EP-ZK, 900W microwave power, 2.45GHz frequency) for melting. The complete melting of the batch was achieved at 40 minutes timer of the microwave oven corresponding to temperature of 1300°C measured by K-type thermocouple. The homogeneous bioglass melt was then quenched rapidly in water to avoid crystallization and obtained bioglass frits, then dried. Figures 1 (a – d) showed the preparation procedure by microwave oven.



(a)



(b)



(c)



(d)

Figure 1. (a) Heating and melting inside microwave oven (b) removal of the crucible containing melt from the microwave kiln (c) quenching in water (d) bioglass frits

2.3. Production of S53P4 BGCs by microwave sintering

In the preparation of the S53P4 BGCs, the bioglass frits initially obtained were pulverized to obtain fine powder. The powdered frits are then compacted into cylindrical shaped pellets (50 x 10 mm) with addition of binder (1% PVA solution) and sintered using microwave energy irradiation in a microwave kiln enclosed inside microwave oven at temperature of 800, 900, 950 and 1050oC respectively. The sintered bioglass-ceramics were then left to cool to room temperature inside the microwave kiln. Figure 2 showed the sintered bioglass-ceramics.



Figure 2. Sintered S53P4 glass-ceramics

2.4. In vitro bioactivity

In this work, two different biological fluids namely: Tris buffer solution and sodium phosphate buffer solution (Na-PBS) were used respectively to assess the in vitro bioactivity of the prepared BAG-S53P4 and their glass-ceramics counterparts. 1M Tris buffer solution was prepared by adding Tris (hydroxymethyl) aminomethane/HCl to de-ionized water while Na-PBS was prepared by dissolving sodium chloride, monosodium phosphate and disodium phosphate into de-ionized water. The ion concentrations of the Tris

buffer and Na-PBS as compared with blood plasma are shown in Table 1. The samples were then immersed in a clean plastic beaker containing the biological fluids (Tri-HCl and Na-PBS) and placed inside water bath at 37°C and pH 7.4 for 6 hours. After the period, respective sample was evacuated and dropped inside acetone for 5 seconds to stop the surface mineralization followed by drying in a desiccator. The samples were afterward analysed by X-ray diffraction to assess its bioactivity by assessment of CHA/HA (carbonate-hydroxyapatite) phase deposited.

Table 1. Ion concentration (mM/ Litre) of Na-PBS, Tris-HCl and human blood plasma

Ion	Na ⁺	K ⁺	Mg ⁺	Ca ⁺	HCO ₃ ⁻	HPO ₄ ²⁻	SO ₄ ²⁻	Cl ⁻	H ₂ PO ₄ ⁻
Na-PBS	156.2	-	-	-	-	24.9	-	100.9	5.5
TRIS	-	-	-	-	-	-	-	45	-
Human Blood Plasma	140.0	5.0	1.5	2.5	27.0	1.0	0.5	103.0	-

2.5. Characterization

X-ray diffractometer (Rigaku miniflex 600, Japan) was used to investigate the crystalline phases before and after sintering. Also, to assess evolution of the hydroxyapatite layer respectively after in-vitro test. The bulk density and porosity of the samples were also evaluated following standard procedures while the hardness of the samples were investigated using Vicker's micro-hardness tester.

3. Results and Discussion

3.1. Physical properties

Figure 3 represents the bulk density and the porosity of the S53P4 BG and BGCs respectively. In term of bulk density, the density of the S53P4 (control) is 2.6 g/cm³ which is close to the theoretical density of bioglass (2.7 g/cm³) in literature. Density of 1.49 g/cm³ is obtained for S53P4/800 sintered at 800°C which might be due to porosity initiated as the binder is removed during sintering leaving behind pores. However, the density increase as the sintering temperature increase. It is also observed that porosity decrease as the sintering temperature increase for the glass-ceramics samples. The increase in density might be attributed to densification resulting from increase in vitreous portion by viscous flow at elevated temperature. The level of porosity also decrease across the S53P4 BGCs as the temperature increase which might be due to sealing of pores from the viscous flow. The precipitation of crystals in the glass enhanced the overall density of the S53P4 BGC samples especially for S53P4/1050 sintered at temperature of 1050°C which showed better density than other BGC samples. This similar trend has been reported by previous works [9, 13].

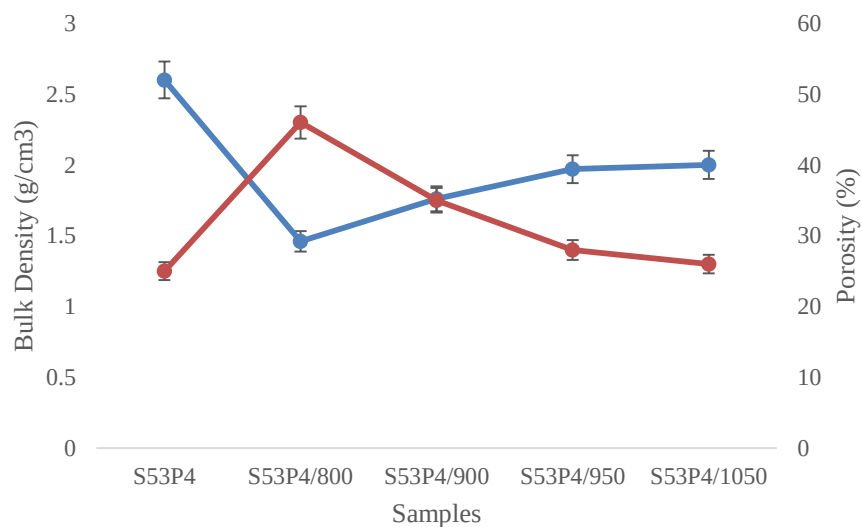


Figure 3. Density and Porosity

3.2. Mechanical property (Hardness)

Figure 4 shows the result of the Vickers hardness (HV) compared with its micro-hardness (GPa) value. The result showed that hardness increase with increase in sintering temperature for the S53P4 BGCs. This improvement in hardness observed for S53P4 BGCs might be attributed to increase in densification and decline in porosity of the samples resulting increased viscous flow at elevated temperature. The improvement of hardness for S53P4 BGCs over the S53P4 bioglass (Control) might be due to precipitation of crystals from the glass during sintering. Similar results have been reported by previous works [9, 14 – 15].

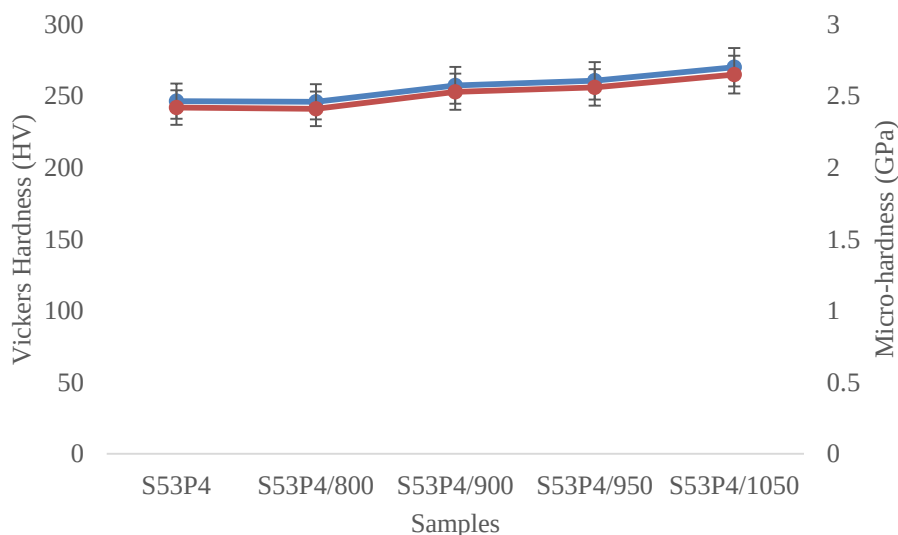


Figure 4. Micro-hardness

3.3. Degradability (weight loss) in biological fluids

Figure 5 represents the result of the weight loss of the bioglass and glass-ceramic samples after immersion in Na-PBS and Tris-HCl respectively for 6 h. It is observed from the results that S53P4 BG showed high weight loss in both Na-PBS and Tris-HCl which might attributed to high release of ions such as Ca, Si, P

and Na from the glass into the solutions [16]. For glass-ceramics version, the degradability (weight loss) is not as high compared to S53P4 BG. The glass-ceramic samples showed minimal weight loss in Na-PBS while their weight loss in Tris-HCl is higher with the exception of S53P4/900 though not pronounced. The small changes in weight loss observed for in Na-PBS might be due to an equal amount of elements dissolving from the glass-ceramics and HAP (hydroxyapatite) forming on the surface [17]. Previous work also reported similar trend in Tris-HCl [17]. Resistance to degradation can be improved through crystallization to obtain glass-ceramics as observed in this work and has previously reported [18].

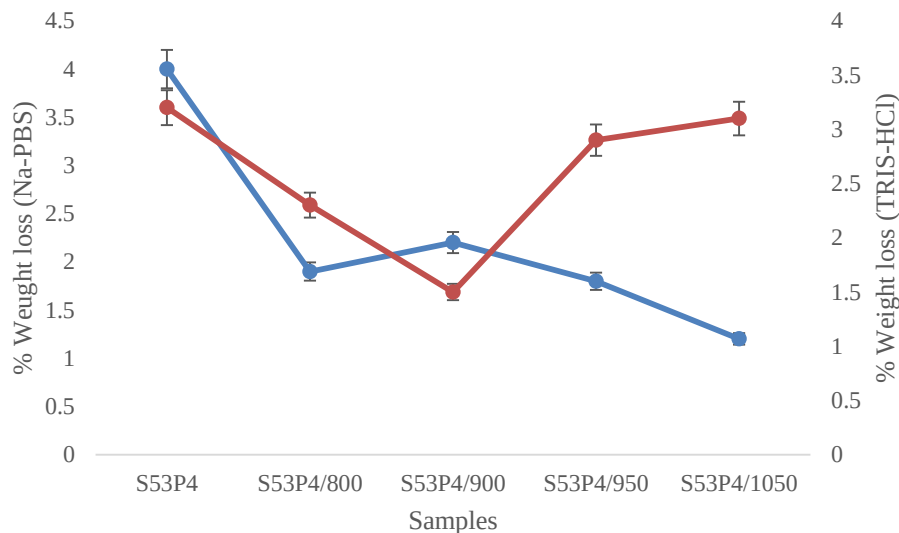


Figure 5. Weight loss of the samples in biological fluids

3.4. pH of the immersion solutions

The result of the pH of the Na-PBS and Tris-HCl buffered solutions after immersion of the bioglass and glass-ceramics version for 6 h is shown in Figure 6. It can be observed that the pH of the Na-PBS increase throughout the immersion period, although not significant (7.6 – 7.9). However, in Tris-HCl, a constant pH within 7.6 – 7.5 was maintained throughout the immersion period. The increase in pH indicates higher reactivity of the glass as reported by Varila et al. [17]. However, since the solutions have differing buffer capacities, the order of reactivity cannot be entirely concluded from pH measurements [17].

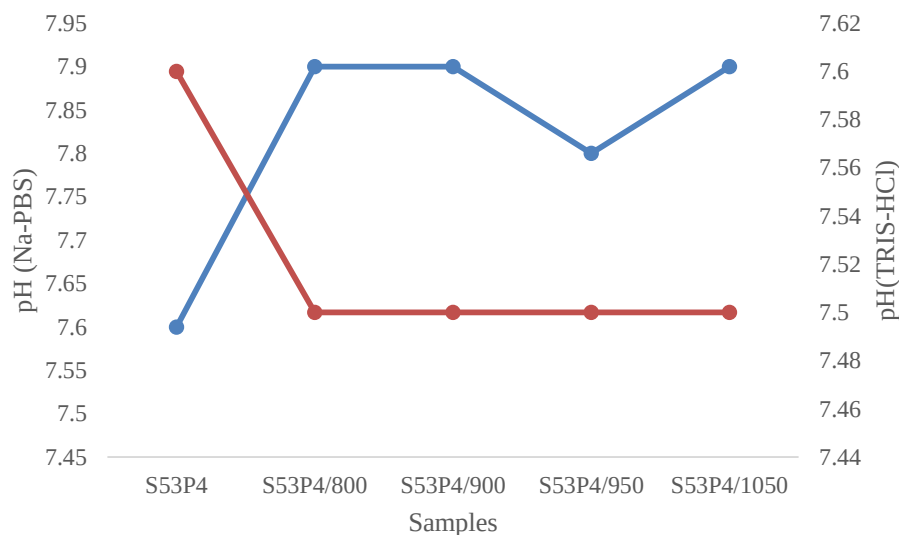


Figure 6. pH of the biological fluids after immersion of samples

3.5. Phase characterization

3.5.1. Before immersion in biological fluids

Figure 7 shows the phase characterization of the S53P4 BG while Figures 8 and 9 indicate the representative diffractogram of the bioglass-ceramic samples sintered at 900 and 950oC respectively. In Figure 7, it is observed that the S53P4 BG showed characteristic amorphous phase with a broad band peaks which affirmed that a bioglass was obtained from the melt-quenching process. However, a low intensity peak at $\theta = 27^\circ$ characteristic of Combeite ($\text{Na}_2\text{Ca}_2\text{Si}_3\text{O}_9$) is obtained as previously reported [19]. In Figures 8 and 9 which represent the S53P4 BG sintered at 900 and 900oC respectively, it is observed that sample sintered at 900oC (S53P4/900) fully crystallized with major peak of Combeite ($\text{Na}_2\text{Ca}_2\text{Si}_3\text{O}_9$) observed. However, for S53P4/950 sintered at 950oC, a broad band peaks between $15 - 32^\circ$ characteristics of amorphous phase can be seen to occur with several crystalline peaks identified with Combeite while peaks of wollastonite (CaSiO_3) are also seen.

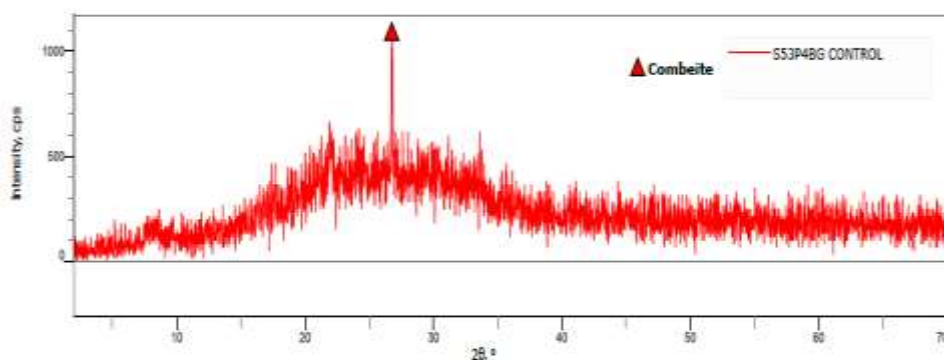


Figure 4.5. XRD pattern of S53P4 bioglass

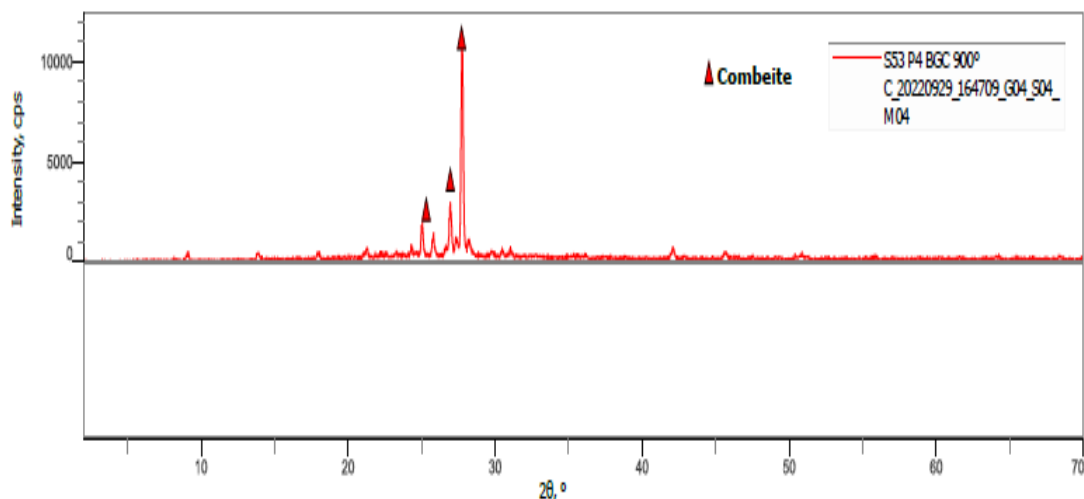


Figure 4.6. XRD pattern of S53P4 bioglass sintered at 900oC

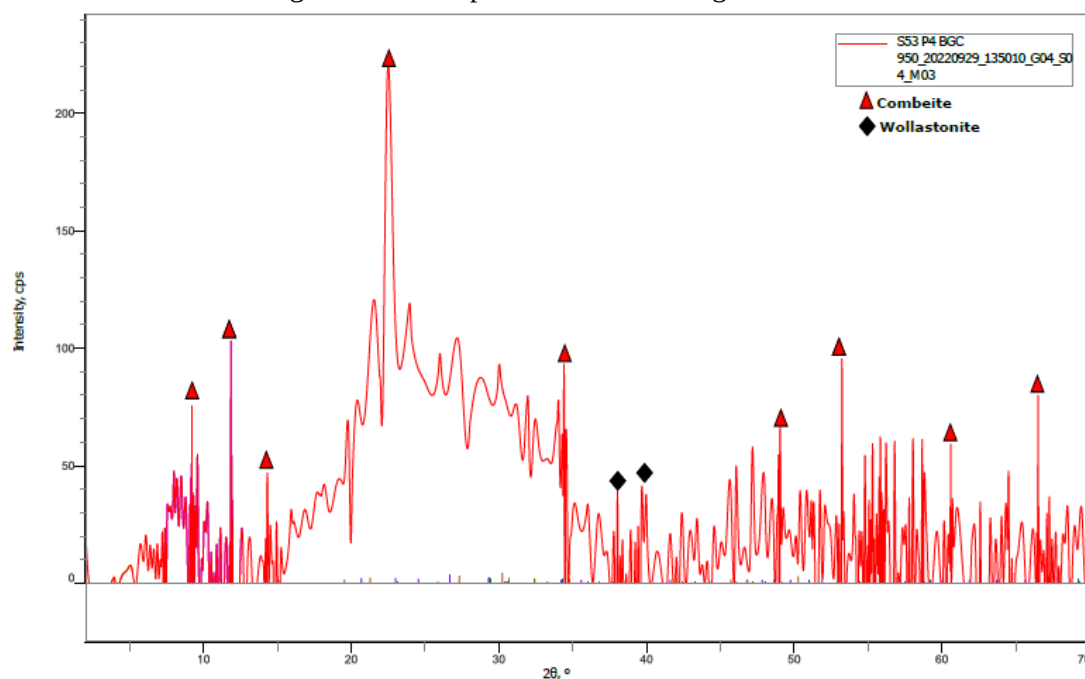
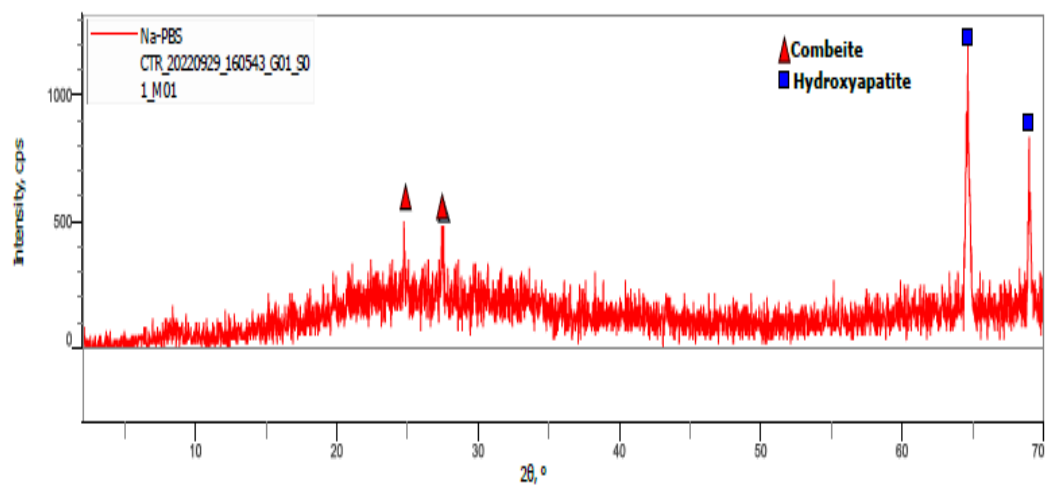


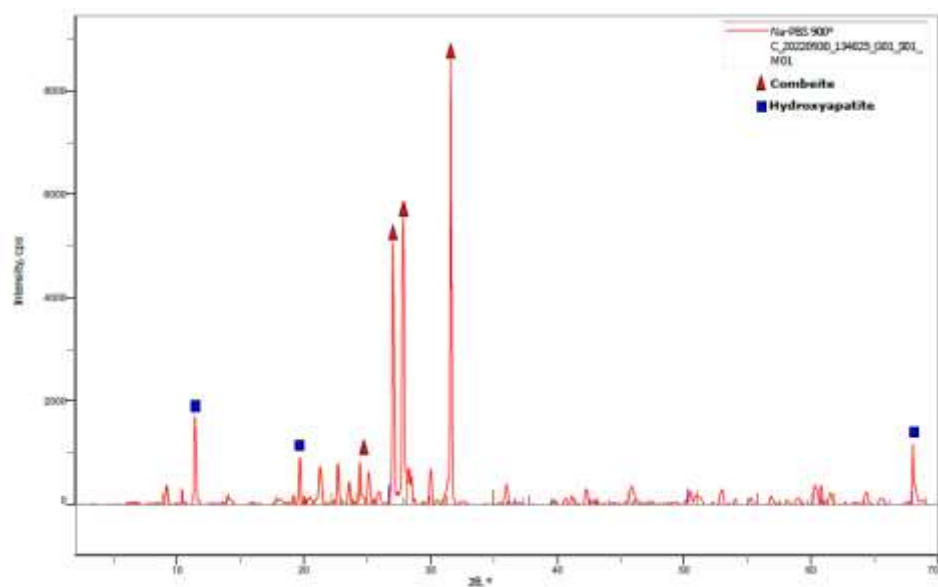
Figure 4.7. XRD pattern of S53P4 bioglass sintered at 950oC

3.5.2. After immersion in biological fluids

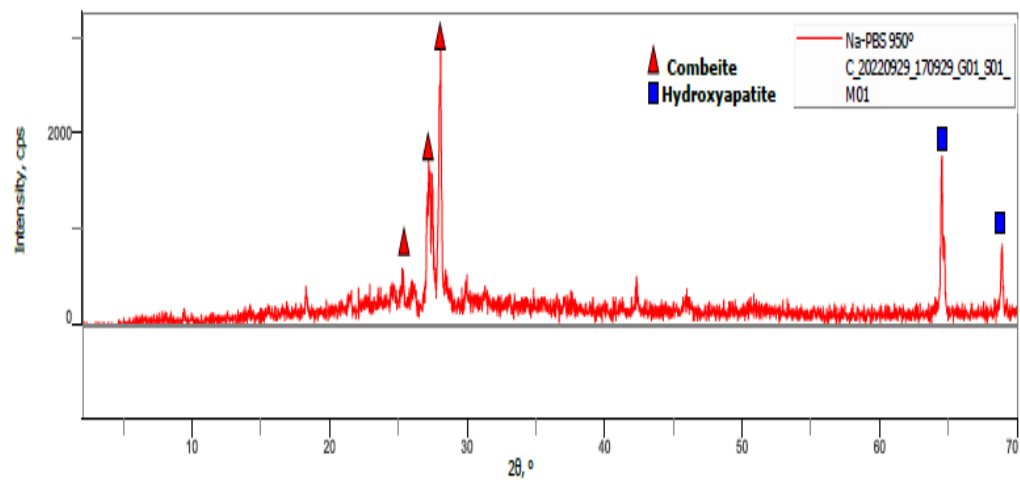
Figure 4.8 (a – c) show the XRD pattern of the samples after immersion in Na-PBS while Figure 4.9 (a – c) represent the XRD pattern of the samples after immersion in 1M Tris-HCl both for 6 h respectively. It is observed for the samples immersed in both Na-PBS and Tris-HCl that new peaks identified to be HAP (Hydroxyapatite) are obtained which indicates the apatite forming ability of the samples in biological fluids and ultimately their compatibility if use in living tissue. However, samples immersed in Na-PBS showed better intensify peaks of HAP than that observed for Tris-HCl, which indicates that hydroxyapatite formation of the samples is more pronounced in Na-PBS probably due to the presence of phosphate in the solution [20].



(a)

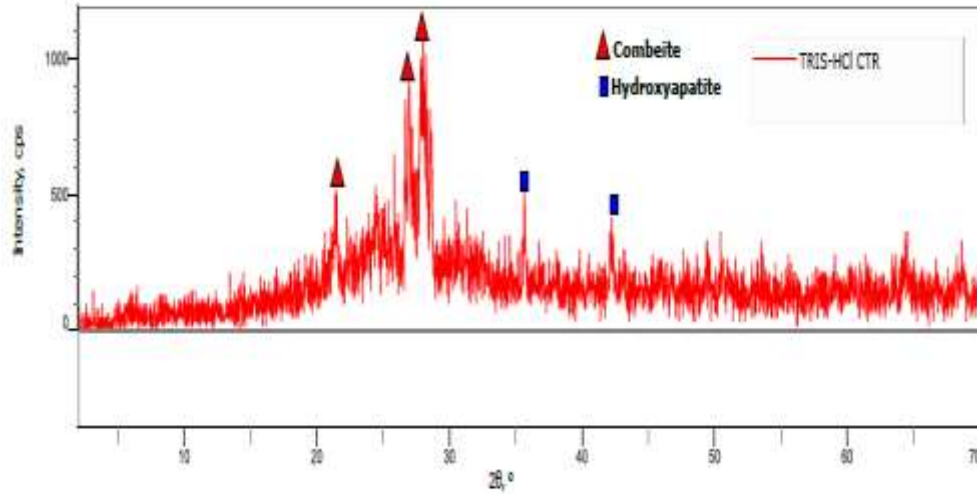


(b)

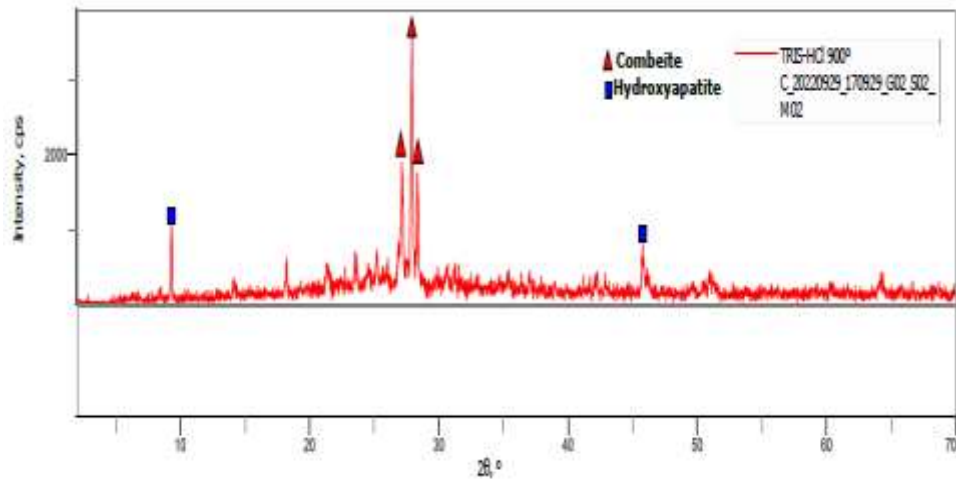


(c)

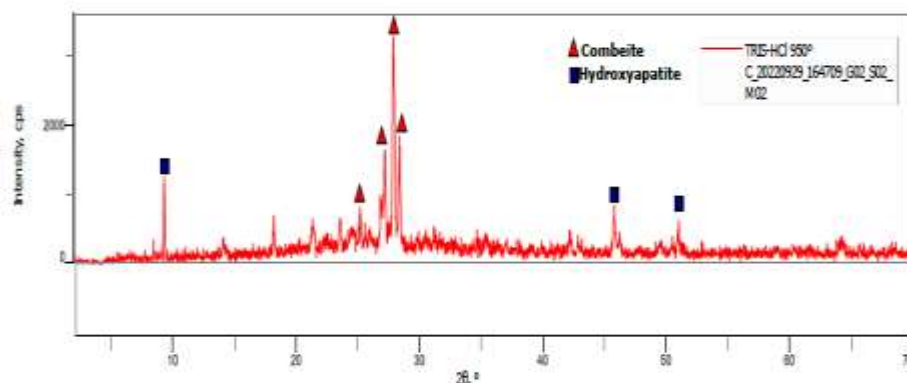
Figure 4.8. XRD pattern of samples immersed in Na-PBS solution (a) S53P4 Control (b) S53P4BGC-900 (c) S53P4BGC-950oC



(a)



(b)



(c)

Figure 4.9. XRD pattern of samples immersed in Tris-HCl solution (a) S53P4 Control (b) S53P4BGC-900 (c) S53P4BGC-950oC

4. Conclusions

The present work has successfully developed S53P4 bioglass using melt-quench approach by microwave assisted irradiation and subsequent sintering at different temperatures using microwave energy irradiation. The following conclusions were drawn from this work:

- Microwave assisted energy irradiation provided easy route to melt bioglass within short possible time and less energy consumption.
- The bulk density of the sintered samples increase while the percent porosity decrease as sintering temperature which is attributed formation of vitreous phase arising from viscous flow during sintering.
- The hardness of the samples improved noticeably as sintering temperature increase compared with control sample
- Weight loss of the sintered samples is considerably lower compared with S53P4 bioglass (control) in biological fluids.
- Hydroxyapatite formation on the samples in Na-PBS is more pronounced compared to Tris-HCl. However, the formation of HAP is well pronounced in non-sintered bioglass compared to sintered bioglass-ceramics.

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SN 19 NIGERIAN FIKA BENTONITE AS AN ALTERNATIVE NATURAL COAGULANT IN WATER CLARIFICATION

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ABSTRACT

This research investigates the potential of Nigerian Fika bentonite as a natural coagulant in water treatment. The analysis revealed that Fika bentonite is composed of 36.26% silica, 12.86% alumina, 9.6% calcium oxide, and 0.13% sodium oxide, confirming it as a calcium bentonite clay. X-ray diffraction indicated a predominantly montmorillonite structure with high levels of smectite clays such as calcite, nontronite, and quartz. Water coagulation tests on a dam water sample showed an 83.2% reduction in turbidity. The study also demonstrated that the treated water met WHO standards, with pH at 7.30, hardness at 44.75mg/l, conductivity at 101.6µs/cm, and TDS at 9.8 mg/l. This research supports the use of local bentonite for cost-effective water treatment.

Keywords: Clay minerals, Nigerian Fika Bentonite, turbidity, ion exchange, coagulation

1. INTRODUCTION

Water is an essential natural resource for the survival of all living species especially human beings that are using the available groundwater as well as surface water for various purposes including drinking, irrigation and different industrial operations. Due to industrialization, urbanization and anthropogenic activities large number of contaminants is added into water. The presence of natural organic matter, heavy metals, pesticides, dye and insecticides make the water unfit for human consumption. These pollutants may have adverse effects on human health and aquatic ecosystems (Reddy and Lee, 2012). With the advancement of technology, a development of more effective, low cost, robust methods for treatment of wastewater have been used which put low impact on environment and human health. Extensive studies have been undertaken in recent years with the aim of finding alternative and economically feasible technologies for water and wastewater treatment. Coagulation is an essential process in the treatment of both surface water and industrial wastewater. Its application includes removal of dissolved chemical species and turbidity from water via addition of coagulants (Vijayaraghavan *et al.*, 2011). Conventional chemical-based coagulants, namely, aluminum sulphate ($\text{Al}_2(\text{SO}_4)_3 \cdot n\text{H}_2\text{O}$), ferric chloride (FeCl_3) and polyaluminium chloride (PAC) are used in most treatment plants. Although these are effective, there are a number of disadvantages associated with usage of these coagulants. Aluminum sulphate for instance has a demand for hydroxide and alkalinity and only works within a certain pH (Dirty water requires large dosage of alum), It also produces a lot of sludge that is not easy to de-water because it becomes very gelatinous. There is strong evidence linking aluminum-based coagulants to the development of Alzheimer's disease in human beings. Ferric chloride on the other hand is highly corrosive and requires special piping, storage and pumping equipment. Synthetic polymer like acrylamide as coagulants create the problem of neurotoxicity and carcinogenicity and significantly contaminate and pollute areas for wild life and vegetation (Yarahmadi *et al.*, 2009). It is therefore necessary to replace these chemical coagulants with safer and effective alternatives to avoid the drawback. Clay minerals, such as bentonite and zeolite, are some of the potential alternatives, as they have large specific surface areas with a net negative charge, which can be electrically compensated for by inorganic and organic cations from the environment (Konig *et al.*, 2012). The use of clay mineral has

undoubtedly become more popular and widely used as an adsorbent and ion exchange for water and wastewater treatment applications especially for removing heavy metal, organic pollutants, and nutrients (Abdelaal, 2004).

Bentonite is a highly effective natural clay mineral, used for the purification of water, wastewater and sludgedewatering and according to Afolabi *et al.*, (2017), deposits of local bentonite clays in Nigeria have been modestly projected to be above 700 million metric tons. These vast deposits of Nigerian bentonite clay have many significant uses in different aspects of industrial fields in the country. They can prove to be a cheaper, widely available and safer option in water treatment since the chemical-based coagulants we know present a range of disadvantages especially to human and environmental health. Additionally, the processing of local bentonite as a coagulant can also bring about employment opportunities and reduce imports thereby improving the country's economy.

Thus, the aim of this study is to investigate the potential effectiveness of Nigerian Fika bentonite as a natural alternative coagulant in water clarification.

2. EXPERIMENTAL PROCEDURE

2.1 Characterization of Fika bentonite clay sample

XRD analysis was carried out to study the structure of the clay minerals. The bentonite sample which was already processed into a fine powder (This helps ensure that the X-rays can penetrate the sample and interact with the atom effectively) was then exposed to X-rays and the resulting diffraction pattern was measured using a diffractometer. This pattern provides information about the arrangement of atoms in the sample.

X-ray fluorescence is used to determine the elemental composition of the sample. The bentonite sample was placed in front of an X-ray source (Benchtop spectrometer), which emits X-rays that interact with the atoms in the sample. The atoms then emitted characteristic X-ray fluorescence which was detected and analyzed to determine the elemental composition.

2.2 Preparation of coagulant samples

The beneficiated Calcium bentonite of Fika origin was obtained in milled powdered form (70 μ m mesh) and was mixed vigorously with distilled water to form a slurry which was then allowed to settle for 30 minutes. The solution was filtered using a cloth to ensure proper separation of bentonite and distilled water. This removes any impurities contained in the sample. The moist bentonite cake was then dried in an oven at 120°C for 15 minutes standard time and temperature and ground to obtain pure powdered form of the coagulant which was stored in an airtight container. Samples of Aluminium sulphate was pulverized into fine particles by means of laboratory mortar and pestle and was sieved through a 150 μ m mesh and stored in an airtight container.

2.3 Water treatment test

Raw water sample was collected from Ahmadu Bello University's Dam. The sample was stored in the refrigerator for 24 hours so as to stabilize it by reducing microbial activity and slow reaction times which can only be achieved at lower temperatures (Z. Jeff 2022). The sample was then collected from the refrigerator and it was measured to have a turbidity of 24.36 NTU, pH of 6.7, conductivity of 84.1 μ S/cm, hardness of 48.24 mg/l of CaCO₃ and TDS level of 41.6 mg/l. To form a standard solution, pre-treated

samples of Aluminum sulphate and Bentonite were collected and 1g of each was measured on a laboratory scale. The measured quantities of coagulants were dosed in two different beakers each containing 100ml of distilled water and mixed properly using a glass rod. The solution was slowly filtered using a filter paper into a conical flask.

The standard solution each of alum and bentonite were dosed into raw water samples in the following doses; 2ml, 4ml, 6ml, 8ml and 10ml each per 200ml of raw water samples in a beaker using a pipette. The samples were then transferred to a flocculator for jar testing. They were rapidly mixed for 5 minutes at 40rpm and then slowly mixed for 20 minutes at 10rpm. The samples were then allowed a settling time for 45 minutes after which the supernatant was filtered with a filter paper into a conical flask and the turbidity, conductivity, hardness, total dissolved solids and pH of the water samples were measured.

3. RESULTS

3.1 Table 1 shows the results obtained from the X-ray fluorescence analysis. The analysis exposed the percentage of chemical oxides present in the bentonite clay samples.

Chemical oxide	Fika Bentonite (wt%)
SiO ₂	36.26
Al ₂ O ₃	12.86
Fe ₂ O ₃	6.80
CaO	9.16
Na ₂ O	0.13
MgO	6.08
K ₂ O	1.60
TiO ₂	0.76
MnO	0.30
P ₂ O ₅	0.33
SO ₃	0.10

Table 1: Chemical composition of Fika bentonite

From Fig 1 the chemical composition of the bentonite sample shows that the most abundant oxides in the sample is SiO₂ and Al₂O₃ having 36.26 and 12.86 wt% respectively. It also showed very low levels of MnO and P₂O₅. The clay is composed of 9.16wt% CaO and 0.13wt% Na₂O, this confirms that the clay is a calcium-based bentonite clay. The results of this analysis strongly agrees with the research of Abdullahi et al 2011, which showed the chemical composition of a local bentonic clay obtained from the Fika region..

3.2 Structure of Bentonite

In Figure 2, the diffractogram shows that the sample presents 66.4% nontronite, 16.5% quartz and 8.1% montmorillonite, and 9% of amorphous material. Nontronite and montmorillonite present intense and very closes peaks. The presence of montmorillonite is expected in every typical bentonite sample and nontronite also belongs to the smectite group of clays which is a common impurity in Nigerian bentonites (Abdullahi

et al 2017). The well-defined peak of quartz occurs because it has a higher degree of crystallinity in relation to the other minerals present in the sample. The results of the X-ray diffraction indicates that the structure of the Fika bentonite clay share similarities with Bentonite clays of Maiduwa, Yobe state as reported by Dewu et al. Both clays contain Montmorillonite, Calcite and Quartz which suggests that clay minerals from the same region share similar characteristics.

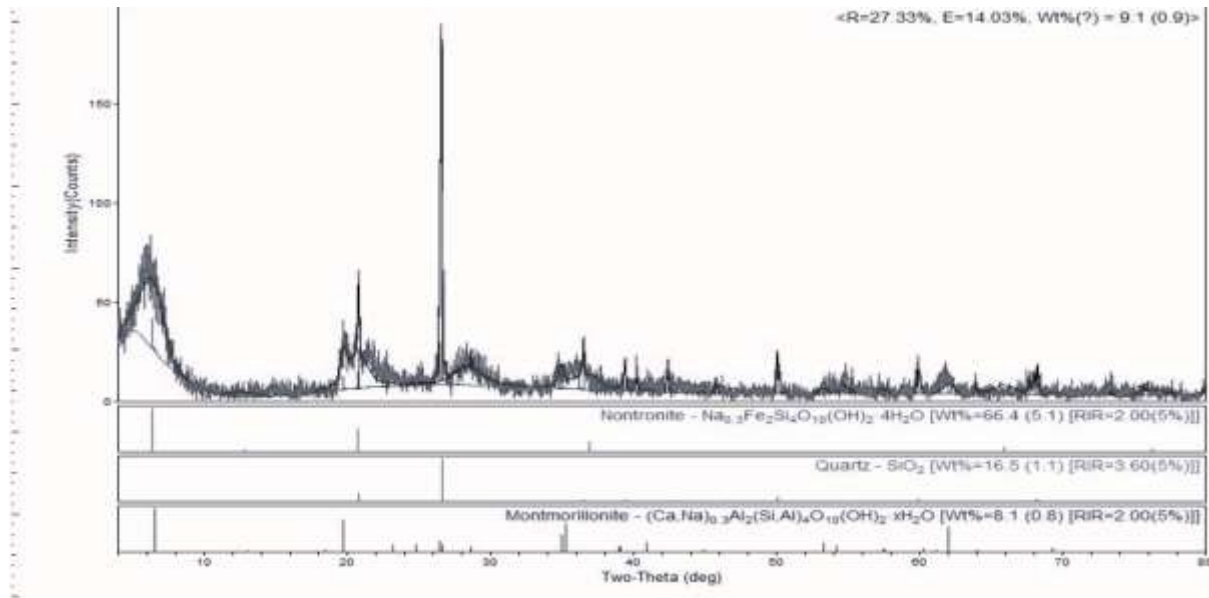


Figure 1: Diffractogram of Fika bentonite sample

3.3 Result of Measurement Water Quality Parameters.

S/no	Raw water data

1	Hardness (mg/l)	48.24
2	Conductivity(μ s/cm)	84.10
3	Turbidity (NTU)	24.36
4	pH	6.7
5	TDS (mg/l)	41.60

Table 1: Hardness, PH, turbidity, conductivity, and TDS of raw water

Dosage (ml)	Hardness (mg/L)		pH		Turbidity (NTU)		Conductivity (μ s/cm)		TDS (mg/l)	
	Alum	Bentonite	Alum	Bentonite	Alum	Bentonite	Alum	Bentonite	Alum	Bentonite
2.00	59.06	47.45	6.43	6.70	0.314	10.901	123.20	89.00	63.90	44.60
4.00	64.29	46.64	5.30	6.90	0.899	7.552	182.50	93.00	92.10	46.70
6.00	67.33	45.49	5.15	7.10	1.375	5.838	238.00	97.50	119.50	49.10
8.00	68.82	44.75	5.12	7.30	1.209	4.027	278.00	101.60	139.10	51.40
10.00	73.59	44.13	5.09	7.40	0.966	4.592	320.00	115.20	154.40	57.50

Table 3: Hardness test, pH, Turbidity, conductivity, TDS data of clarified water

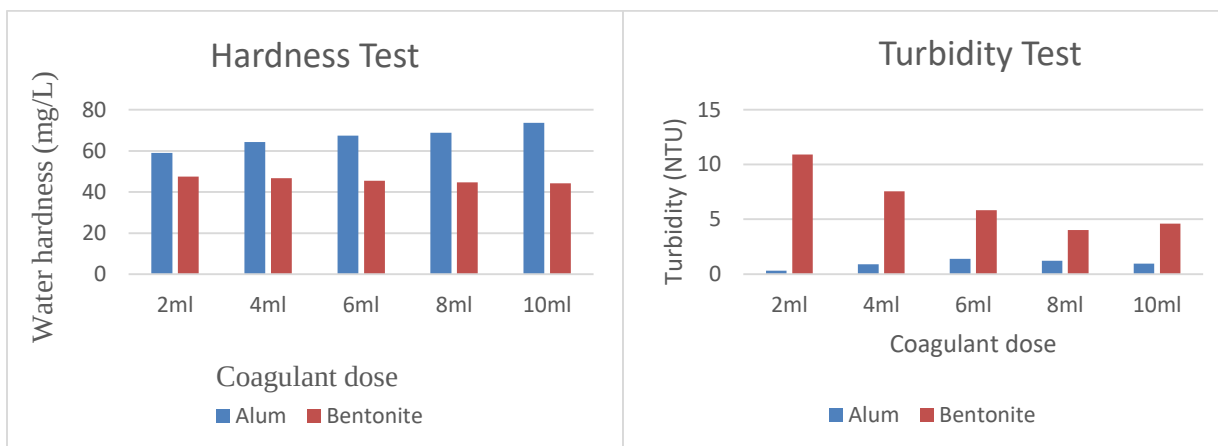


Fig 3: Effects of alum and bentonite solution on hardness and turbidity of water

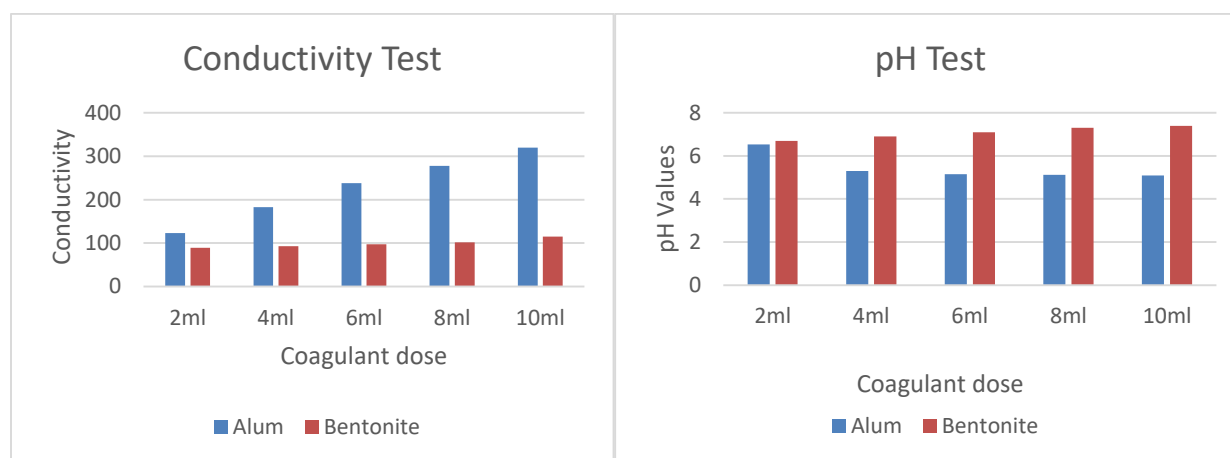


Fig 4: Effects of alum and bentonite coagulants on conductivity and pH of water

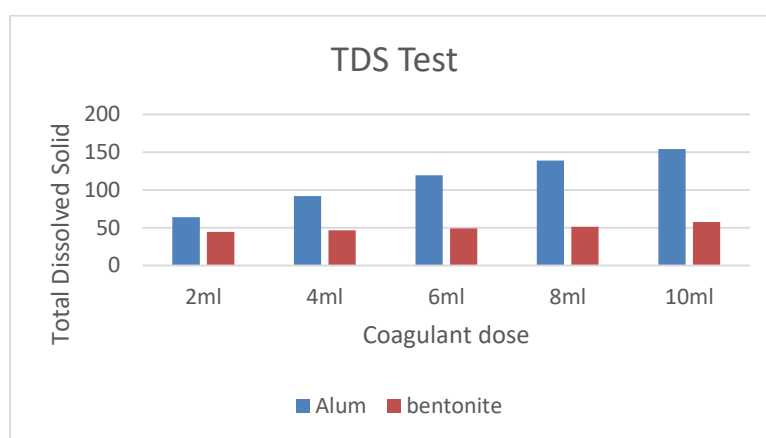


Fig 5: Effects of alum and bentonite coagulants on Total dissolved solidsin water

Aluminum sulphate (Alum) performed better in terms of removal of turbidity since it reduced the turbidity by 98.75% at a small optimum dose of 2ml, compared to the bentonite clay which reduced turbidity by 83.2% at 8ml. This is because with higher dosages of bentonite, greater electrostatic force is generated causing more flocs to settle, thereby removing a lot more turbidity than the smaller doses. However, Bentonite at very high dose begins to impart more turbidity to the water, this is because the sample was a low turbid water and higher doses of bentonite are more effective for high turbid waters. Alum at optimum dosage lowered the pH of the water from 6.70 to 6.43; a level not recommended by WHO(6.5-8.5), unlike bentonite clay which raised the pH of the water to 7.30 at optimum dosage without deviating from WHO permissible limits. The reduction in pH after treatment with alum implies that alum imparts acidity in water. However, the increase in pH after treating the water with bentonite coagulant indicates that bentonite has

the potential of rendering water alkaline. Hence, the treatment cost associated with the use of lime to raise water pH in water treatment plant can be averted by utilizing the bentonite which have demonstrated the potentials of raising water PH unlike alum. Alum also increased the hardness of water by 22.42% at optimum dosage while bentonite clay was seen to lower hardness by 7.23%. The decrease in hardness level of the water with increase in bentonite solution dosage, suggests that the bio-coagulant contains bonding sites that might have absorbed the divalent metallic ions (Ca^{2+} and Mg^{2+}) associated with carbonate and bio-carbonate responsible for temporary hardness. This suggests that bentonite solution could be as well used as an adsorbent in absorption of metallic ions, thus affirming previous reports by snavada *et al* 2020. At Optimum dosage, Aluminum sulphate was also detected to have significantly increased the conductivity by 96.87%. The excessive increase in conductivity of the water by the alum is due to the fact that it is a salt compound composed of aluminum and sulfate ions. When alum is added to water, it dissociates into aluminum ions (Al^{3+}) and sulphates ions (SO_4^{2-}). These ions increase the electrical conductivity of the water. Aluminum ions, in particular, have a relatively high charge density, and they can carry a significant electrical charge, contributing to increased conductivity. Bentonite on the flip side is a type of clay mineral, which unlike alum does not introduce highly charged metal ions into the water. Instead, it works by adsorbing and removing suspended particles and impurities through a physical mechanism. Alum also increased the Total dissolved solids present in the water by 97.4mg/l, parameters which indicate high presence of inorganic salts and chlorides, while bentonite clay only showed a slight increase in conductivity by 8% as well as a slight increase of 9.8mg/l in TDS.

4. CONCLUSION

Nigerian Fika Bentonite was successfully prepared, characterized and utilized as an alternative coagulant in water clarification. Due to drawbacks of alum with respect to pH reduction, hardness formation and high increment in electrical conductivity and Total dissolved solid presence, aspects which bentonite clay have been observed to perform better, it has been concluded that bentonite clay could be used to replace alum successfully since it also requires small optimum dosage of 8ml to produce acceptable water quality, and its amount of turbidity removal is still within recommended limits (<5NTU).

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SN 20 EFFECTS OF WATER SEAL ADMIXTURE ON THE COMPRESSIVE STRENGTH OF CONCRETE

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ABSTRACT

This paper aimed at evaluating the effects of water seal on the compressive strength of concrete as an admixture. The preliminary investigations was based on experimental and laboratory tests, concrete cubes of 150mm x 150mm x150mm were cast using a mix ratio of 1:2:4 for grade 20 concrete with addition of different percentages of water seal admixture (0.0%, 1.0%, 1.5%, 2.0%,2.5%and 3.0% respectively). Workability and compressive strength at various curing ages of 7days, 14days, 21days, and 28days were

tested. The results indicated that the addition of water seal increased the workability and the compressive strength of concrete. The highest compressive strength for 28days was found to be 23.41N/mm² at 2.0% water seal as an admixture, which was concluded to be the optimum percentage to be used in the production of concrete.

Keywords: Admixture, Compressive Strength, Workability, Water Seal,

1. Introduction

Concrete technology has created a revolution in producing concrete with lower water/cement ratio compared to the standard without jeopardizing the original strength and workability. However, there are still uncertainties on the exact quantity and quality of the admixtures used due to inadequate data that explains the effects of using these admixtures on the strength and workability of the concrete. Hassan and Hamza (2004). Concrete, generally, is a product made from cement, water and aggregates and an additional material known as admixture, is sometimes added to modify certain properties of concrete. Cement is the chemically active constituent but its reactivity is only brought into effect upon mixing with water. The aggregate plays no important roles in chemical reaction but its usefulness arises because it is an economical filler material or hard composite material with good resistance to volume changes which take place within the concrete after mixing, besides improving durability of concrete. Jackson and Dhir (1996). Concrete is a building material composed of cement, sand as fine aggregate, crushed rock as coarse aggregate and water. High performance concrete (HPC) is defined as a concrete meeting special combination of performance and uniform characteristics that cannot always be achieved routinely using conventional constituents, and normal mixing, placing and curing practices (Mehta, 1999). High performance concrete is a concrete in which certain characteristics are developed for a particular application and environment, for example placement with ease, compaction without segregation, early age strength, long term strength, long life in severe environment etc. High performance concrete possesses high workability, high strength and durability (Plank *et al* 2008). The concrete mix with an addition of appropriate chemical admixtures often improves its plastic properties such as workability, pump ability, cohesion and adhesion. Addition of admixtures will also reduce the bleeding of concrete and gives fine surface finish (Metwalli 2013). This research aimed at investigation the effect of commercially available water seal admixture on the compressive strength of concrete. The admixture was added at 1.0%, 1.5%, 2.0%, 2.5% and 3% respectively to evaluate the compressive strength and determine the optimum dosage of the water admixture in concrete production.

2. Material and Methods

2.1 Materials

The materials use in this study include: cement, fine and coarse aggregates, water and water seal admixture. The cement used was Dangote 3X cement (CEM 11-42.5N) cement with a specific gravity of 3.13. Natural occurring sand (fine aggregate) was sourced from a river in Samaru Zaria, Kaduna State. The Coarse aggregate was of crushed grade obtained from the local dealers in Kaduna state. The size of aggregate used ranges between 19.05 and 12.01mm having an aggregate crushing (ACV) and impact value (AIV) of 23.5% and 25% respectively.

The admixture used in this research work was suphonated melamine with empirical formula CHZNZ which is colourless to white solid powder (while monoclinic crystal). The chemical composition of water seal admixture was determined by XRF analysis using thermo scientific ARL performed X sequential XRF on

molten disc prepared by mixing sample and fluxana (FX – X50 – 2, lithium tetraborate 50% lithium metaborate 50%) the data were evaluated using unquant program as shown in table 1.

Table 1: Oxide Composition of the Water Seal Admixture

Oxide	Percentage (%)
SiO ₂	13.50
CaO	46.74
Al ₂ O ₃	3.47
Fe ₂ O ₃	1.58
MgO	3.70
MnO	0.09
Na ₂ O	9.30
K ₂ O	0.63
SO ₃	2.42
Loss on ignition	18.11

2.2 Concrete Mix Proportions

The mix proportion used was calculated using absolute volume method using mix ratio of 1:2:4 for grade 20 concrete. The concrete mix proportions is presented in Table 2.

Table 2: Concrete mixProportions

Material	0%	1.0%	1.5%	2.0%	2.5%	3.0%
Cement (kg)	13.884	13.884	13.884	13.884	13.884	13.884
Fine Aggregate (kg)	27.768	27.768	27.768	27.768	27.768	27.768
Coarse Aggregate (kg)	55.536	55.536	55.536	55.536	55.536	55.536
Water Seal Admixture (kg)	0	0.139	0.208	0.278	0.347	0.417
Water (kg)	6.942	6.942	6.942	6.942	6.942	6.942
Number Of Cubes	12	12	12	12	12	12

2.3 Workability Test

This test was conducted in accordance with (BS 1881: Part 102), in order to determine the workability of the fresh concrete made with water seal admixture,

2.4 Compressive Strength Test

The test was conducted in accordance with BS EN 12390-3 (2002). Concrete samples were cast and cured in water, and a total of 3 cubes were considered for an average.

3. Results and Discussions

3.1 Workability of Concrete

The result of the slump test which determines its workability is classified according to some ranges of slump values as: Very Low Workability (0-25mm), Low Workability (25-50mm), Medium Workability (50-100mm) and High Workability (100-175mm). Table 3 shows the slump values obtained at various percentage addition of water seal admixture.

Table 3: Results of slump test

S/N	% of Water Seal	Slump Value (mm)	Type Of Slump	Remark
1	0	39	True slump	It is workable
2	1.0	45	True slump	It is workable
3	1.5	49	True slump	It is workable
4	2.0	58	True slump	It is workable
5	2.5	59	True slump	It is workable
6	3.0	62	True slump	It is workable

The trend showing workability with percentage water seal admixture dosages can be seen clearly in figure 1.

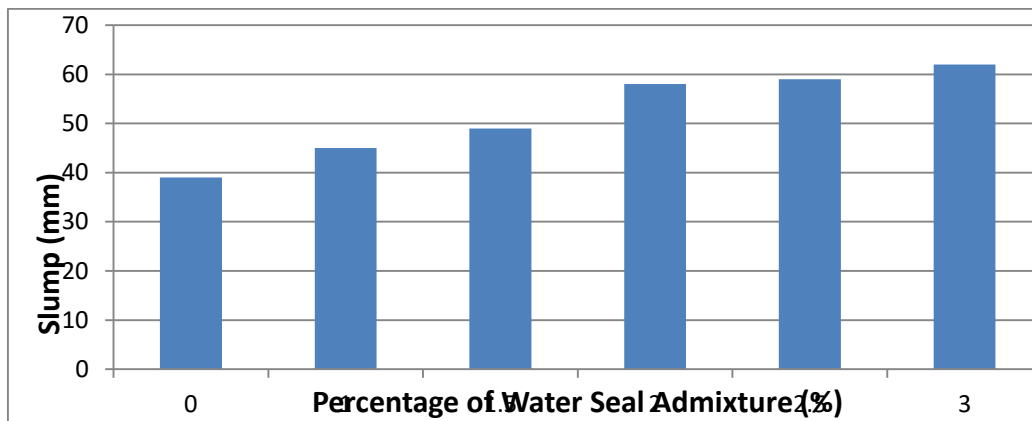


Figure 1: Slump against % addition of water seal admixture

From Figure 1, there is drastic increase in slump from 0 to 2% admixture dosage. However, the increase of slump from 2 and above is not so significant.

3.2 Compressive Strength of Concrete

The results of the compressive strength obtained at different curing age and percentage addition of water seal is presented in Table 4 to 7 and Figure 2. It was observed that addition of water seal enhanced the compressive strength of concrete.

Table 4: Compressive Strength of Concrete for 7 Days

% of Water Seal	Density (kg/m ³)	Compressive Strength (N/mm ²)
0.0	2246.92	8.52
1.0	2539.51	10.67
1.5	2459.26	11.40

2.0	2469.14	13.74
2.5	2378.27	13.16
3.0	2595.56	12.44

Table 5: Compressive Strength Concrete for 14 Days

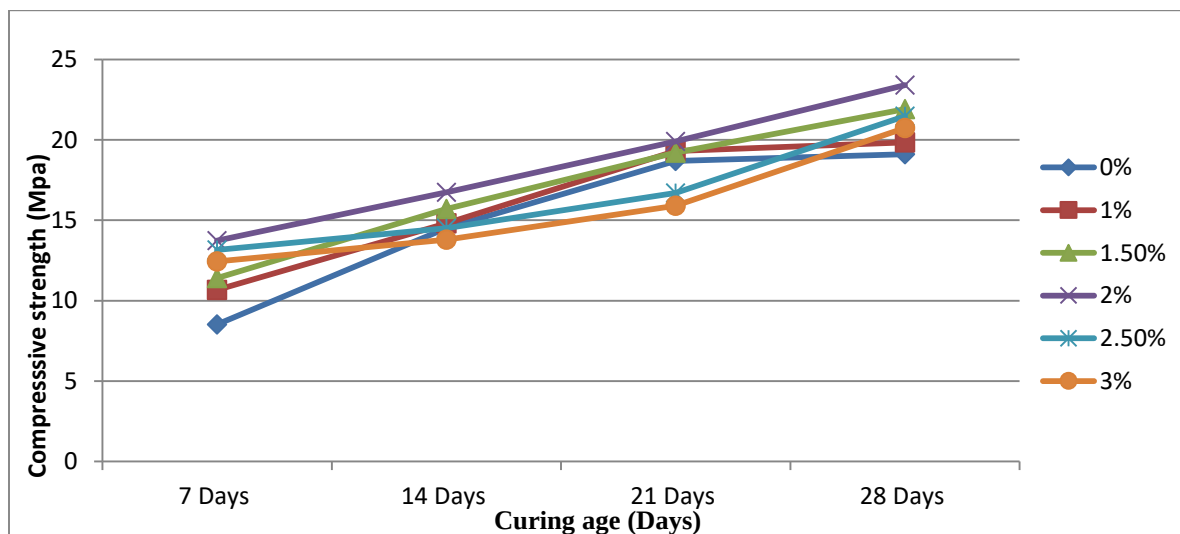
% of Water Seal	Density (kg/m³)	Compressive Strength (N/mm²)
0.0	2488.89	14.52
1.0	2409.87	14.81
1.5	2390.12	15.70
2.0	2469.20	16.74
2.5	2378.27	14.51
3.0	2459.26	13.38

Table 6: Compressive Strength of Concrete for 21 Days

% of Water Seal	Density (kg/m ³)	Compressive Strength (N/mm ²)
0.0	2390.12	18.7
1.0	2449.38	19.03
1.5	2464.20	19.25
2.0	2459.26	19.85
2.5	2464.20	17.15
3.0	2612.35	17.03

Table 7: Compressive Strength of Concrete for 28 Days

% of Water Seal	Density (kg/m ³)	Compressive Strength (N/mm ²)
0.0	2524.24	19.11
1.0	2469.13	19.85
1.5	2467.16	21.92
2.0	2409.87	23.41
2.5	2459.29	21.48
3.0	2404.94	20.59

**Figure 2: Variation of compressive strength with curing age at different % of admixture**

It was observed from Figure 2 that the compressive strength of concrete increased as the curing age increased. On the other hand, addition of water seal increased the compressive strength of concrete. The increase in the compressive strength of concrete may be due to hydration of cement, and it was concluded that the optimum percentage addition of the admixture is 2.0% having the highest compressive strength.

Conclusions

Based on the tests carried out, the following conclusion were made;

- i. Addition of water seal as admixture increased the workability of concrete
- ii. Addition of the water seal admixture increased the workability of the concrete
- iii. It was concluded that the optimum percentage of water seal to be used in the production of concrete should not be higher than 2.0 %.

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SN 21 BIOSYNTHESIS OF ZINC OXIDE USING AQUEOUS EXTRACT OF *SENNA SIEBERIANA* NANOPARTICLES AND CHARACTERIZATION FOR UV-VISIBLE SENSING STUDIES OF AMMONIUM NITRATE

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ABSTRACT

Biosynthesis of Zinc oxide nanoparticles (ZnO NPs) using aqueous extract of *Senna sieberiana* for detection of ammonium nitrate was achieved in this study using standard methods. Characterization of the ZnO NPs was done by multiple spectroscopic analyses using UV-Visible Spectrophotometer, Fourier Transform Infrared Spectrophotometer (FTIR), X-ray diffraction (XRD), Brummer-Emmett-Teller (BET) and Scanning Electron Microscope (SEM) with EDS profile. The SEM-EDS result showed the average size of ZnO NPs to be 9 nm – 17 nm with elemental composition profile of 80.08% Zinc and 18.55% oxygen. The XRD studies revealed the crystalline nature of the synthesized ZnO NPs which absorbed maximally at 372 nm with irradiated UV-Visible light. The FTIR analysis reportedly reveals the ZnO bending and other functional group peaks on the mesoporous sized ZnO NPs as obtained by BET analysis. The absorbance spectra of ZnO NPs, were recorded as a function of different ammonium nitrate concentration (10-100 ppm) using a UV-Visible Spectrophotometer. From the result of UV-Visible sensing study of ammonium nitrate, it was observed that the maximum absorbance of ZnO NPs, shift to a lower wavelength with decreasing intensity upon addition and increase in concentration of ammonium nitrate from 10 to 100 ppm. The study

demonstrates that the prepared ZnO NPs, have a good sensory performance to ammonium nitrate and is recommended as a sustainable material for fabrication of sensors for explosive materials. This can add value to the protection of life and environmental remediation.

Keyword: Nanoparticles, Spectroscopy, Sensors, Explosives

1.0 INTRODUCTION

The consumption of ammonium nitrate (NH_4NO_3) in the formulation of ammonium nitrate-based explosives for industrial and defence operational purposes have increased greatly due to its commercial availability, inexpensive and ease in manufacturing (Haruna, 2016). Ammonium nitrate has been used globally as an explosive chemical in addition to other explosive items such as artillery shells and mortar bombs for explosive device fabrication (Small Arms Survey Research, 2014). Ammonium nitrate although safe to use when handled properly is itself, a hazardous material as explosion of a small quantity may initiate and enhance the propagation of further explosion with recent explosions recorded in Beirut port explosion of August, 2020 and Tiajin port, 2015 (Negavanovic, 2015). The potential of nanomaterials for chemical sensing is particularly desirable for significant application in security detection devices to deal with the challenges of trace detection of NH_4NO_3 (Christophe *et al.*, 2017). The optical properties of nanomaterials which enable them useful for chemical sensing can be related to their small size, high surface to volume ratio and porosity thus, allowing more surface availability for interactions with explosive analytes even at lower concentrations (Xiao *et al.*, 2015).

Studies have reported that zinc oxidenanomaterials have great potential for chemical sensing applications (Protimaet *al.*, 2016). Nano-zinc oxide superior sensing properties over other metal oxides nanomaterialsis due to its high surface defect density which provides a large surface area for the adsorption of chemical species (Ahmed *et al.*, 2017). ZnO nanoparticles have a stable wurtzite structure with a band gap of about 3.35eV and exciton binding energy of 60 meV which allows excitonic transitions and high radiative combination efficiency for spontaneous emission at room temperature (Singh, 2013). Studies have reported the biosynthesis of Zinc oxide nanoparticles [Azeezet *al.* (2019), Awwadet *al.* (2020), Ezealisijiet *al.*

(2019), Ogunyemiet *al.* (2019), and Muhammad *et al.* (2019)] and the important benign role phytochemicals present in plants which include flavones, polyphenols played for bio-reduction of the metal ions to nanoparticles.

Studies have also reported the detection of explosive analytes using zinc oxide nanoparticles. Ahmed *et al.* (2017) reported the electrochemical sensing application of ZnO nanoparticles synthesized by a simple hydrothermal process for the detection of picric acid. Geetha *et al.* (2019) synthesized fluorescent zinc oxide nanoparticles using aqueous extracts of *Boswellia ovalifoliolata* for electrochemical detection of picric acid. In a research by Singh (2013), zinc oxide (ZnO) nanorods (NRs) and its composite thin films with ZnO polypods were successfully synthesized for sensing 2,4,6-trinitrotoluene and cyclotrimethylenetrinitramines (RDX). The sensitivity of the ZnO nanomaterials sensor was found to be good towards detection of these explosive analyte.

Zinc oxide nanoparticles are continuously studied for explosive detection, however its reports are mostly focused on Nitro based compounds like 2,4,6-trinitrotoluene (TNT), dinitrotoluene (DNT), pentaerythritol tetranitrate (PETN), cyclotrimethylenetrinitramine (RDX), with few reports on ammonium nitrate detection (Silva *et al.*, 2014). Hence, the need to study and contribute to knowledge on the detection of ammonium nitrate using biosynthesized zinc oxide nanoparticles, it is in light of this that the study is embarked.

2.0 EXPERIMENTAL PROCEDURES

2.1 Materials

NaOH (VWR Chemicals, 98%, 40.00), NH₄NO₃ (VWR Chemicals, 99%, 80.04), Zn(NO₃)₆H₂O (VWR Chemicals, 98 %, 297.49), Distilled water, *Senna sieberiana* leaves.

2.2 Sampling

2.2.1 *Senna sieberiana* plant collection and pre-treatment

Senna sieberiana plant was collected from the Botanical Garden of Ahmadu Bello University, Zaria, Kaduna. Plant sample was identified and given the voucher number: ABU900202 at the Herbarium of Botany Section, Department of Biological Sciences, Ahmadu Bello University, Zaria, Kaduna. Fresh *S. sieberiana* leaves were selected and washed thoroughly with tap water followed by distilled water to remove dirt. It was air-dried under shade for two weeks, pulverized using a wooden mortar and pestle and stored in an air-tight container for further use.

2.3 *Senna sieberiana* Leaves Aqueous Extract Preparation

The aqueous extract of *S. sieberiana* leaves was obtained by weighing exactly 10.00 g of the powdered leaves and transferred into 250 ml beaker containing 100 ml distilled water. The mixture was homogenized thoroughly and boiled for 45 minutes at 60°C using a hot plate magnetic stirrer. The extract was obtained

by subjecting the homogenates to filtration using a Whatman No. 1 filter paper to remove insoluble fractions and to get a clear solution. The solution was used for the synthesis of Zinc oxide nanoparticle and about 10 ml of the leaves extract was used for qualitative phytochemical screening (Akhileshet *al.*, 2014).

2.4 Phytochemical Screening of *Senna sieberiana* Aqueous Extract

The aqueous extract obtained from *S. sieberiana* was screened qualitatively for the presence of naturally occurring biologically active compounds (phytochemicals) like flavonoids and phenolic compounds by using procedures described by Banu and Catherine (2015).

2.4.1 Estimation of total tannin content

According to Wadhai *et al.* (2019) the tannin content of SSBT extract was determined. Exactly 0.20 g of the extract was weighed into a 50 ml beaker and 20 ml of 50% methanol was added to it, covered with parafilm and heated in a water bath at 80°C for 1 hour. The reaction mixture was shaken thoroughly to ensure uniformity. The extract was then filtered into a 100 ml volumetric flask, and 20 ml of distilled water, 2.50 ml of Folin-Denis' reagent, and 10 ml of sodium carbonate were added and mixed properly. The reaction mixture was then allowed to stand for 20 minutes at 30°C for the development of bluish-green coloration. The absorbance was taken at 750 nm using a double beam Shimadzu Ultraviolet (UV) spectrophotometer (UV-1800, Japan). The tannin in the extract was then determined using the absorbance on a calibration curve. The calibration curve was prepared using standard tannic acid.

2.4.2 Estimation of total phenols content

The method described by Hasperu  *et al.* (2016) was used to determine the total phenol content of *S. sieberiana* extract. 0.01 g of *S. sieberiana* aqueous extract was dissolved in 10 ml of distilled water and oxidized with 2.50 ml of 10% Folin-Ciocateu reagent, which was then neutralized with 2.00 ml of 7.5% sodium carbonate. The reaction mixture was incubated at 45°C for 40 minutes. Absorbance was read at 750 nm, using double beam Shimadzu UV spectrophotometer (UV-1800, Japan). The calibration curve was prepared using standard garlic acid.

2.4.3 Estimation of total flavonoid content

Total flavonoid content of the aqueous extract of *S. sieberiana* was determined using the method of Chang *et al.* (2002). 0.50 ml of the extract was added to a test tube containing 1.50 ml of methanol, 0.10 ml of 10% aluminum chloride, 0.10 ml of 1.00 M sodium acetate and 2.80 ml of distilled water and incubated at ambient temperature for 30 minutes. The absorbance was read at 415 nm with double beam Shimadzu UV-spectrophotometer, UV-1800.

2.5 Synthesis of Zinc Oxide Nanoparticles

Exactly 1.00 M of zinc nitrate solution was freshly prepared and stored in a 250 ml of volumetric flask. 50 ml of the leaves extract was added to 50 ml of the prepared zinc nitrate solution in a beaker under continuous stirring by the use of glass stirring rod at room temperature. Approximately 0.50 M NaOH solution was added dropwise to the mixture to adjust the pH to the alkalinity range and stirred continuously using a

magnetic stirrer for 30 minutes. The precipitate obtained was washed thoroughly with deionized water. Finally, the precipitate was dried in an oven at 120°C for 1 hour. The obtained ZnO nanoparticles were annealed at 350°C for 45-60 minutes in muffle furnace and kept in a sample bottle until use. The equation of reaction is represented using equation 3.1 – 3.3 (Azeezet al., 2019):

Equation of Reaction

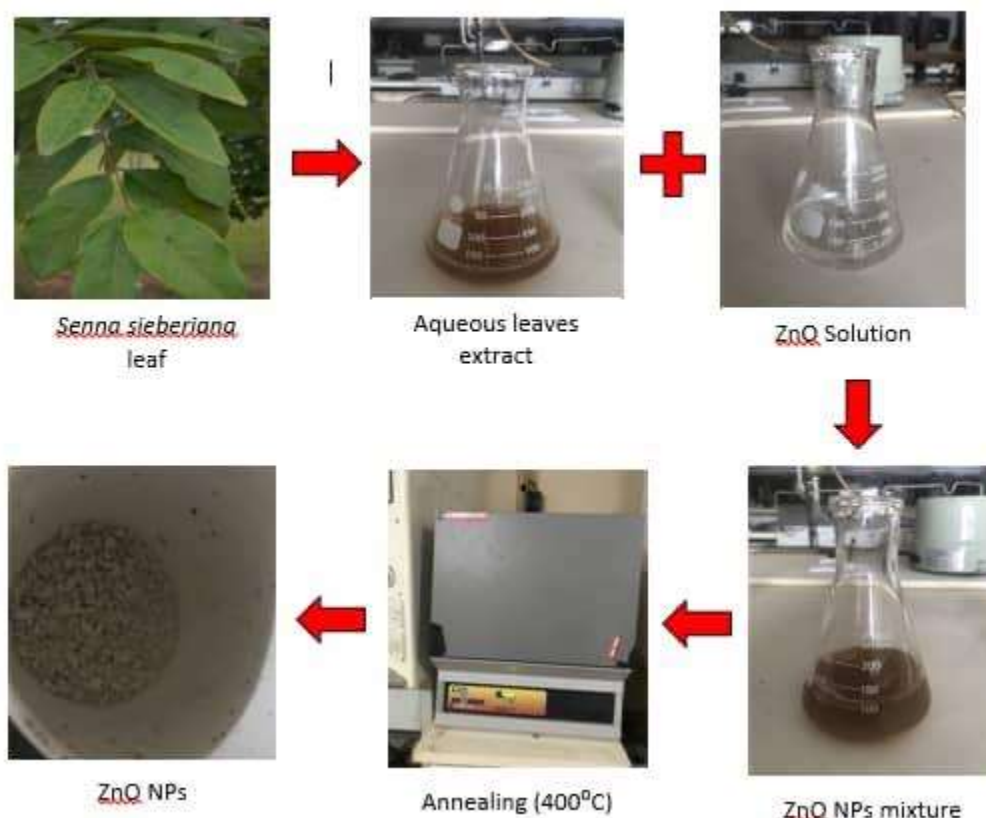


Plate1: Schematic representation of ZnO NPs synthesis

2.6 Characterization of the ZnO Nanoparticles

The morphologies and elemental compositions of the ZnO nanoparticles were obtained by using Scanning Electron Microscope (SEM) Zeiss AurigaM12-051 operating at 18 keV equipped with energy dispersive spectrometer (EDS) at the University of Capetown, Pretoria, South Africa.

The crystal structures of the ZnO nanoparticles were determined by using an XRD diffractometer Empyrean Joel Japan operating in Bragg–Brentano geometry mounting a Cu-anode X-ray source ($K\alpha$, $\lambda = 1.5418\text{\AA}$) at National Geosciences Space Agency, Barnawa, Kaduna. Shimadzu Japan UV-1800 UV–visible spectrophotometer obtainable at Defence Industries Corporation, Kaduna was used from a range of 200 nm – 700 nm to confirm the formation of ZnO nanoparticles. Agilent Technologies Cary 630 Fourier Transform Infrared spectrometer using KBr pellets method within a fixed spectral range, i.e. 4000–400 cm^{-1} obtainable

at Umaru Musa Yar'Adua University, Katsina was used for confirmation of functionalizing group on the ZnO nanoparticles.

2.7 UV-Visible Sensing Study of Ammonium Nitrate

A series of ammonium nitrate concentration in 10 ppm, 25 ppm, 50 ppm, 75ppm, and 100 ppm was prepared. The response of the synthesized ZnO nanoparticles to various concentrations of ammonium nitrate was performed using a UV-Visible spectrophotometer. 1.50ml of the various analyte concentrations was added to 1.50ml of the ZnO nanoparticles aqueous solution in a 4.00 ml Quartz cuvette and its UV-Visible spectra recorded (Muhammed *et al.*, 2018). The sensing studies were performed using the Stern-Volmer equation according to Xiancheng (2015) to assess the response and limit of detection of the prepared ZnO nanoparticles to different ammonium nitrate concentrations.

3.0 RESULTS AND DISCUSSION

3.1 Phytochemical Screening of Aqueous Extract of *Senna sieberiana* Leaves

3.1.1 Qualitative phytochemical screening of aqueous extract of *Senna sieberiana* leaves

The phytochemical screening of aqueous extract of *Senna sieberiana* leaves showed the presence of significant reductants which include phenol, flavonoids and tannin in considerable quantities as shown in Table 1. The quantitative presence of these bioactive compounds contained in *S. sieberiana* is in agreement with study on stem-bark composition in *Senna* species by Mohammed *et al.* (2013). The presence of these biomolecules in the aqueous extracts of *Senna sieberiana* explains the importance of plant in the biosynthesis of zinc oxide nanoparticles without the need of introducing additional chemical or stabilization agents (Kamalpreet and Kaushal, 2019).

Table 1: Phytochemical Constituents of Aqueous Leaf Extract of *Senna sieberiana*

S/No.	Phytochemical Constituents	Sample concentration (mg/100g)
1	Tannin	172.08 ±1.63
2	Phenol	493.03 ±1.72
3	Flavonoids	116.89 ±1.50

3.2 Characterization Analysis of Synthesized ZnO Nanoparticles

3.2.1 Scanning electron microscopy (SEM)/energy dispersive spectrum (EDS) of synthesized ZnO nanoparticles

The morphology of the synthesized ZnO nanoparticle was examined by SEM and the observed results shown in Plate 2. The observed SEM images revealed that the synthesized ZnO nanoparticles were spherical

in shape, possessing porous surfaces with rough edges and the average sizes of the nanoparticles ranging from 9nm – 17 nm which is consistent with average particle size obtained in a study carried out by Awwad *et al.* (2020) for the synthesis of Zinc oxide nanoparticles using aqueous *Ailanthus altissima* Fruit Extracts. The analysis of the samples by Energy Dispersive Spectrometer (EDS) confirms the elemental components observed in the sample. The EDS spectrum shows the peak of zinc and oxygen elements to be 80.08% and 18.55%, respectively for ZnONPs synthesized using the aqueous extracts of *S. sieberiana* as shown in Figure 1. The EDS analysis obtained shows that zinc oxide nanoparticles synthesized using *S. sieberiana* contains Zinc and oxygen which are in agreement with study on green synthesis of ZnO NPs using different plant extracts by Solabomi *et al.* (2019).

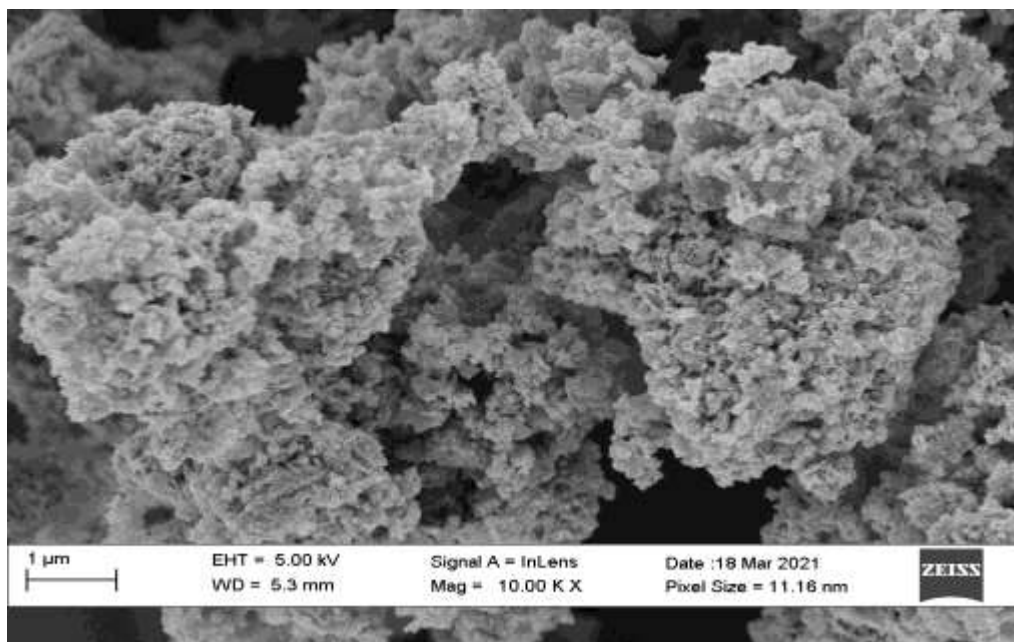


Plate 2: SEM micrograph of synthesized ZnO NPS at 10000x

Element	Wt %
Na	11.09
C	8.76
O	18.55
Mg	0.97
Si	1.44
Cl	0.32
Ca	1.42
Zn	80.45
Total:	100

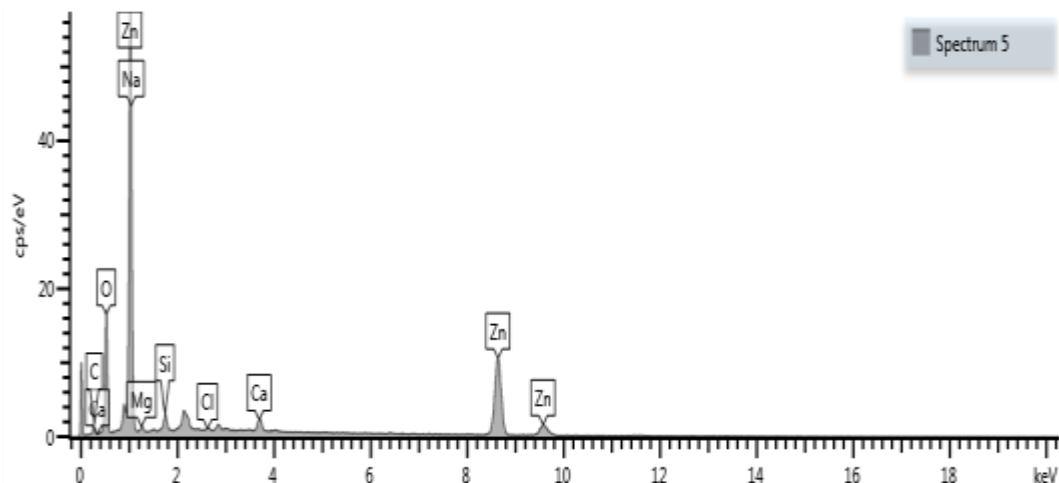


Figure 1: EDS spectrum of synthesized ZnO nanoparticles

3.2.2 UV-Visible spectrum of synthesized ZnO nanoparticles

UV-Visible spectroscopy recorded over the range of 200–700 nm range was further used to confirm the formation of ZnO NPs. In this study, the biosynthesized ZnO NPs using the aqueous extracts of *S. sieberiana* revealed absorption peak maxima at 372 nm indicating the formation of ZnO nanoparticles which is consistent with the studies of Solabomi *et al.* (2019).

The energy band gap of ZnO nanoparticles was computed by means of equation(1) shown below:

$$E = \frac{hc}{\lambda}$$

where, h is planks constant ($6.626 \times 10^{-34} \text{ J/s}$), c is the speed of light ($3 \times 10^8 \text{ m/s}$) and λ is the wavelength (372 nm) of the synthesized ZnO nanoparticles as represented in Figure 2. The energy band gap of ZnO was found utilizing equation (4.1) to be 3.29 eV which is consistent with result obtained by Shaheen *et al.*(2020) in the study of synthesis and application of Zinc Oxide nanoparticles as sustainable materials in

the fabrication of supercapacitor electrode.

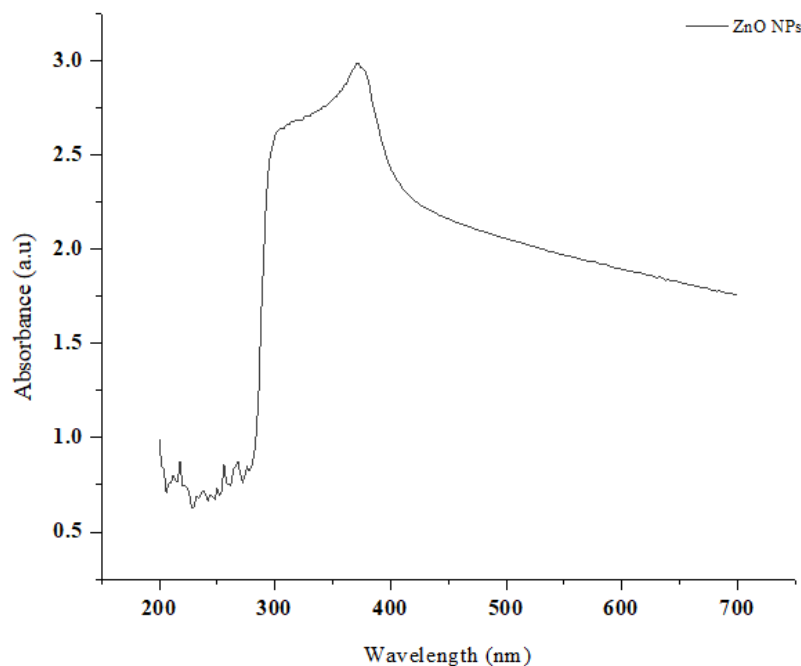


Figure 2: UV-Visible spectrum of synthesized ZnO Nanoparticles

3.2.3 Fourier transform infrared spectrum of synthesized ZnO nanoparticles

FTIR is used as a confirmatory technique to the nanoparticle formation and offers an impression to the vibrational modes of the existing molecules; hence it helps to identify the functional and possible phytochemical molecules present in the aqueous extract of *S. sieberiana* involved in the bio-reduction of Zinc nitrate to ZnO NPs. The ZnO NPs FTIR spectrum of this study reveals the functional group present in the aqueous *S. sieberiana* extract as represented in Figure 3. The FTIR spectrum of the synthesized ZnO NPs showed a weak peak at 672 cm^{-1} which corresponds to the hexagonal ZnO nanoparticles symmetric bending vibration and a peak at 702 cm^{-1} due to stretching vibration of ZnO nanoparticles, the region between $400\text{--}700\text{ cm}^{-1}$ is assigned for metal-oxygen bond (Awwad *et al.*, 2020). The peak present at 1428 cm^{-1} reflect the presence of --C=C vibrations, peak at 3428 cm^{-1} represent the $\equiv\text{C-H}$ vibration, the presence of C-H bond produced a peak at 2884 cm^{-1} and the peak at 2393 cm^{-1} shows the presence of $\text{--C}\equiv\text{C}$ bond, respectively contained in the aqueous extract.

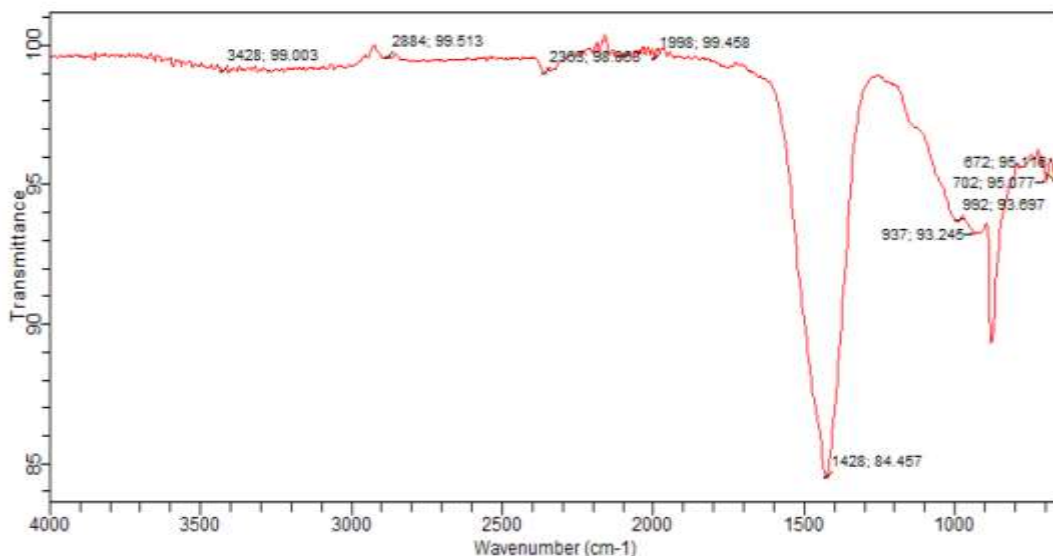


Figure 3: FTIR spectrum of synthesized ZnO Nanoparticles

3.2.4 X-Ray diffraction pattern of synthesized ZnO nanoparticles

X-ray diffraction pattern of synthesized ZnO NPs was obtained as displayed in Figure 4. The crystalline peaks positioned at (2θ) peaks angles of 31.74°, 34.42°, 36.23°, 47.52°, 56.64°, 62.84°, 66.30°, 67.89°, 69.01° correspond to the reflection from (100), (002), (101), (102), (110), (103), (200), (112), (201) crystal planes, respectively. By using the Debye-Scherrer's equation in equation (2), the average crystallite size of ZnO NPs was derived by calculating the Full Width at Half Maximum of the peaks and it was estimated to be between 15.41 nm – 24.82nm. These values obtained are consistent with the studies of Awwad *et al.* (2020).

Debye- Scherrer's equation:

$$L = \frac{K\lambda}{\beta \cos \theta} \quad (2)$$

Where, λ is the wavelength of X-ray source (Cu-K α line) and is a constant value of 0.1541 nm,

K is a constant value of 0.94

β is the full width at half maximum (FWHM) in radians and

θ is Bragg's diffraction angle.

3.2.5 Brummer-emmett-teller of synthesized ZnO nanoparticles

The BET analysis provided a description of the textural properties of the prepared ZnO nanoparticles with respect to the specific surface area, pore volume and pore size distribution. The surface area was given to be 481.465 m²/g, pore diameter was 2.116 nm, pore volume to be 0.240 cc/g. The BET characterization revealed the prepared ZnO nanoparticles is mesoporous in nature based on the IUPAC classification of material with pore size within 2-50nm classified as mesoporous materials.

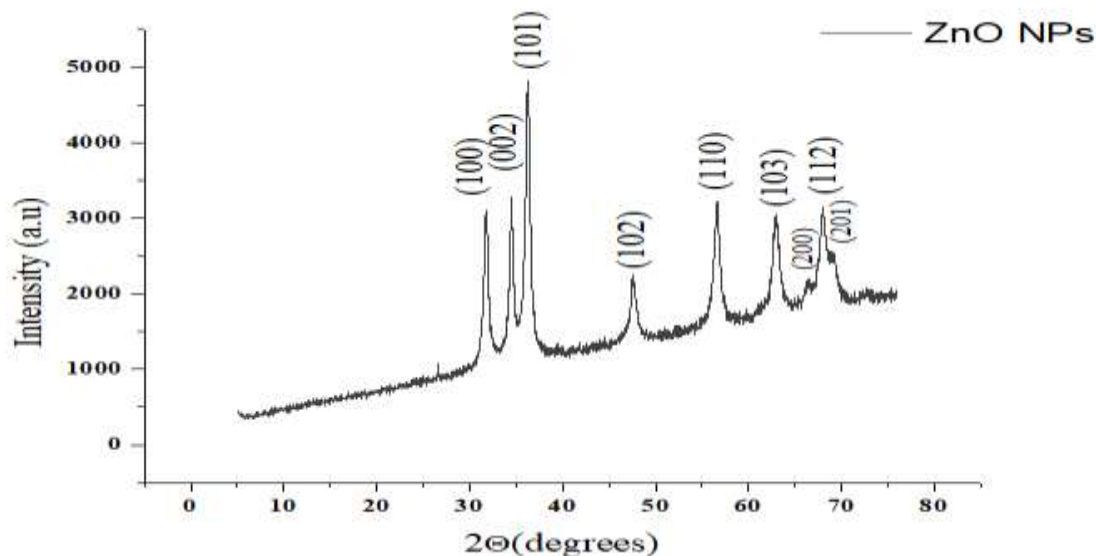


Figure 4: XRD spectrum of synthesized ZnO Nanoparticles

3.2.6 UV-Visible Sensing Study of NH_4NO_3 using Synthesized ZnO Nanoparticles

The ammonium nitrate sensing study was performed through UV-Visible measurement of the absorbance spectra of the carbon dots as a function of different ammonium nitrate concentration. (100 ppm, 75 ppm, 50 ppm, 25 ppm and 10 ppm). Figure 5 presents the UV-Visible measurement showing the shift in the peak wavelength value for ZnO Nanoparticles from 372 nm to 304 nm after the addition of ammonium nitrate solution.

It was also observed that the peak intensity of ZnO NPs at 304 nm decreases with an increase in concentration of the ammonium nitrate solution from 10 ppm to 100 ppm. The absorbance ratio of the various ammonium nitrate concentrations with ZnO NPs ($\text{abs}_{372}/\text{abs}_{304}$) when analyzed showed a linear relationship with a coefficient of multiple determination (R^2) value of 0.803 and negative gradient (Figure 6). The limit of detection (LOD) for the ZnO NPs was calculated to be -129.71 ppm, which suggests that the sensitivity of the ZnO NPs is at the level of a few parts per billion (Zhong, 2004). This is indicative of interaction, also photoinduced creation of electron hole pairs between the ZnO NPs and NH_4NO_3 solution as analyte concentration increases. Irradiation of the ZnO nanoparticles with UV-light enhances the response of the ZnO NPs sensor by reducing the surface band bending, thereby promoting better intergrain charge transport of the NH_4NO_3 analyte, thus improving the sensor signal and the profile of the signal (Lydon *et al.*, 2019).

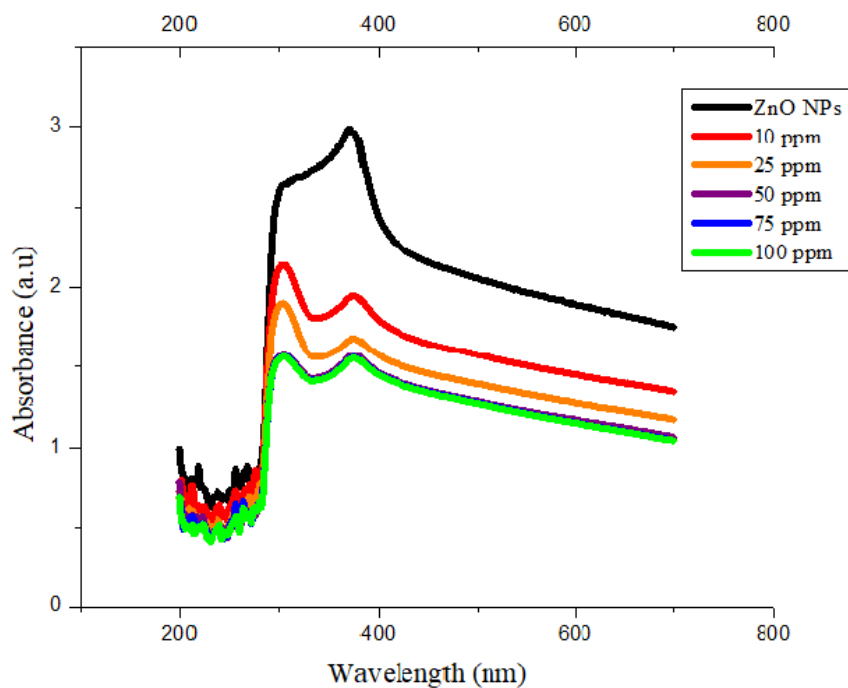


Figure 5: Change in the UV-Visible Spectra of ZnO NPs as a function of different concentrations of ammonium nitrate (10 – 100 ppm)

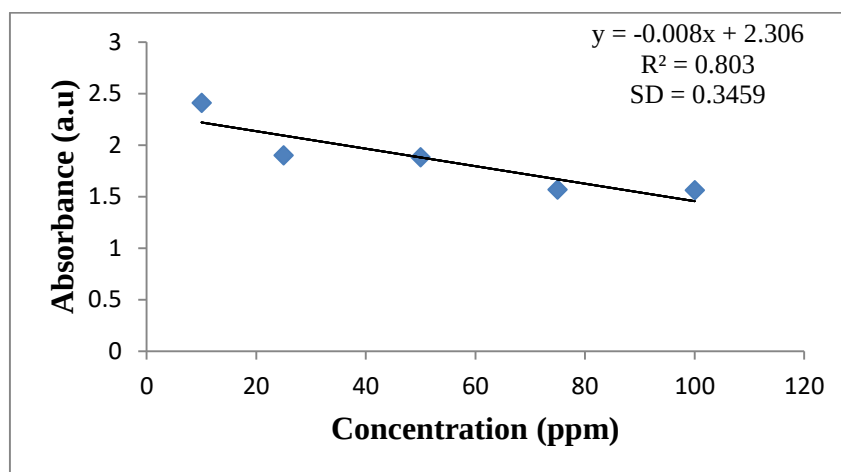


Figure 6: Absorbance ratio linear relationship plot of zinc oxide nanoparticles with ammonium nitrate (10-100 ppm)

4.0 CONCLUSION

The biosynthesis of Zinc oxide nanoparticles using aqueous extract of *Senna sieberiana* leaves. The presence of biomolecules in the aqueous extract of *Senna sieberiana* leaves were important for the biosynthesis of Zinc Oxide nanoparticles without the need of introducing additional chemical reducing agent, making the synthesis eco-friendly. Characterization using SEM, BET, FTIR, UV and XRD

confirmed the formation and properties of the ZnO nanoparticles. The sensitivity profile could be achieved as a result of the porosity and high surface volume ratio of the as-synthesized ZnO nanoparticles. This provide a sufficiently large surface active sites for intermolecular filling of the explosive analyte, which further facilitates a charge transfer thus, producing a measurable signal for its UV-Visible sensing studies. It is thus concluded that Zinc oxide nanoparticles is a sustainable materials in the fabrication of sensing materials for ammonium nitrate and other explosive analyte. It is recommended that ZnO nanoparticles-based sensors, be constructed as hybrid sensors, with other mesoporous nanomaterials for enhanced sensory performance.

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SN 22 PH-CONTROLLED SYNTHESIS AND SINTERING OF HOMOGENEOUS $\text{MgHf}_4\text{P}_6\text{O}_{24}$ POWDER

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Abstract

$\text{MgHf}_4\text{P}_6\text{O}_{24}$ is a Mg^{2+} ion conductor with an isotropic three-dimensional network structure. In this study, we examined the effect of pH adjustment on the synthesis of fine $\text{MgHf}_4\text{P}_6\text{O}_{24}$ xerogel powders by sol-gel chemical method from calculated stoichiometric amounts of analytical grade of $\text{Mg}(\text{NO}_3)_2$, HfCl_4 and $\text{NH}_4\text{H}_2\text{PO}_4$ precursor powders. Thermal analysis (DSC-TGA), X-ray diffraction (XRD) and Transmission Electron Microscopy (TEM) analyses revealed that controlling the pH from ~ 0.2 to ~ 8.9 with NH_3 solution during the sol-gel synthesis was favorable for obtaining fine homogeneous $\text{MgHf}_4\text{P}_6\text{O}_{24}$ xerogel powders, and it was also beneficial for obtaining a stable single phase sintered $\text{MgHf}_4\text{P}_6\text{O}_{24}$ pellets after calcination at 900 °C. Sintering of the pH-controlled xerogel powders after pelletisation at 1300 °C for 24 h resulted in $\sim 98\%$ dense $\text{MgHf}_4\text{P}_6\text{O}_{24}$ solid electrolyte which had an electrical conductivity of $4.52 \times 10^{-4} \text{ Scm}^{-1}$ at 747 °C and activation energy of $0.74 \pm 0.02 \text{ eV}$.

Keywords: Synthesis, pH, Calcination, Sintering, Electrical Conductivity, Activation Energy

1.0 INTRODUCTION

Improved data on sol-gel synthesis and its influence on the structural and electrical behaviour of $\text{MgZr}_4\text{P}_6\text{O}_{24}$ solid-state electrolyte have been well published (Adamu and Kale, 2016; Adamu *et al.*, 2020; Kale *et al.*, 2004; Fergus, 2009; Pet'kov *et al.*, 2014; Kale and Jacob, 1989; Kale *et al.*, 1996; Mudenda and Kale, 2017). However, as a larger part of our research interest of the investigation of phosphate solid-state electrolytes and their applications, we report on the sol-gel synthesis of $\text{MgHf}_4\text{P}_6\text{O}_{24}$ solid-state nanopowders because of the improvement on the structural and electrical behaviour reported earlier (Adamu and Kale, 2016; Adamu and Kale, 2020; Kakihana, 1996). The sol-gel synthesis has brought improvement in the homogeneity of xerogel powders, better density, ionic mobility, and conductivity of the Mg^{2+} -ion conducting species in $\text{MgHf}_4\text{P}_6\text{O}_{24}$ solid-state electrolyte (Adamu and Kale, 2016; Adamu *et al.*, 2020; Adamu and Kale, 2020).

Temperature, stoichiometric compositions and pH were some factors relied on while sintering of the pelletised $\text{MgHf}_4\text{P}_6\text{O}_{24}$ nanopowders into dense electroceramics for impedance measurement. In the following sections we present the details of pH-controlled sol-gel synthesis, characterisation techniques incorporating $\text{MgHf}_4\text{P}_6\text{O}_{24}$ solid-state electrolyte for impedance measurement.

2.0 EXPERIMENTAL PROCEDURE

2.1 Materials preparation

All chemicals are analytical grade and used as received without further purification. Homogeneous $\text{MgHf}_4\text{P}_6\text{O}_{24}$ xerogel powders were synthesised using sol-gel method, and this was achieved through mixing on an atomic scale by combining aqueous solutions of precursor soluble salts at relatively low crystallisation temperature and, it produces chemical compositions not always possible by solid-state fusion method. The stoichiometric amount of pure chemical solutions from the precursors $\text{Mg}(\text{NO}_3)_2$, HfCl_4 and $\text{NH}_4\text{H}_2\text{PO}_4$, in aqueous form were mixed separately in stoichiometric proportion to synthesis $\text{MgHf}_4\text{P}_6\text{O}_{24}$ xerogel powders at a pH of ~ 0.2 which was later neutralised to ~ 8.9 using dilute NH_3 solution, and the wet xerogel was dried on a hot plate at 100°C . The resulting dried xerogel powders were calcined at 900°C , then pelletised and sintered at 1300°C , using data extract from TGA-DSC profiles. Furthermore, the sintered dense pellet of $\text{MgHf}_4\text{P}_6\text{O}_{24}$ solid-state electrolyte was further characterised for their ionic conductivity. The impedance spectroscopy measurement in this study was achieved using two-probe analysis at an impedance temperature range from 182 to 764°C at a frequency range from 100 MHz to 32 MHz .

2.2 Materials characterisation

Simultaneous Thermal Analyser, STA 8000 (PerkinElmer, Seer Green, UK) was used to measure the TGA-DSC which was used to analyse the weight loss and thermal oxidation behaviour of the dried xerogel powders. In this analysis, effective optimisation calcination condition of the xerogel powders in a controlled atmosphere at a flow rate of 50 mL min^{-1} using constant heating-cooling rate at $10^\circ\text{C min}^{-1}$ with temperature range of $30 - 1000^\circ\text{C}$ is akin to that described in our recent papers (Adamu *et al.*, 2020; Adamu and Kale, 2020). Based on this analysis, the resultant dried xerogel powders were calcined at 900°C , and the calcined nanopowders were pelletised and sintered at 1300°C , using the same heating-cooling condition.

Powder x-ray diffractometer (Bruker D8 advance, Karlsruhe, GmbH) equipped with $\text{CuK}\alpha 1$ ($\lambda = 1.5406\text{ \AA}$) radiation source operating at 30 kV and 45 mA , calibrated against Si standard was deployed to analyse the phase structure of $\text{MgHf}_4\text{P}_6\text{O}_{24}$ xerogel powders over $10^\circ \leq 2\theta \leq 80^\circ$ scan range.

Impedance analyser, Solartron SI1260 FRA (Hampshire, UK) was used to analyse the electrical behaviour of the solid-state electrolyte. Sintered pellets of $\text{MgHf}_4\text{P}_6\text{O}_{24}$ solid-state electrolyte was mildly ground to achieve a flat surface area without diminishing the pellets thickness. Platinum paste (Sigma-Aldrich, UK) was lightly applied to the opposite parallel faces of the sintered pellets and allowed to dry before firing in a tube furnace (Fig. 1) at 800°C for 0.5 h to form contact electrodes on both surfaces of the pellets. Ionic conductivity was thereafter recorded as a function of temperature and frequency in 182 to 764°C temperature and 100 MHz to 32 MHz frequency range, respectively.

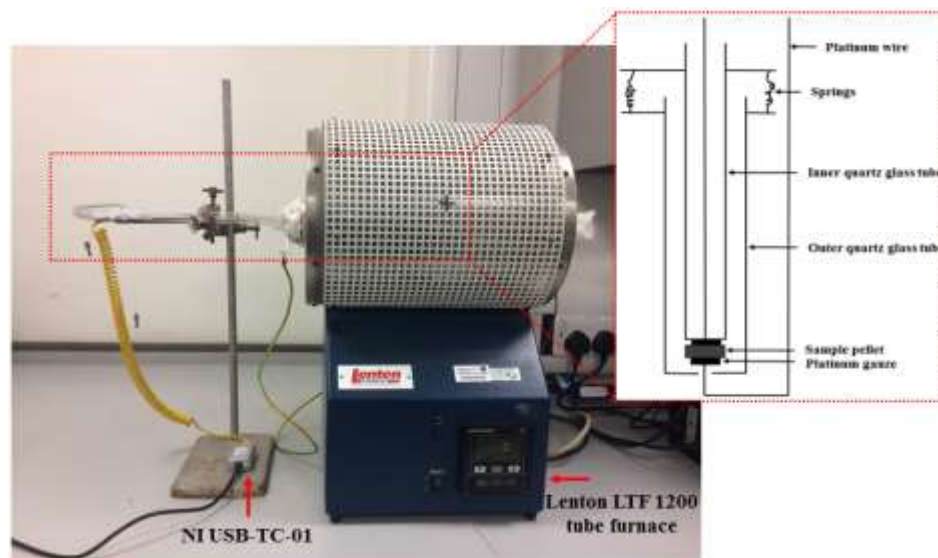


Figure 1. Quartz assembly rig for impedance measurements in a Lenton LTF 1200 tube furnace.

3.0 RESULTS AND DISCUSSIONS

3.1 Thermal analysis (TGA-DSC)

Thermal analysis (TGA-DSC) profile curves in Fig. 2 shows the main decomposition changes in the $\text{MgHf}_4\text{P}_6\text{O}_{24}$ xerogel powders. The TGA decomposition in this study is presented in three different regions: The first region within 30 - 100 oC corresponds to the removal of lattice H_2O . The second region shows weight loss in the 150 - 500 oC temperature range which is because of the decomposition or oxidation of gelled inorganic precursor materials such as $\text{Mg}(\text{NO}_3)_2$, HfCl_4 and $\text{NH}_4\text{H}_2\text{PO}_4$. In the third region, there was no further reduction in weight above 500 ± 25 oC for the $\text{MgHf}_4\text{P}_6\text{O}_{24}$ xerogel powders. Similarly, the DSC profiles of $\text{MgHf}_4\text{P}_6\text{O}_{24}$ xerogel powders in Fig. 2 clearly shows two endothermic decomposition peaks at 150 °C and 350 °C, and an exothermic peak at 900 oC. Moreover, it is known that the inorganic precursor, $\text{NH}_4\text{H}_2\text{PO}_4$ decomposes into $(\text{NH}_4)_3\text{H}_2\text{P}_3\text{O}_{10}$ and H_2O molecules at 140 - 170 oC which could be responsible for the endothermic peak at 150 oC. $\text{Mg}(\text{NO}_3)_2$ compound also decomposes into MgO , NO_2 , and O_2 at a temperature above 300 oC, this could be responsible for the endothermic peak at 350 oC. The reactive oxide HfO_2 formed by oxidation of HfCl_4 at 432°C yields $\text{MgHf}_4\text{P}_6\text{O}_{24}$ after stoichiometric composition reaction with MgO and P_2O_5 reactive oxides at 900 oC. Therefore, the exothermic peak observed at 900 oC indicates the formation of a single phase $\text{MgHf}_4\text{P}_6\text{O}_{24}$ nanoparticles with full crystallinity. In this study however, the TGA-DSC measurement was limited to 1000 oC because of the heating capacity range of the equipment.

Based on this TGA-DSC analysis for $\text{MgHf}_4\text{P}_6\text{O}_{24}$ xerogel powders, it was resolved that a pure single phase was fully crystallised at 900 oC.

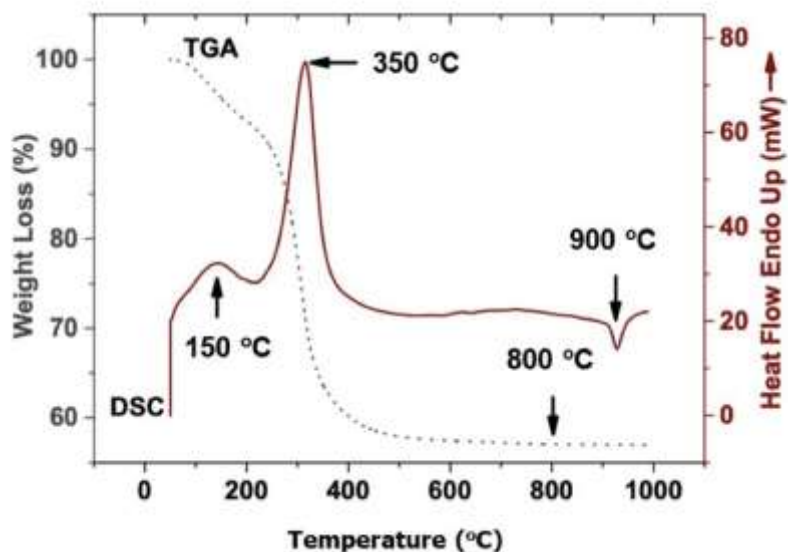


Figure 2. TGA-DSC profiles of $\text{MgHf}_4\text{P}_6\text{O}_{24}$ dried xerogel powders at a scan rate of $10^\circ\text{C min}^{-1}$ in the air.

3.2 X-ray diffraction (XRD)

X-ray diffraction data of calcined and sintered $\text{MgHf}_4\text{P}_6\text{O}_{24}$ nanoparticles presented in Fig. 3 also corroborated the conclusion arrived at using Fig. 2, which shows single-phase formation for the dried xerogel powders calcined at 900°C and the corresponding pelletised nanopowders, sintered at 1300°C , with majority of the peaks matched and indexed appropriately.

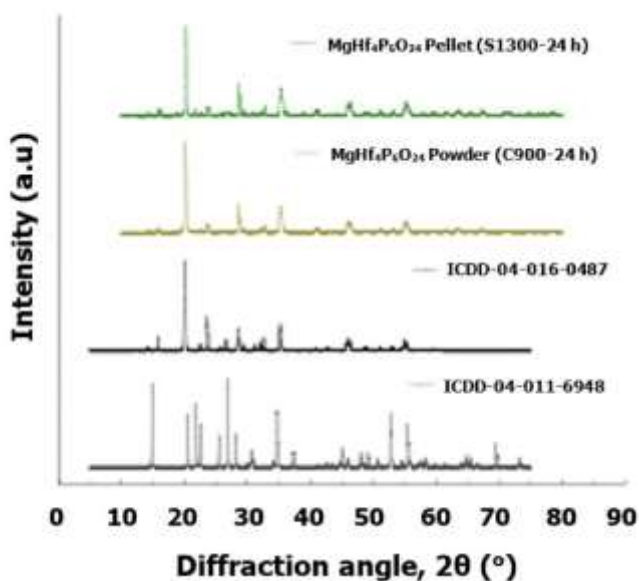


Figure 3. X-ray diffraction peaks of $\text{MgHf}_4\text{P}_6\text{O}_{24}$ nanopowders calcined at 900 °C and sample pellets sintered at 1300 °C. All peaks were indexed to $\text{Mg}_0.5\text{Zr}_2(\text{PO}_4)_3$ [ICDD-04-016-0487] and $\text{Zr}_2(\text{PO}_4)_2\text{O}$ [ICDD-04-011-6948].

3.3 Relative density

$\text{MgHf}_4\text{P}_6\text{O}_{24}$ sample pellets in Fig. 4 shows that relative density increases with sintering temperature at a constant annealing time. In this study, the sample pellets were subjected to sintering temperatures of $1000^\circ\text{C} \leq T \leq 1500^\circ\text{C}$ at 24 h annealing time. In Fig. 4, the sample pellet begins to show some densification (~95%) at temperature higher than 1100°C and exhibited an optimum density of about 98% at 1300°C for 24 h. Furthermore, the increment in density between 1300-1500°C is only ~1%, signifying that a saturation point has been reached for the densification of $\text{MgHf}_4\text{P}_6\text{O}_{24}$ sample pellets. The porosity of ~2% was achieved at 1300°C which is considered good enough for the solid-state electrolyte sample pellets in electrochemical applications. In this study, 1300°C sintering temperature at annealing time of 24 h was considered suitable for purpose of comparison and that since the difference in percentage-relative density is only ~1% from 1300-1500°C, a saturation point was already achieved at 1300°C. Using 1300°C as sintering temperature according to the density profile, a pure stable phase was also achieved for the characterised solid-state electroceramics.

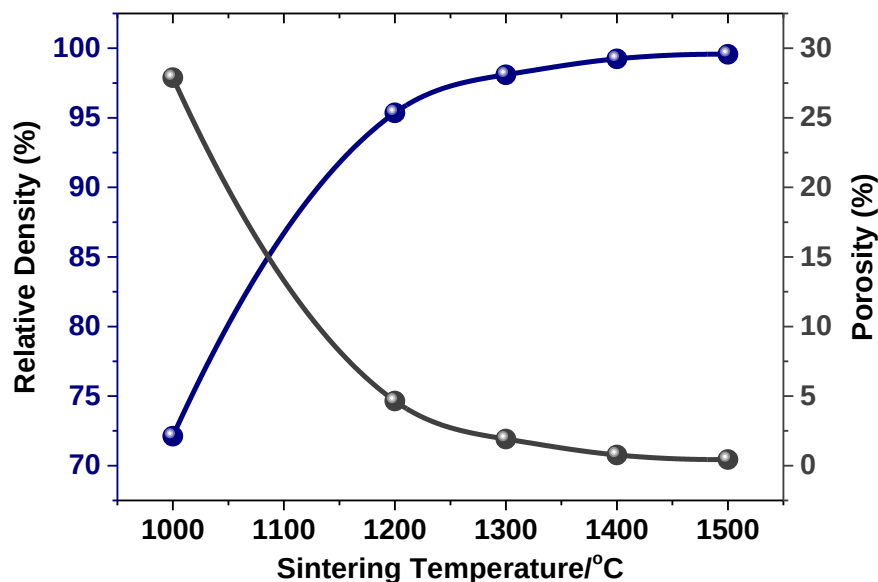


Fig. 4. Dependence of percentage-relative density and porosity of the sample pellets of $\text{MgHf}_4\text{P}_6\text{O}_{24}$ compound on sintering temperature

3.4 Temperature dependence of ionic conductivity

Figure 5 shows the ionic conductivity of sintered $\text{MgHf}_4\text{P}_6\text{O}_{24}$ solid-state electrolyte as a function of temperature. In this study, the ionic conductivity of $\text{MgHf}_4\text{P}_6\text{O}_{24}$ solid-state electrolyte was measured showing potential of being used interchangeably in both structural and electrochemical applications. In Fig. 5, the linearity of the plot suggest there are no significant structural and phase changes noticed in the impedance temperature range. The activation energy, E_a includes energy of the formation and migration of ions in the solid-state electrolyte was determined from the gradient of Arrhenius plot by fitting the ionic conductivity data with Arrhenius equation in Eq. 1

$$\sigma T = \sigma_0(T) \exp\left(-\frac{E_a}{kT}\right) \quad (1)$$

Figure 5 shows that the ionic conductivity of the solid-state electrolyte increases exponentially as the impedance temperatures increase, and the bulk $\text{MgHf}_4\text{P}_6\text{O}_{24}$ solid-state electrolyte exhibits an ionic conductivity of $4.52 \times 10^{-4} \text{ Scm}^{-1}$ at 747°C . In addition, the bulk activation energy, E_a of $\text{MgHf}_4\text{P}_6\text{O}_{24}$ solid-state electrolyte shown in Fig. 5 deduced from the slope of $\ln \sigma T - 1000/T$ plots are $0.74 \pm 0.02 \text{ eV}$ and this signifies greater mobility of the Mg^{2+} ions.

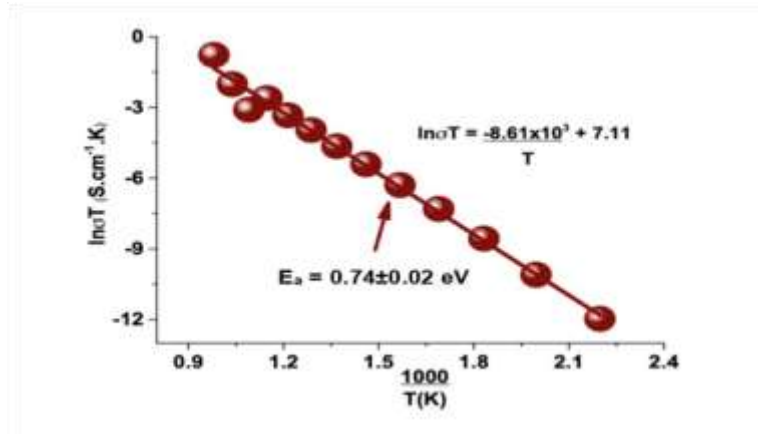


Figure 5. Bulk ionic conductivity of $\text{MgHf}_4\text{P}_6\text{O}_{24}$ solid-state electrolyte as a function of temperature

CONCLUSION

We have examined the effects of pH control on the synthesis of homogeneous $\text{MgHf}_4\text{P}_6\text{O}_{24}$ powders using sol-gel synthesis. This study however shows that a weakly basic sol-gel condition at $\text{pH} \sim 8.9$ was favourable to the synthesis of homogeneous single phase $\text{MgHf}_4\text{P}_6\text{O}_{24}$ nanopowders and sintered pellets with a relative density of $\sim 98\%$ and ionic conductivity of $4.52 \times 10^{-4} \text{ Scm}^{-1}$ at 747°C .

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This research material is based entirely upon our research findings of the phosphate electroceramic electrolytes and their applications, and as such, we sincerely thank all those who have been directly or indirectly involved in it.

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SN 23 THE CHEMICAL AND MINERALOGICAL ANALYSIS OF CALCINED PALM BUNCH ASH AND BONE POWDER WASTES FOR CEMENT REPLACEMENT IN CONCRETE AND MORTAR DEVELOPMENT AND PRODUCTIONS

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Abstract

Cement is one of the vital building materials whose continuous production has put the world at risk of the effects of global warming. Also the high cost of this conventional building material has increased the construction cost of buildings. The study involves the chemical, thermal and mineralogical analysis of the calcined palm bunch ash and bone powder wastes (CPBABPW) and their suitability in partial replacement of Portland cement. The chemical and mineralogical properties of calcined Palm bunch ash and bone powder were determined with an X-ray fluorescence spectrophotometer and X-ray diffractometer respectively. To determine the thermal properties and mass evolution of the samples at a given temperature, the thermal analysis of the samples was done with the DSC / TGA. The Calcined palm bunch ash and bone powder were mixed in the percentage ratio of 10:90, 30:70 and 50:50 respectively and the mixing ratio of M20 (1:2:4) was used with a water to cement ratio of 0.6 and partial replacement of the Portland cement with the (CPBABPW) were in 0, 5, 10, 15, 20, 25, 30, 35, 40, 45 and 50 percentages (%). Standard cubes of 50*50*50mm were used for casting the concrete. The results of the chemical, mineralogical and thermal characterizations of calcined palm bunch ash reveal the elemental compositions as follows Al₂O₃ (0.56%), K₂O (44.44%), SiO₂ (17.81%), CaO (14.22%), MgO (1.92%) and P₂O₅ (2.18%) while that of bone powder waste are; Al₂O₃ (0.67%), SiO₂ (2.81%), CaO (49.72%), MgO (0.48%), F₂O₃ (0.14%) and P₂O₅ (33.39%). The results show a predominance of pozzolanic oxides. The thermal analysis results show a small loss of mass of 8 % at 1000 °C for CPBA and BP, a total mass loss of 16% was observed. The permeability, porosity and water absorption increase slightly with the increase in the admixtures while the bulk density and the comprehensive strength slightly decrease with the increase in the admixtures. The results of the study show that calcined palm bunch ash wastes combined with bone powder can be used as a partial replacement for cement up to 40% could be alternative building materials for sustainable concrete production and economic disposal of waste materials.

KEYWORDS: Palm bunch; Bone powder; calcined wastes; pozzolanic; Mineralogical; Analysis.

1. INTRODUCTION

The rate of demand for cement is increasing astronomically due to the increase in industrialization, globalization, and structural development. As a result, the production of cement has been the major cause of global warming because of the high energy demand and subsequent emission of CO₂ (Govind Singh et al., 2020). Also, cement, which is the conventional material for concrete production, is scarce

and, at the same time, expensive. The use of abundant waste materials as substitutes becomes paramount due to the sustainability of the production (Uzoho *et al.*, 2019).

The poor solid waste management in developing countries is an issue of great concern because of the unimaginable degradation these wastes are causing within their environs. The waste materials have been used as a substitute for one or more concrete constituent materials (Auwal *et al.*, 2022).

In the work done by Auwal *et al.* (2022), the suitability of animal bone ash as a partial replacement of cement in concrete production was investigated, and from the results of their studies, it was found that animal bone ash reduces the strength of the concrete. It is observed that the compressive strength reduces from 0%, 5%, 10%, 15%, and 20%. Also worthy of note is that concrete mix containing not more than 5% of animal bone ash showed a little reduction in the final strength, and thus bone powder alone can be used for light construction work.

Pande and Makarande (2013), studied the effect of rice husk ash on concrete development. According to the results of the research, rice husk ash waste can be utilized in concrete production as a partial replacement for Portland cement and serves to improve the strength of the concrete and waste management control. The mixing proportion was done based on the various ratios of the rice husk ash being used to replace the cement in this order: 0, 12.5, 25, and 37.5% by mass. In this research, it was found that cement use and costs are reduced when 12.5% of the cement is replaced with rice husk ash in the matrix. (Vasoya & Varia, 2015). Akinyele *et al.* (2016) worked on the utilization of animal bone ash and wood ash as the replacement of cement in concrete production; it was found that the animal bone ash contains much more pozzolanic properties when compared with the wood ash. Therefore, it was used as the best replacement, which shows good results at 10% replacement of cement among the range of 0–25% used in the research work (Auwal *et al.*, 2022).

From the literature, it is found that one material cannot satisfy the pozzolanic qualities required in inorganic binding materials; hence, the need for exploration, chemical, and mineralogical analysis of calcined palm bunch ash and bone powder wastes for their suitable replacement of cement in concrete development and production informed this work.

2.0 Materials and Method

2.1 Materials

The materials used in this work were Dangote Cement, Nsude sand (fine aggregate), gravel (0.2-0.5mm), palm bunches, cow bones and water.

2.2 METHOD

2.2.1 The samples collection, Preparation and physicochemical Analysis

The samples of palm bunches were collected in the village of Nike Abakpa, Enugu State, and brought to the PRODA Ceramics workshop, where the palm bunches were burned to ashes. The ashes were then packed in a bisque pot, loaded in a kiln, and calcined at 500 oC. The cow bones were bought at Mami Market in Abakpa Enugu and loaded into the kiln, where they were calcined at 800 oC and subsequently crushed to powder form.

The powdered samples were all sieved with a 100-mesh sieve for the homogeneity of the mixtures. The prepared samples were characterized to determine the elemental composition using EDX3600B X-ray fluorescence (XRF) spectrometer. The samples were mixed with a cellulose binder and pelletized in an XRF pellet press. The samples were loaded into the EDX3600B sample holders for the analysis, and

the mineralogical phase elucidation was done with an Australian GBC Enhance Mini-Material Analyzer (EMMA) X-ray diffractometer. The degree of crystallinity was measured using MATCH crystal impact identification from a powdered diffraction software package (version 3.4.2 Build 96) utilizing the FullProof Suit program (2.05) for Rietveld refinement.

Thermo-analytical characterizations of the samples were done using the SDT Q600 V20.9 Build 20 instrument. The sample was heated at a rate of 10 °C/min, reaching a maximum temperature of 1000 °C, and then cooled to room temperature. The DSC and TGA data were registered.

2.2.2 THE PHYSICAL ANALYSIS OF THE PRODUCED CONCRETE SAMPLES

Making moisture determination

This was determined by weighing the concrete immediately after molding and recorded as the wet weight, W_o . The test pieces air-dried for 24hrs and then dried in an oven at 105°C until a constant weight was recorded. After drying the test pieces were weighed and the dried weight recorded as W_i . The making moisture was then calculated.

$$\text{Making Moisture (\%)} = \frac{[W_o - W_i]100}{W_o} \quad 1$$

Determination of water of absorption

The concrete test pieces obtained after drying were then weighed and the weight recorded as dry weight, M_1 (g). Thereafter, the test pieces were soaked in water for one hour, then removed, cleaned and weighed immediately and recorded as soaked weight, M_2 (g). The water of adsorption was then calculated:

$$\text{Water of Absorption (\%)} = \frac{100 [M_2 - M_1]}{M_1} \quad 2$$

Porosity and density determination

After the procedure described above was completed, the suspended weight of the test pieces was then determined by the use of a lever balance and recorded as M_3 (g). After the procedure described above was completed, the suspended weight of the test pieces was then determined by the use of a lever balance and recorded as M_3 (g). The apparent density of the sample is dependent on the external volume of the sample; it is defined as the weight of a given volume divided by the volume, while the bulk density is dependent on the overall space occupied by the materials of the sample. It is based on how the samples are packed; that is, a closely packed sample of a material would have a higher bulk density than a normally poured sample. Density is a concept defined for any substance, while bulk density is only used in cases where the particles of matter are packed with space for air within. The bulk density of a substance varies with the state the sample is in. Therefore, it is not an intrinsic property of a material, whereas density is an intrinsic property. The apparent porosity, apparent density, and bulk density were then calculated:

$$\text{Apparent Porosity (\%)} = \frac{100 [M_2 - M_1]}{M_2 - M_3} \quad 3$$

$$\text{Apparent Density} = \frac{M_1}{[M_1 - M_3]} \quad 4$$

$$\text{Bulk Density} = \frac{M_1}{[M_2 - M_3]} \quad 5$$

2.2.3 MIXED PROPORTION

Tables 2, 3, and 4 show the formulations of different mixes using calcined palm bunch ash and bone powder in a percentage ratio of 10:90, 30:70, and 50:50 to have admixtures A to C, respectively. Each of the admixtures was used to partially replace the Portland cement in 0, 5, 10, 15, 20, 25, 30, 35, 40, 45, and 50 percentages (%) to have ten samples per admixture and we have a total of 30 samples produced altogether. The mixing ratio of M20 (1:2:4) was used with a water-to-cement ratio of 0.30, and standard cubes of 50*50*50mm were used for casting of the concrete. Control mixes designated as A0, B0 and C0 were made without admixture of A, B and C respectively

2.2.3 Formulation of the samples

Table 1: Formulation of concrete using admixture A

Code	Admixture 1(%) (%)	Cement 14.26% (1)	Fine sand (%)(2)	Coarse aggregate (%) (4)	Water (%)
A0	0	100	28.6	57.14	0.3
A1	5	95	28.6	57.14	0.3
A2	10	90	28.6	57.14	0.3
A3	15	85	28.6	57.14	0.3
A4	20	80	28.6	57.14	0.3
A5	25	75	28.6	57.14	0.3
A6	30	70	28.6	57.14	0.3
A7	35	65	28.6	57.14	0.3
A8	40	60	28.6	57.14	0.3
A9	45	55	28.6	57.14	0.3
A10	50	50	28.6	57.14	0.3

Admixture A is the mixture of calcined palm bunch ashes and animal bone powder at 10% and 90% respectively.

Table2: Formulation of concrete using admixture B

Code	Admixture Cement (%)	B (%) 14.26% (1)	Fine sand (%) (2)	Coarse aggregate (%) (4)	Water (%)
B0	0	100	28.6	57.14	0.3
B1	5	95	28.6	57.14	0.3
B2	10	90	28.6	57.14	0.3
B3	15	85	28.6	57.14	0.3
B4	20	80	28.6	57.14	0.3
B5	25	75	28.6	57.14	0.3
B6	30	70	28.6	57.14	0.3
B7	35	65	28.6	57.14	0.3
B8	40	60	28.6	57.14	0.3
B9	45	55	28.6	57.14	0.3
B10	50	50	28.6	57.14	0.3

Admixture B is the mixture of calcined palm bunch ashes and animal bone powder at 30% and 70% respectively

Table 3; Formulation of concrete using admixture C

Code	Admixture Cement (%)	C (%) 14.26% (1)	Fine sand (%) (2)	Coarse aggregate (%) (4)	Water (%)
C0	0	100	28.6	57.14	0.3
C1	5	95	28.6	57.14	0.3
C2	10	90	28.6	57.14	0.3
C3	15	85	28.6	57.14	0.3
C4	20	80	28.6	57.14	0.3
C5	25	75	28.6	57.14	0.3
C6	30	70	28.6	57.14	0.3
C7	35	65	28.6	57.14	0.3
C8	40	60	28.6	57.14	0.3
C9	45	55	28.6	57.14	0.3
C10	50	50	28.6	57.14	0.3

Admixture C is the mixture of calcined palm bunch ashes and animal bone powder at 50% and 50% respectively

3. RESULTS AND DISCUSSION

Results of Chemical and Mineralogical Analysis of Calcined Palm Bunch and Bone Powder

Table 4: Chemical Composition of calcined palm bunch ash, bone powder and portland cement

Composition (%)	Calcined palm bunch ash	Bone powder	Portland Cement (Almabrok&Khashin.,2019)
SiO ₂	17.81	2.87	17-25
Al ₂ O ₃	0.58	0.67	3.0-8.0
K ₂ O	44.44	0.00	0.4-1.3
CaO	14.22	49.72	60-67
TiO ₂	0.0	0.00	
P ₂ O ₅	2.18	33.39	
Fe ₂ O ₃	1.86	0.14	0.5-6.0
MgO	1.92	0.48	0.1-4.0

The chemical compositions of the calcined palm bunch and bone ash were determined with X-ray fluorescence. The results are shown in Table 1.

It is observed that PBA has more potassium oxide (K₂O) at 44.4%, followed by SiO₂ and CaO at 17.81% and 14.22%, respectively. The chemical composition of bone powder is presented, as shown in Table 4. It is seen that the bone powder has mainly lime (CaO) and Phosphorus pentoxide (P₂O₅) as chemical oxides. This suggests that the major inorganic component of bone ash may be hydroxyapatite (Ca₅(PO₄)₃OH) which is consistent with the results of the X-ray diffraction and in agreement with other researchers' reports (Bih *et al.*, 2021, Zhao *et al.*, 2018). The main oxides present in Portland cement which include CaO, SiO₂, Al₂O₃, Fe₂O₃, MgO and K₂O were also present in calcined palm bunch ash and bone powder when put together as shown in Table 4. It is observed that the CaO content in the samples is within the specified limits of the ASTM C150 standard (ASTM, 2012).

The silica (SiO₂) content for the two samples when mixed is expected to be within the range of ASTM C150 standard. The calcined palm bunch ash has more silica content than bone powder. Silica (SiO₂) gives strength to cement due to the formation of dicalcium and tricalcium silicate. Also, silica determines the fineness and the grinding ability of the cement and imparts strength to cement (ASTM, 2012). Excess alkaline in a binder gives rise to cracking and general weakness due to the contraction and expansion reaction of the alkaline oxide resulting from the hygroscopic nature of the oxides, though the alkaline oxides (K₂O and Na₂O) help in the quick setting of the concrete or mortar when it is within the range of (0.3 – 0.2%) (Almabrok and Khashin, 2019) (Bediako and Amankwah., 2015). The alkaline oxide was not detected in the bone powder as shown by the XRF results in Table 1 above while the Palm bunch has high alkaline oxide (K₂O) contents and was added to introduce the alkaline oxides into the admixtures.

Alumina (Al₂O₃) and magnesia (MgO) are important requirements in the strength enhancement of concrete. It can be seen from Table 4, that both palm bunch and bone powders have less content of Al₂O₃ and MgO when compared with the standard cement compositions.

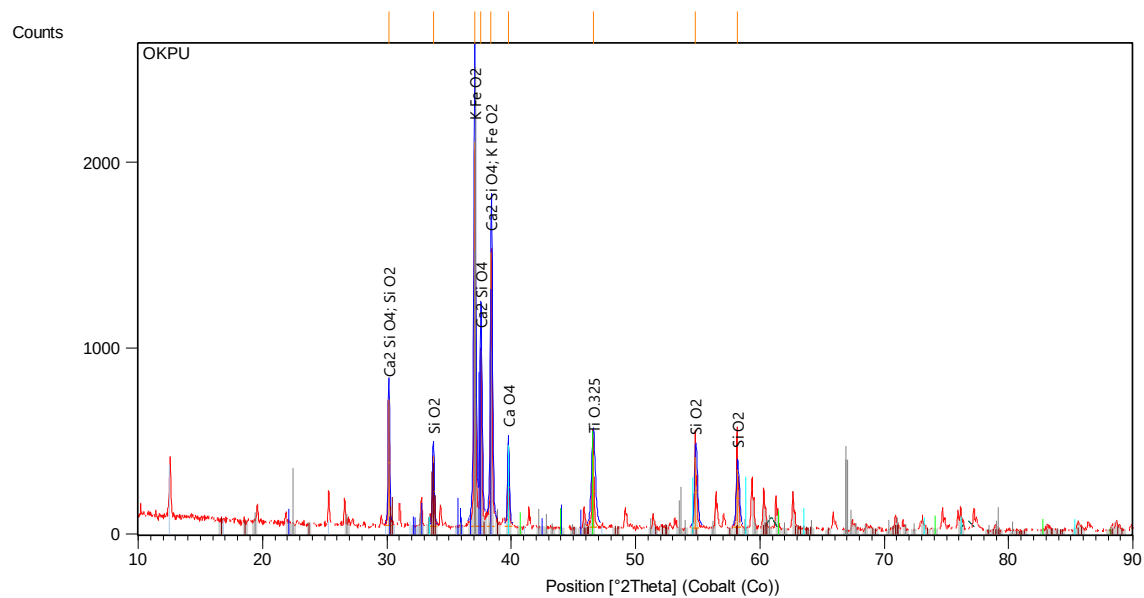


Figure 14: X-Ray Diffractogram of the Calcined bone powder sample

The result of the mineralogical analysis of calcined bone powder is shown in the X-ray diffractogram above (Fig. 1). The peaks revealed in the XRD patterns indicate predominantly calcium oxide ($2\theta = 30.14518^\circ$, $d = 3.44233$). Other diffraction peaks at 2θ values of 33.72° , 37.05° , 37.55° , 38.39° , 39.75° , 46.58° , 54.82° and 58.18° with corresponding d -spacing values of 3.086, 2.817, 2.78, 2.72, 2.63, 2.26, 1.94 and 1.84 confirm the presence of hydroxyapatite ($\text{Ca}_5(\text{PO}_4)_3\text{OH}$) with some minor Quartz (Malla *et al.*, 2020). The characterization of calcined bone powder by X-ray diffraction shows that the analysis obtained in the present research is in good agreement with the ones reported by Bih *et al.* (2022). The bone ash serves as a good source of calcium oxide, which is an integral part of mortar for construction, and it improves the mechanical properties and setting time of cement. Calcium hydroxide (portlandite) also reduces the water absorption of the concrete (Nwakwo *et al.*, 2020)

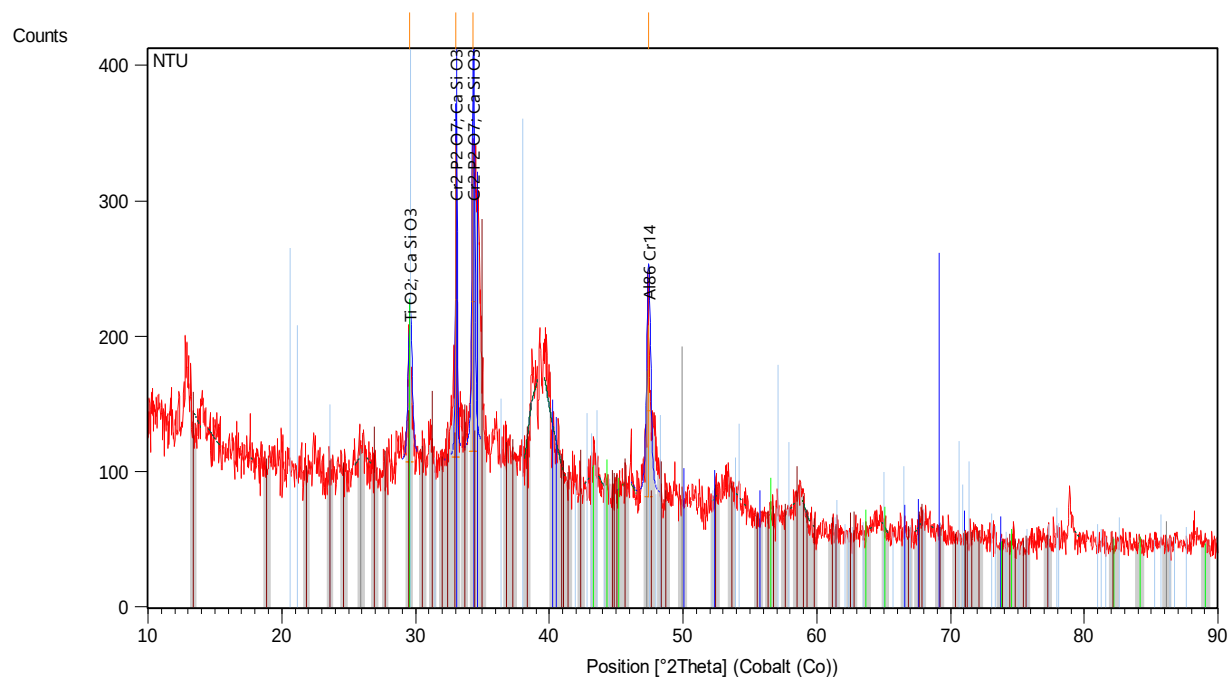


Figure 15: X-Ray Diffractogram of the Calcined Palm bunch ash sample

The result of the mineralogical analysis of calcined palm bunch ash is shown in fig2. The diffractogram indicates the presence of potash (K_2O) crystalline and amorphous phase of silica in the Palm bunch ash. The diffraction peaks at 2θ values of 29.58, 33.03, 34.31 and 47.39 with corresponding d-spacing values of 3.50, 3.15, 3.03 and 2.22 confirmed the samples to be more K_2O origin with other crystals; SiO_2 , CaO , and TiO_2 (Yaacob *et al.*, 2011) The XRD result of the calcined palm bunch ash agrees with the one reported by Nelson *et al* (2023). The amorphous silica increases with increase in the calcination of palm bunch ash. The results from the XRD and XRF show that the bone powder has more pozzolanic properties due to the high concentrations of CaO

Sample: OKTU
Size: 3.6920 mg
Method: Ramp

DSC-TGA

File: C:\...Results\DR VIC\2022\NEWRH@450.002
Operator: MESHACK
Run Date: 15-Nov-2022 16:42
Instrument: SDT Q600 V20.9 Build 20

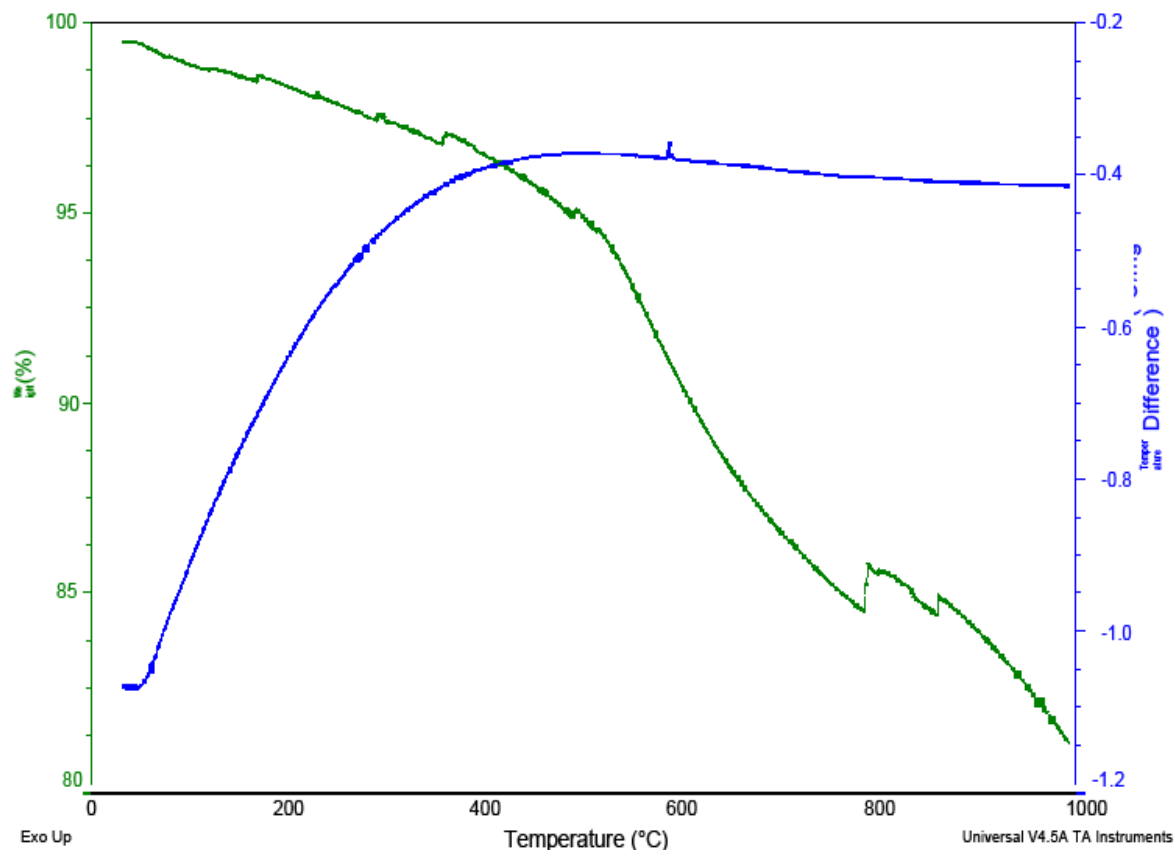


Figure 16 The DSC-TGA of the Bone powder

The thermogravimetric and differential scanning calorimetry (DSC / TGA) thermal analysis of Bone powder is shown in fig3. It is observed from above that the total weight loss is 16% at 1000 °C occurring in several steps. The first weight loss is associated with endothermic peak due to evaporation of absorbed moisture which is between 50 to 350 °C. The decomposition of the material occurred from 450–800 °C which is attributed to the dehydroxylation and decomposition carbonate compounds and the release of carbon dioxide (Olsen et al., 2008, Miculescu *et al.*, 2011)

Sample: NTU
Size: 3.6540 mg
Method: Ramp

DSC-TGA

File: C:\...Results\DR VIC\2022\NEW\RH@550.001
Operator: MESHACK
Run Date: 16-Nov-2022 15:23
Instrument: SDT Q600 V20.9 Build 20

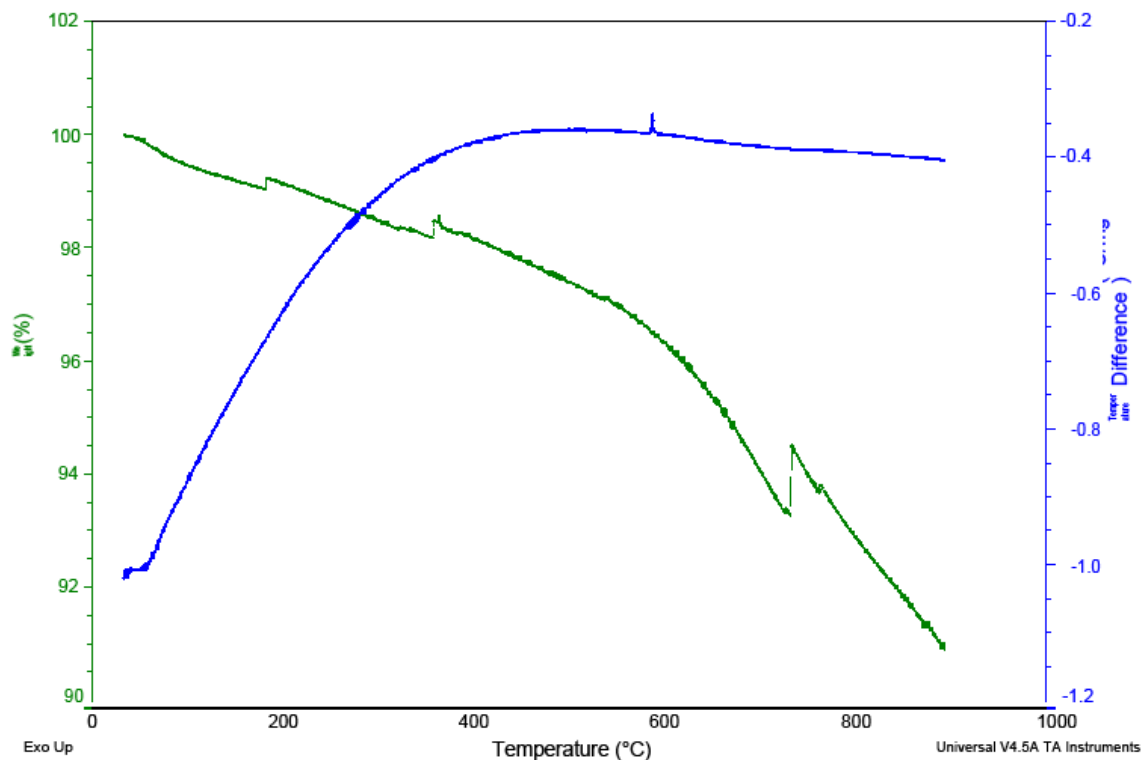


Figure 17 The DSC-TGA of the calcined palm bunch ash

The Differential scanning calorimetry and thermogravimetric (DSC / TGA) thermal analysis of the calcined Palm bunch ash. The first mass loss is due to the dehydration of water molecule absorbed on the compound because of its hygroscopic nature from 50 to 250°C with 2% loss of mass. The total mass loss is 9%. The endothermic peak at 600 and 700 °C corresponds to $\alpha \leftrightarrow \beta$ quartz transformation. The loss in mass is less than the one reported by Claoston *et al* (2014) and in an agreement with the work by Nelson *et al* (2023) on the calcined Palm bunch ash. The calcined Palm bunch ash contains less organic and volatile materials, thus more thermally suitable at high temperatures changes.

Table 5 Physical analysis of samples A

Code	Apparent porosity (%)	Water absorption (%)	apparent density	Bulk density	% making moisture
A0	5.217683	2.678725	2.055049	1.947823	0.426395
A1	8.101187	4.221593	2.088153	1.918988	1.75091
A2	7.491487	3.891509	2.080982	1.925085	1.558815
A3	7.042092	3.649548	2.075756	1.929579	1.331431
A4	9.453078	4.961024	2.1044	1.905469	2.431791
A5	7.606466	3.953598	2.082327	1.923935	1.759965
A6	10.52838	5.556705	2.117673	1.894716	1.965327
A7	5.21636	2.678028	2.055034	1.947836	1.440454
A8	6.666895	3.448398	2.071431	1.933331	2.174761
A9	7.859439	4.090463	2.085298	1.921406	1.41645
A10	7.280702	3.777879	2.078524	1.927193	1.537061

Table 6 Physical analysis of samples B

Code	Apparent porosity (%)	Water absorption (%)	apparent density	Bulk density	% making moisture
B0	5.217683	2.678725	2.055049	1.947823	0.426395
B1	7.476116	3.883215	2.080802	1.925239	2.768054
B2	6.044087	3.116217	2.064329	1.939559	3.369168
B3	7.522742	3.90838	2.081347	1.924773	2.913584
B4	8.210816	4.281168	2.089453	1.917892	3.056021
B5	9.112528	4.77377	2.100262	1.908875	3.712129
B6	9.924405	5.221294	2.110179	1.900756	6.118875
B7	8.434877	4.403138	2.092119	1.915651	3.954343
B8	8.843389	4.626253	2.097013	1.911566	4.333789
B9	10.08262	5.308952	2.112132	1.899174	4.707362
B10	10.43195	5.503012	2.11647	1.89568	4.336556

Table 7 the physical analysis of the samples C

Code	Apparent porosity (%)	Water absorption (%)	apparent density	Bulk density	% making moisture
C0	5.217683	2.678725	2.055049	1.947823	0.426395
C1	7.438808	3.863088	2.080366	1.925612	0.997728
C2	7.288592	3.782128	2.078616	1.927114	1.454921
C3	6.626273	3.426667	2.070965	1.933737	1.38
C4	8.617124	4.502557	2.094297	1.913829	2.265687
C5	6.975027	3.613536	2.07498	1.93025	1.492018
C6	7.651943	3.978175	2.08286	1.923481	1.695559
C7	8.725966	4.562023	2.095602	1.91274	1.908985
C8	9.02059	4.723331	2.09915	1.909794	2.882677
C9	7.657068	3.980946	2.08292	1.923429	2.381763
C10	8.558377	4.470489	2.093594	1.914416	2.480876

The Table 5, 6 and 7 show results of the physical analysis of the admixture A to C respectively. The result of the water absorption and apparent porosity of the concrete produced with admixture A is shown

in Table 5. This property is important in concrete development as the strength of the concrete produced varied directly with the apparent porosity of the materials. These physical properties determine the insulative properties of concrete cast. The use of admixture A, which is the mixture of 10% calcined palm bunch ash and 90 % bone powder used to replace 30% of Portland Cement showed to have the same water absorption and apparent porosity with the control (Ao) which is without admixture. The water of The values of apparent porosity and water absorption within the recommended values for the engineering and building concrete (5.21-10.52%) and (2.65%-5.55%) respectively (Hafidh *et al.*, 2021).

The result of the bulk density of the samples slightly decrease with increasing the percentage admixtures as shown in Tables 5, 6 and 7 where the density is a strong linear function in the amount of admixture added. The bulk density of the samples with admixture (A) decreased smoothly until 30% addition where the bulk density increased sharply while the water absorption and porosity decreased at that point to the same value with the control. The effect of admixture in A as shown in Table 5 is small even when the addition of admixture was 50%. This could be due to high concentration of CaO from bone powder which is pozzollanic in nature and acts as strong binder, hence, reduces the pores of the mixtures (Nwakwo *et al.*, 2020). Thus the effect of admixtures increase from Admixture A to C as shown in Table 5, 6 and & respectively. The porosity and water absorption observed in this study is less than the ones reported for light concrete except for B9 and B10 with 45 and 50% admixture B (Hosny *et al.*, 2023).

4.0 CONCLUSION

The chemical, thermal and mineralogical analysis of the calcined palm bunch ash and bone powder wastes (CPBABPW) was done to determine their suitability in partial replacement of Portland cement. The results show that the bone powder, though having a high concentration of lime (CaO), similar to that of cement oxides, does not have significant alkali oxide and silica, which give rise to quick setting and strength to the mortar and concrete. The analysis indicates that the calcined palm bunch is rich in alkaline oxides and silica and becomes the best complement to substitute cement in concrete and mortar development and production.

The analysis and experimental work done show that the utilization of these waste admixtures in concrete development will save the cost of building structures, decrease the depletion of our natural resources and help reducing disposal problems.

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SN24 EXPERIMENTAL STUDY AND MODELLING OF MECHANICAL PROPERTIES OF EPOXY-SHEEP HORN-COCONUT SHELL PARTICLES HYBRID COMPOSITES

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Abstract: Employment of natural fibers as alternative reinforcement in polymeric composites became crucial owing to the growing concerns regarding the environmental impact associated with the use of synthetic fibers. Balance of ecology and economy can only be sustained through proper utilization of natural resources and waste materials. Thus, this work investigates the effects of sheep horn and coconut shell particles on the mechanical properties of epoxy based composites. Both sheep horn and coconut shell particles were characterized using TGA and XRF analysis, and blended in predetermined proportions before impregnation into the epoxy resin to produce various hybrid composite samples. The composites were produced using open mould casting technique and the impact energy, tensile strength and flexural strength were evaluated. Maximum impact energy, tensile strength, and flexural strength of 15.57J, 36.52MPa, and 67.93MPa respectively, representing 83.8%, 74.3%, and 35.6% improvement, compared to the impact energy, tensile strength, and flexural strength of the control sample were obtained with the hybrid composite sample containing a blend of 5 wt.% sheep horn and 3 wt.% coconut shell particles. The results showed that the hybrid composites had superior properties compared to individual fiber reinforced composites. Regression model equations generated using design expert software showed good agreement between the experimental responses and the model predicted responses.

Keywords: polymeric composite, sheep horn, coconut shell, natural fiber, hybrid, biodegradable

1.0 Introduction

Rising preference for polymer based composite as alternative material for structural application in a good number of weight critical components in the aerospace and automobile industries is driven by its remarkable combination of properties. Traditionally, synthetic fibers such as glass or carbon fibers are incorporated into polymers to improve or modify their mechanical properties. Limited availability and high cost of these synthetic fibers as well as their processing difficulties among other shortcomings necessitated the search for suitable natural fibers as alternative and low cost reinforcement. Natural fibers of interest are majorly bio-waste materials which includes shells of nuts (coconut, palm kernel, etc.), corncob, wood dust, coconut husk fiber, shells of mollusks (periwinkle, snail, etc.), and animal wastes (horns, hooves, etc.). These substances constitute nuisance in the environment as they pollute the air when burnt, and serves as breeding ground for mosquitoes, cockroaches, and rodents when dumped. Also, the products derived from synthetic fibers reinforced polymers poses a serious concern to the environment after their useful lives as they constitute major source of municipal solid wastes since they are not biodegradable (Mark *et al.*, 2019). Therefore, there is a need for conversion of the biodegradable natural fibers into value-added engineering materials applicable in polymer industries as low cost reinforcement, and also serve as part of the solution to waste disposal issue. However, natural fibers have some disadvantages which include higher water

absorption, lower thermal stability, and lower mechanical properties, compared to their synthetic fibers counterparts (Senthilkumar *et al.*, 2022). To overcome some of these challenges, hybrid natural fibers are incorporated into a single matrix with a view to obtain a synergistic effect, leading to enhanced properties (Palta *et al.*, 2018; Abdulrahim *et al.*, 2021).

Coconut (*cocos nucifera*) shell structurally composed of cellulose, hemicellulose, and lignin. Among the various agricultural wastes, coconut shell could be very interesting material as reinforcement in biodegradable polymeric composites, due to its good thermal stability and high mechanical strength compared to other agricultural wastes (Sarki *et al.*, 2011). Also, over the last few years, structural biological materials such as bones, mollusk shells, and hooves have attracted the attention of materials researchers. However, very few literatures exist on the use of animal horns sheath as filler in polymeric composites. Sheep (*ovis aries*) horn's sheath in particular is very strong, and highly resilient. During a fight, sheep horns clash together at high speeds (up to 5.5 m/s), resulting in forces up to 3400 N (Johnson *et al.*, 2016), making it a good structural material, suitable as reinforcing fiber in the manufacture of polymer matrix composites for structural applications.

A significant number of researches had been carried out on natural fibers reinforced polymeric composites. Obiukwu *et al.*, (2016), investigated the properties of coconut shell powder reinforced high-density polyethylene (HDPE) composite and reported that the hardness of the composite increases with increase in coconut shell powder content, while the impact strength and ductility decreases. Reddy and Dhoria (2018), studied the effect of alkaline treatment on the mechanical properties of kenaf fiber reinforced polyester composites and reported that the composites made of chemically treated fibers have good mechanical properties compared to untreated fibers. Somashekhar *et al.*, (2018), studied the mechanical properties of coconut shell powder and tamarind shell powder reinforced epoxy composites. They reported that the combined tamarind shell powder and coconut shell powder increases the tensile properties of the composite by around 50%. Bosenbecker *et al.*, (2019), carried out the mechanical characterization of high-density polyethylene (HDPE) reinforced with cellulose from rice husk bio-mass. It was reported that the addition of rice husk cellulose in the HDPE matrix had good effect on the elastic modulus of the composites. However, the impact strength decreases as the rice husk cellulose content increases in the HDPE matrix. Setty *et al.*, (2020), developed vinyl ester based composites reinforced with raw and chemically treated *limonia acidissima* shell powder, and reported that the properties of the composites filled with NaOH treated filler were supreme compared to untreated filler. Abdulrahim *et al.*, (2021), conducted an experiment on hybridization of polyester/banana stem fiber and cow horn particulate composite for possible production of military helmet. They reported that the values of the impact energy, hardness, and strength obtained are within the range for the production of military helmet. Naik *et al.*, (2021), carried out experimental investigation on tribological properties of orange peel particulate-epoxy composite and concluded that the orange peel particulates filler is a suitable and sustainable option for improving the tribological properties of polymer-based composites.

The literature listed above gives a brief overview of the effects of natural fibers addition on the properties of polymeric composites. To the best of author's knowledge, no work has been done on the effects of sheep horn and coconut shell particles as hybrid reinforcement on the mechanical properties of epoxy based composites. Against this background, the present work was carried out to explore the potential of using sheep horn and coconut shell particles as hybrid reinforcement in epoxy based composites.

2.0 Materials and Methods

2.1 Materials

The materials used in this study were epoxy resin, amino based hardener, sheep horn, coconut shell, sodium hydroxide and distilled water. Epoxy resin and hardener were procured from Tony chemical store in Ojota, Lagos, Nigeria, while sheep horn, coconut shell, sodium hydroxide and distilled water were sourced in Ilorin, Kwara State, Nigeria.

2.2 Methods

2.2.1 Preparation of reinforcing materials

Sheep horns and coconut shells were cleaned with water to remove foreign materials and sun-dried for 8 weeks with average daily temperature of 28°C and relative humidity of 22%, after which they were manually broken into chips using sledge hammer, and milled into microparticles using hammer mill.



Figure 1: (a) sheep horn (b) sheep horn particles (c) coconut shell (d) coconut shell particles

2.2.1.1 Chemical treatment of the coconut shell particles

Chemical treatment of the coconut shell particles became imperative because plant based natural fibers are less compatible with the polymer matrix and thus require some surface treatment or chemical modification. This was done by soaking the coconut shell particles in NaOH solution of 5% concentration for 60 minutes at room temperature (Arthanarieswaran *et al.*, 2015; Rajkumar *et al.*, 2016; Herlina-Sari *et al.*, 2018; Samaei *et al.*, 2020). After which the coconut shell particles were sieved and rinsed repeatedly in distilled water until a neutral pH value was obtained. The treated coconut shell particles were then, dried at room temperature for 48 hours, and followed by oven drying at 60°C for 8 hours (Kumar *et al.*, 2016).

2.2.1.2 Production of coconut shell nanoparticles

Nanoparticles were produced by continuous breaking of NaOH treated coconut shell particles of initial particle size of 43 µm with hardened steel balls of 50mm diameter in a ball milling chamber rotating at 110 rpm. The milling duration was 72 hours with ball to powder weight ratio of 10:1, in line with the work of Bello *et al.*, (2015). Particle size analysis of the produced nanoparticles was carried out using Zetasizer particle size analyzer (serial number: MAL1084260).

2.2.2 Characterization of sheep horn and coconut shell particles

2.2.2.1 Thermo-gravimetric analysis (TGA)

Quantitative measurements of the mass changes associated with thermal degradation of the sheep horn and coconut shell particles were carried out using Perkin Elmer TGA-4000 thermo-gravimetric analyzer. Sample of each material was taken and heated up to a final temperature of 900°C and a residence time of 1 minute at 900°C was allowed. The temperature was increased at a rate of 10°C/minute from room temperature to 900°C during the analysis to determine the thermal stability of the materials.

2.2.2.2 X-ray fluorescence analysis (XRF)

The x-ray fluorescence (XRF) analysis was conducted on the sheep horn and the coconut shell particles using x-ray fluorescent (Nitron 3000). Each sample, prepared into pellets was placed on the sample holder and the ray point was positioned over it. The ray button was pressed to start taking data. The data were collected in triplicates, and the average was automatically taken to determine the percentage chemical composition in oxide and elemental form.

2.3 Production of the composites

Sheep horn microparticles and coconut shell nanoparticles of 43µm and 50nm average particle sizes respectively, were utilized as hybrid reinforcement. Blending of coconut shell nanoparticles with sheep horn microparticles as hybrid reinforcement was adopted due to high propensity of nanoparticles to agglomerate. Randomised mixture formulation of the matrix and the two reinforcement phases was done using design expert software (version 12.0.12.0). Weight fraction of epoxy resin was varied from 90 to 100 weight %, while that of each of the sheep horn and coconut shell particles were varied from 0 to 5 weight %. During the production of each formulation of the composites, calculated amount of the hybrid reinforcing particles were thoroughly blended to obtain homogenous mixture, using Rico electric blender (serial number: MG1701), rotating at 1500 rpm. The blend was then gradually added to a weighed amount of epoxy resin while stirring it manually to avoid clustering, using a glass rod until homogenous mixture was obtained, and followed by motorized stirring to ensure homogenous dispersion of the reinforcement in the epoxy resin. Then, measured amount of hardener equivalent to ratio 2:1 (resin:hardener) by weight was added to the mixture of epoxy resin and reinforcement, then stirred manually for about 5 minutes using a glass rod, followed by motorized stirring for about 10 minutes at 300 rpm, after which the mixture was poured steadily into the mould and left in the mould for 24 hours to set and harden at room temperature. Prior to the casting of the composites, the mould cavities were neatly coated with masking tape to facilitate easy removal of the composite samples after curing. Same process was repeated for the production of all the composite formulations.

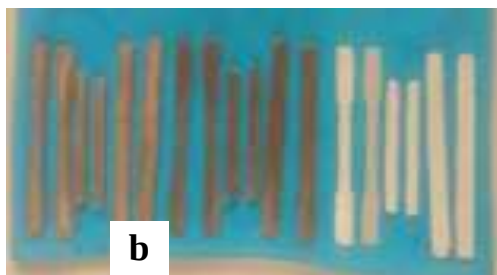
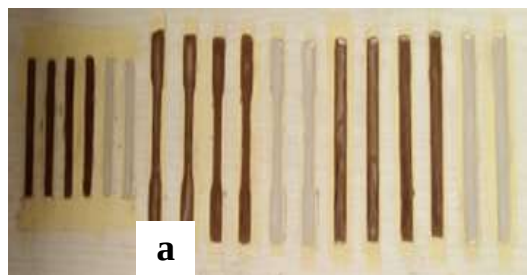


Figure 2: Some of the composites (a)during casting (b)after removal from the mould

2.4 Testing and modelling of mechanical properties

The composites were tested for the three important mechanical properties of impact energy, tensile strength, and flexural strength, according to ASTM D256, D638, and D790 respectively. For each composite formulation, three samples were tested, and the average results were taken into account. Regression models were generated, using design expert software (version 12.0.12.0). Quadratic model was selected for the theoretical predictions of impact energy, tensile strength, and flexural strength of the composites. The models were evaluated using ANOVA, which showed their significances.

3.0 Results and Discussion

3.1 Thermo-gravimetric analysis (TGA)

Figures 3a and 3b depicted the thermo-gravimetry (TG) and derivative thermo-gravimetry (DTG) curves of sheep horn (*ovis aries*) and coconut shell (*cocos nucifera*) particles.

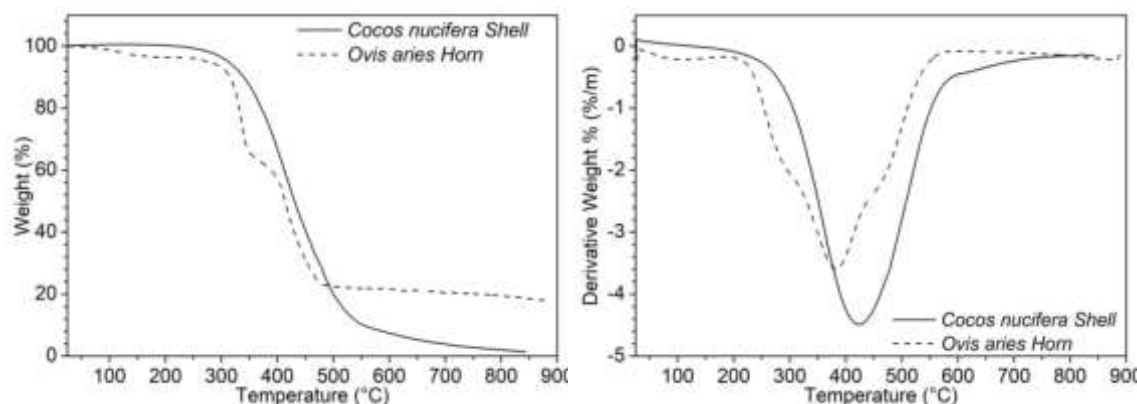


Figure 3: (a) TG curve (b) DTG curve

TG curve of sheep horn particles indicated initial weight loss between approximately 100 - 300°C, due to evaporation of residual moisture and loss of the light volatiles. Whereas, coconut shell particles remained thermally stable up to a temperature close to 300°C. This may be attributed to absence of moisture and its relative high thermal stability. The coconut shell particles had the first phase of weight loss at approximately 300 - 550°C. Here, the weight loss was remarkably accelerated, and this was attributed to the degradation of hemicellulose and cellulose mainly, and part of lignin. The degradation pattern was found to be in good agreement with the work of Andezai *et al.*, (2020). The second phase of weight loss began at approximately 550°C, indicating gradual degradation of lignin into a carbon rich residual solid. As indicated in the TG curve, thermal degradation and the main weight loss of sheep horn particles took place in two stages. The first stage which occurred between approximately 300 - 375°C, is attributed to denaturation of protein (Prochon *et al.*, 2012). While the second stage which took place between approximately 375 - 475°C resulted in total destruction of protein. Appreciable thermal stability was recorded after the two thermal degradation stages. DTG curve of sheep horn particles was also characterized by multi-stage degradation events, indicating that the decomposition products were released in steps. The DTG curves of both samples peaked around 400°C, indicating that 50% weight loss in both samples occurred around this temperature.

Thus, the two bio-waste samples possessed appreciable thermal stability for hybridization in polymeric composites.

3.2 X-Ray fluorescence analysis (XRF)

Table 1: Elemental composition (weight %) of sheep horn and coconut shell particles

Elements	O	Mg	Al	Si	S	Cl	K	Ca	Fe	Ru	Rh	Others
Horn	46.8	3.7	4.6	4.7	21.2	9.3	4.7	2.5	-	-	-	2.5
Coconut	36.3	14.0	5.8	10.3	-	2.8	11.0	2.2	3.3	6.3	2.8	5.2

3.3 Mechanical properties

3.3.1 Impact energy

The influence of single and hybrid reinforcement content on the impact energy absorbed by the composite are illustrated in Figure 4. It was observed that composite samples with single reinforcement; 2 wt.% horn, 2 wt.% coconut shell, 4 wt.% horn, and 4 wt.% coconut shell, absorbed higher impact energy compared to the control sample (100% epoxy). The control sample absorbed impact energy of 8.47J, whereas, impact energy of 9.82J and 10.26J, which is 15.9% and 21.1% higher than the impact energy of the control sample were respectively recorded with the addition of 2 wt.% horn, and 2 wt.%coconut shell. Incorporation of 4 wt.% horn, and 4 wt.%coconut shell further increased the impact energy to 10.97J and 10.72J respectively, which is 29.5% and 26.6% higher than the impact energy of the control sample. It could be seen that the impact energy of the composite increases with increasing reinforcement addition. Peak impact energy of 15.57J was however recorded for the hybrid composite sample containing a blend of 5 wt.% horn and 3 wt.% coconut shell particles, which is 83.8% higher than the impact energy of the control sample. Reduction in impact energy of the hybrid composite was observed at higher concentration of coconut shell particles. This is possibly due to agglomeration/clustering at higher concentration of the nanoparticles, which may results in the region of stress concentration. Similar observation was reported by Akaluzia *et al.*, (2020).

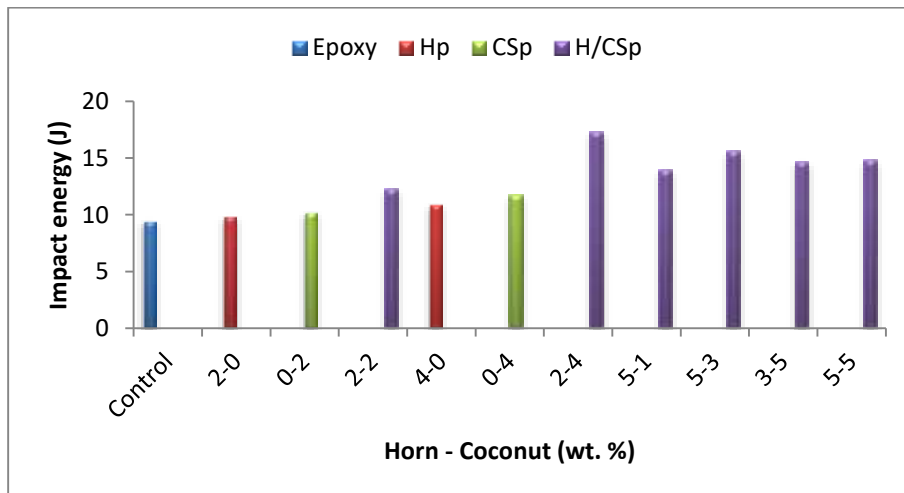


Figure 4: Impact energy of the composites

3.3.2 Tensile strength

The variation in tensile strength with percentage weight addition of the single and hybrid reinforcements are illustrated in Figure 5.

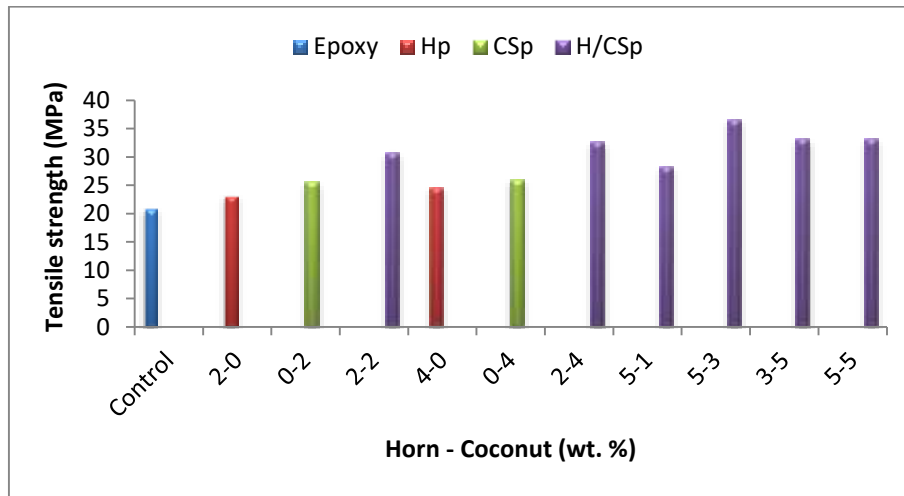


Figure 5: Tensile strength of the composites

It was observed that composite samples with single reinforcement; 2 wt.%horn, 2 wt.%coconut shell, 4 wt.%horn, and 4 wt.%coconut shell, exhibited improved tensile strengths compared to the control sample (100% epoxy). Tensile strength of 20.95MPa was obtained for the control sample, while tensile strengths of 23.08MPa and 25.53MPa, which is 10.2% and 21.9% higher than the tensile strength of the control sample were recorded with the addition of 2 wt.% horn, and 2 wt.% coconut shell particles respectively. Incorporation of 4 wt.% horn, and 4 wt.% coconut shell further increased the tensile strength to 24.51MPa and 25.94MPa respectively, which is 17.0% and 23.8% higher than the tensile strength of the control sample. Higher tensile strength obtained for the coconut shell reinforced composite samples may be linked to its finer particle size. From the results obtained for the hybrid composite samples, synergistic effect was suspected with the interaction of the two reinforcing particles as the hybrid composite sample containing a blend of 2 wt.% horn and 2 wt.% coconut shell particles, possessed superior tensile strength (30.67MPa) compared to the composite samples with 4 wt.%horn (24.51MPa), and 4 wt.%coconut shell (25.94MPa), having single reinforcement of equal weight fraction as that of the hybrid composite sample. Maximum tensile strength of 36.52MPa was obtained with hybrid composite sample containing a blend of 5 wt.% horn and 3 wt.% coconut shell particles. This amount to 74.3% improvement, compared to the tensile strength of the control sample.

3.3.3 Flexural strength

The effect of addition of different weight fractions of the single and hybrid reinforcements on the flexural strength of the composite are illustrated in Figure 6.

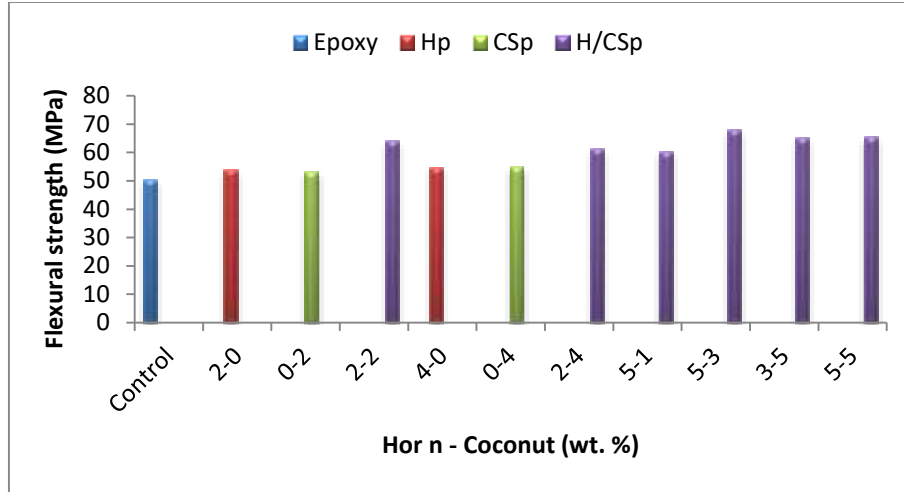


Figure 6: Flexural strength of the composites

Composite samples with single reinforcement; 2 wt.%horn, 2 wt.%coconut shell, 4 wt.%horn, and 4 wt.%coconut shell particles, were found to possess improved flexural strengths, compared to the control sample (100% epoxy). Flexural strength of 50.08MPa was obtained for the control sample, while flexural strengths of 53.65MPa and 52.97MPa, which is 7.1% and 5.8% higher than the flexural strength of the control sample were respectively recorded with the addition of 2 wt.% horn, and 2 wt.% coconut shell particles. Addition of 4 wt.% horn, and 4 wt.% coconut shell particles, increased the flexural strength of the composite to 54.58MPa and 54.65MPa respectively, which is 9.0% and 9.1% higher than the flexural strength of the control sample. This behavior means that the reinforcement addition enhances the resilience or elastic toughness of the composites. Optimum flexural strength of 67.93MPa was obtained with the hybrid composite sample containing a blend of 5 wt.% horn and 3 wt.% coconut shell particles, which represents 35.6% improvement in flexural strength, compared to the flexural strength of the control sample. The observed decrease in flexural strength of the hybrid composite sample incorporating 5 wt.% coconut shell particles may be due to clustering/agglomeration at higher concentration of the nanoparticles, resulting in increased void content (micro-pores), which reduces the stress transfer efficiency of the composites.

3.3.4 Regression models

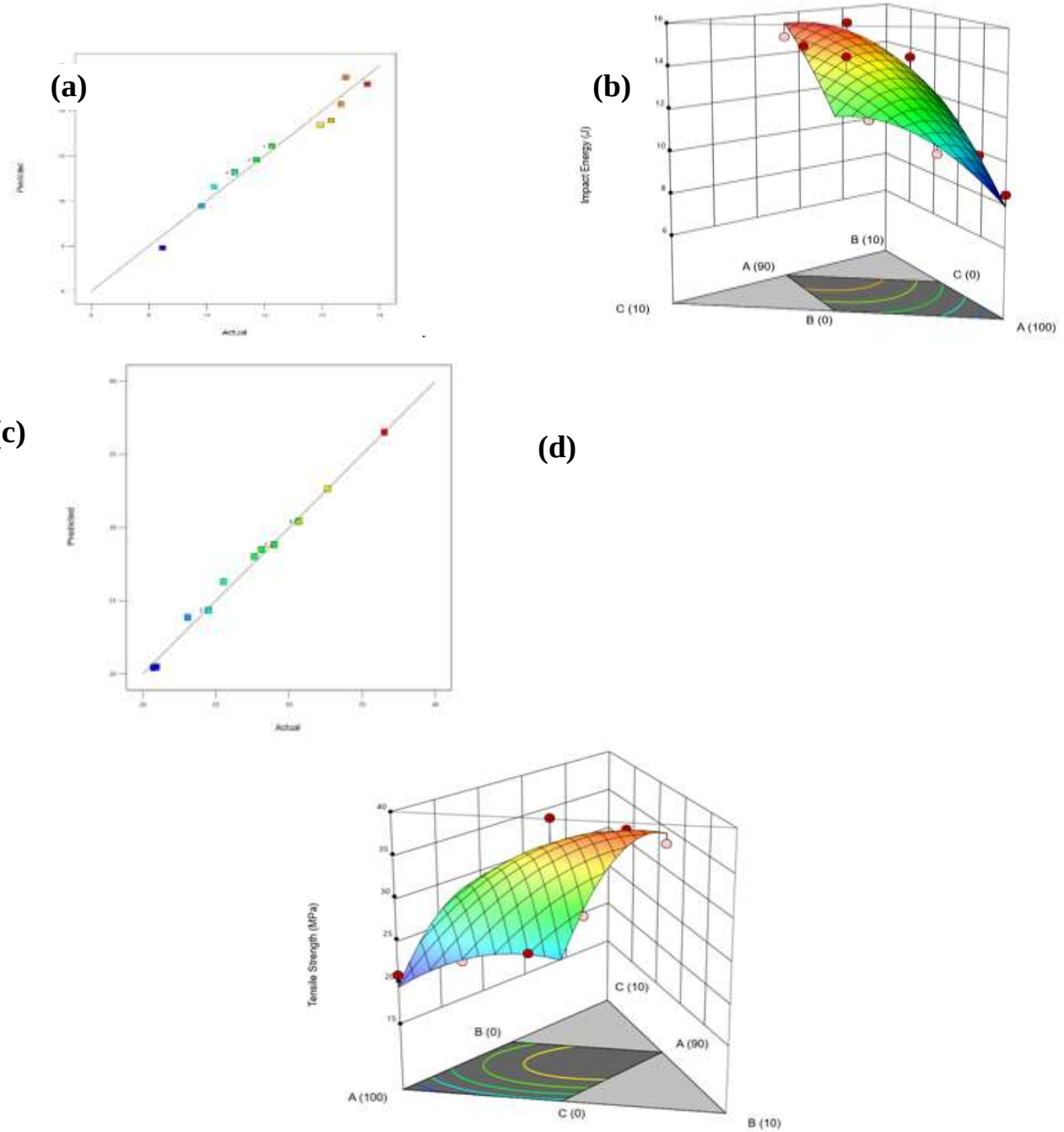
The regression models for theoretical predictions of impact energy, tensile strength, and flexural strength of the composites are presented in equations 1, 2, and 3 respectively. Graphs of experimental (actual) responses versus the predicted responses were also presented in addition to the 3D surface plots showing the effect of interaction of epoxy, horn, and coconut shell particles on the mechanical properties.

$$\text{Impact energy} = 0.079285E - 3.22793H - 17.12154C + 0.043186EH + 0.189335EC + 0.218799HC \quad (1)$$

$$\text{Tensile strength} = 0.195253E - 30.96729H - 64.25673C + 0.337408EH + 0.696049EC + 1.11733HC \quad (2)$$

$$\text{Flexural strenght} = 0.482905E - 67.65766H - 104.88444C + 0.727410EH + 1.11266EC + 2.21295HC \quad (3)$$

Where E, H, and C are the mixture components representing epoxy, horn, and coconut shell particles respectively.



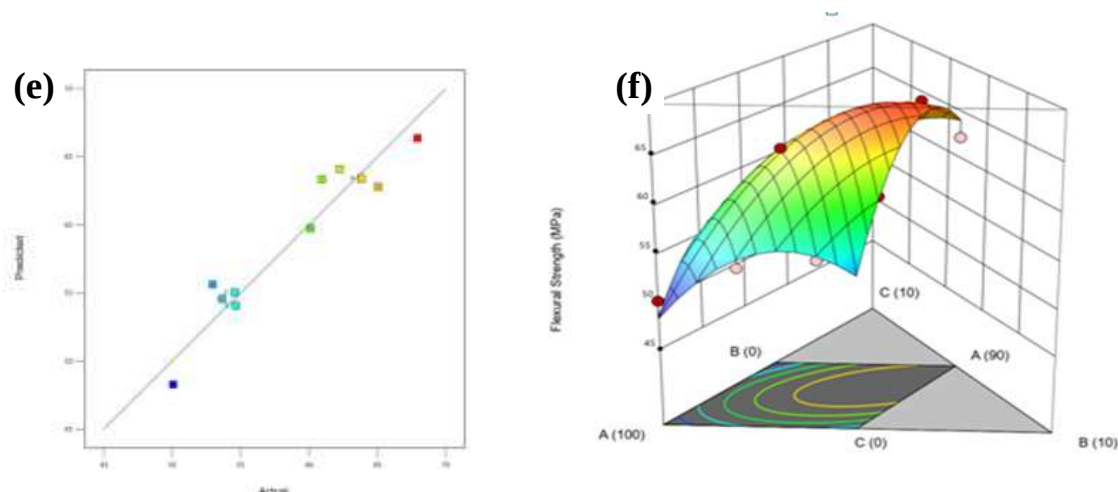


Figure 7: (a) Experimental versus predicted impact energy (b) Effect of interaction of epoxy, horn and coconut shell particles on impact energy (c) Experimental versus predicted tensile strength (d) Effect of interaction of epoxy, horn and coconut shell particles on tensile strength (e) Experimental versus predicted flexural strength (f) Effect of interaction of epoxy, horn and coconut shell particles on flexural strength

4.0 Conclusions

Mechanical properties of hybrid sheep horn and coconut shell particles reinforced epoxy composite were evaluated to establish the possibility of using it as a new material for engineering application. The results showed that the hybrid composite had superior properties compared to individual fiber reinforced composites. Maximum impact energy, tensile strength, and flexural strength of 15.57J, 36.52MPa, and 67.93MPa respectively, representing 83.8%, 74.3%, and 35.6% improvement, compared to the impact energy, tensile strength, and flexural strength of the control sample were obtained with the hybrid composite sample containing a blend of 5 wt.% sheep horn and 3 wt.% coconut shell particles. Regression model equations generated using design expert software showed good agreement between the experimental responses and the model predicted responses.

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**SN25 VALORIZATION OF ORANGE RESIDUES FOR POLYMER COMPOSITE
DEVELOPMENT**

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Abstract

This mini review thoroughly elucidates sustainable valorisation routes for orange residues in polymer composite development and exploring potential applications. Various plastics and epoxy types are highlighted, and their combining efficiency in polymer composite development. It is however established that less usage has been made of polystyrene based resin as sustainable matrix in orange residue valorisation for composite development. The mechanical, microstructural and thermal properties of the composites explored confirm their suitability in diverse load bearing and sound proofing applications.

1 Introduction

Agricultural processing industry and crop cultivation generate a substantial amount of waste biomass, which has been identified as a major contributor to environmental degradation worldwide [1]. This waste comprises various plant components such as leaves and roots, as well as byproducts like orange remnants, including peels and albedo, sawdust, rice straw, and similar materials [2]. In particular, the consumption of oranges (*Citrus sinensis*), a widely consumed fruit in West Africa, result in residual waste products notably peels and albedo, which have been found to contain essential oils with significant biological activities, including antioxidant, anti-carcinogenic, and germicidal effects [3, 4].

The appropriate management of agricultural waste, specifically orange peel, is a growing concern within the realm of waste management and environmental sustainability [2, 5]. Prior to proposing any strategy for the valorization of this waste material, it is imperative to attain a comprehensive understanding of its physicochemical properties. Existing literature indicates that orange peel consists of approximately 23% sugar, 22% cellulose, 12% acetate, 11% hemicellulose, and 25% pectins [6].

In contemporary times, there has been a substantial increase in the utilization of plastic composites across various industries, underscoring the significance of their unique properties. Composites are a class of construction materials characterized by the presence of two or more distinct constituents that do not dissolve in each other and are combined at a macroscopic level. Composites typically consist of a discontinuous or reinforcing phase, composed of materials like metal, ceramic, or fiber, embedded within a continuous phase or matrix, which can be made from either thermosetting or thermoplastic materials [7, 8]. Notably, composites featuring synthetic or mineral fillers and a high-modulus reinforcement within a relatively lower-modulus matrix, such as polystyrene, have gained increased attention [9, 10].

In this mini review, the utilization of waste valorisation techniques for orange peels is elucidated in their various usages in different polymer matrixes to obtain polymer composite.

2 Orange

Citrus sinensis is commonly known as the orange fruit, and is recognized as the most extensively cultivated citrus crop worldwide. The United States stands as the foremost producer of oranges, while Colombia is also known to produce this fruit in substantial amounts. Additionally, the Mediterranean region, Australia, the Union of South Africa, the Caribbean, the Far East, and the subtropical areas of South America are also significant cultivators of oranges. The fruit is typically grown in countries that possess hot and humid climatic conditions. In the year 2016-2017, the global production of sweet oranges recorded a total of 49.6 million metric tons(USDA, 2017).

Citrus is a genus belonging to the *Rutaceae* or *Rue* family comprising about 140 genera and 1,300 species (Yerou et al., 2017). Some important fruits of the genus *Citrus* are; *Citrus sinensis*(Orange), *Citrus reticulate* (tangerine), *Citrus paradise* (grapefruit), *Citrus limon* (Lemon), *Citrus grandis* (shaddock), *Citrus aurantifolia* (lime), and *Citrus medica* (Citron). For this review, we will be considering the fruit *Citrus Sinensis* (Orange). Figure 2.1 shows the picture of an orange.

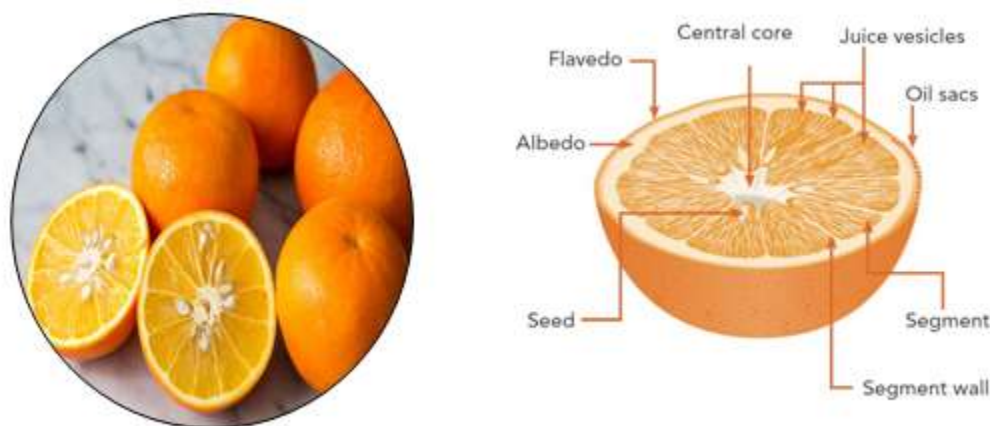


Figure 2.1 Orange (*Citrus sinensis*)

2.1 Orange residues

The fruit of *Citrus sinensis*, commonly referred to as the orange, is highly valued for its desirable properties, which include a sweet flavor, rich aroma, and abundance of vitamin C. It is widely employed in various commercial applications, with the food and beverage industries as well as the cosmetics sector being the primary users. The orange fruit is composed of two distinct anatomical parts, namely, the pericarp, which encompasses the peel, skin, or rind, and the endocarp, which comprises the pulp with juice sac glands[11]. The outermost layer of the skin, known as the epidermis, is comprised of epicuticular wax and features a vast number of minuscule aromatic oil glands that are accountable for the characteristic scent. The pericarp, which constitutes the outer flavedo or epicarp, primarily comprises parenchymatous cells and cuticle. The distinguishing features of orange peel from its albedo is depicted in Figure 2.2.

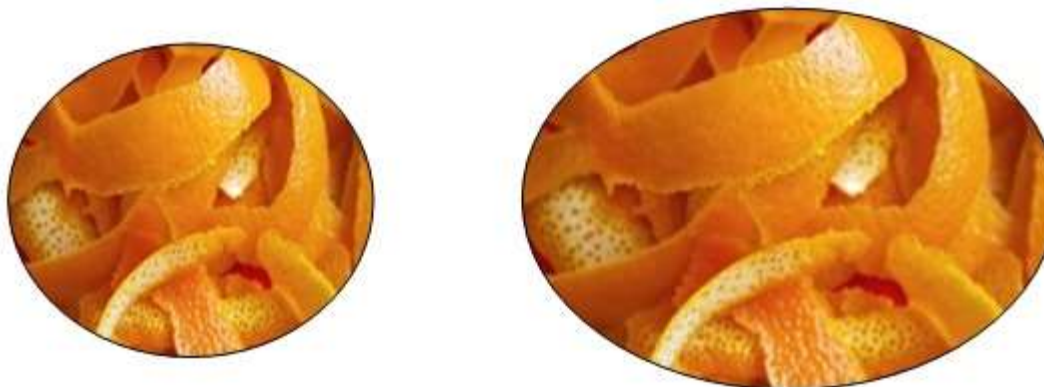


Figure 2.2 Orange peel

An orange is estimated to contain approximately 60 flavonoids and 170 phytonutrients [6, 12](Ibri et al., 2017). Orange residues have been employed for their anti-inflammatory, anti-cancer, antibacterial, and germicidal effects [4]. Orange peels can be used as animal feeds, fertilizers, feedstock for the growth of single-cell protein [6], and others.

2.2 Content in Orange (*Citrus sinensis*)

In order to propose an effective method for the valorization of orange peel waste, it is crucial to first comprehend its underlying physicochemical properties. Based on existing literature, orange peel is composed of 23% sugar, 22% cellulose, 12% acetate, 11% hemicellulose, and 25% pectins[6].

Cellulose

Cellulose, a glucose polymer composed solely of β -(1,4)- linkages, exhibits a markedly linear structure that facilitates robust hydrogen bonding between individual chains of cellulose. This high degree of intermolecular hydrogen bonding renders cellulose highly resistant to degradation via chemical or biological means. Within this array of methods, cellulose content is determined by quantifying the glucose that is liberated via a two-stage acid hydrolysis process [13].

Hemicellulose

Hemicelluloses denote compounds that can be isolated by ethanol precipitation subsequent to the extraction of cell walls mediated by dilute alkali. In such procedures, after the removal of the pectin component of the walls through the use of aqueous solvents and calcium chelators, the hemicelluloses are extracted. However, maintaining the structural integrity of numerous polysaccharides after their extraction from the cell wall matrix using alkali can be challenging. As a substitute for alkali extraction, enzymes can be employed to liberate hemicellulose fragments from the cell wall matrix (Mohnen, 1999).

Lignin

Lignin, a biopolymer characterized by high energy content, is produced through the polymerization and cross-linking of phenylpropanoids. Within this methodological framework, the quantification of lignin is performed in two stages. The majority of lignin is measured gravimetrically as the organic matter that remains insoluble subsequent to the hydrolysis of carbohydrates. In herbaceous materials, it is assumed that all protein is insoluble, and the corresponding weight is subtracted from the acid-insoluble residue to report

the lignin content. In certain biomass samples, a fraction of the lignin is solubilized during the hydrolysis process and is quantified via ultraviolet (UV) spectroscopy (Hames, 2009).

3 Waste Valorization

Waste refers to any solid, liquid, or gaseous material deemed undesirable [14]. Improper handling of wastes has adverse impacts on the environment, including humans, animals, and plants, as established by prior research [15, 16]. Organic waste constitutes approximately 50% of all waste generated, highlighting its potential to reduce the pollution resulting from inadequate waste management significantly. Effective management of organic waste, therefore, presents a viable strategy to mitigate the volume of pollution arising from waste mismanagement (Getahun et al., 2012; Sharholy et al., 2008).

Waste management aims to reduce waste generation while maximizing resource recovery from waste. One effective approach to waste management is waste valorization, which involves recovering value from waste materials rather than solely disposing of them. By adopting this approach, the volume of waste destined for landfills can be minimized, natural resources can be conserved, and greenhouse gas emissions related to waste management can be curtailed.

The conversion of waste materials, including chemicals, fuels, and other substance, into more valuable products is referred to as waste valorisation. Although not a new concept, its renewed interest stems from the depletion of primary resources, the escalating volume of waste generation and disposal worldwide, and the demand for environmentally friendly and economically viable waste management protocols. Numerous waste valorisation methods have been proposed and are showing potential in meeting industrial needs. One such promising technique is the application of flow chemistry technology to convert waste into valuable products, as documented in previous research (Arancon et al., 2017).

In recent years, waste valorization has emerged as a critical research area due to the rapid depletion of natural resources and the increasing environmental concerns. A promising approach to waste valorization is exemplified in research that explores the use of orange peel and polystyrene to produce orange peel polystyrene (OPBC) composites, which offer a sustainable and eco-friendly alternative to traditional raw materials. OPBC composites exemplify waste valorization by utilizing discarded orange peels that are rich in cellulose fibers, which can be extracted and employed as reinforcement in OPBC composite production. The polystyrene serves as a matrix material, bonding the orange peel fibers together to form a composite material. This is as illustrated in Figure 3.1

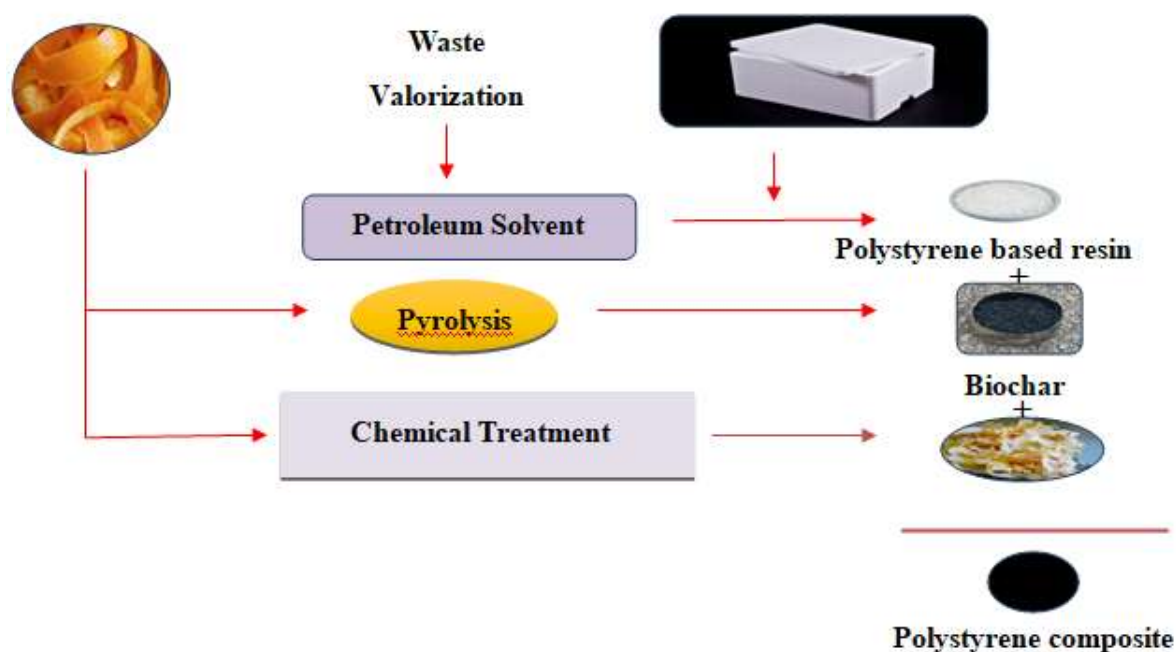


Figure 3.1: Waste valorization techniques of orange peel and polystyrene

4 Orange Residue Filled Polymer Composite

The study by Ojha et al. (2012), focused on the fabrication and mechanical properties of orange peel-reinforced polymer composite. The study prepared new sets of composites using varying weight fractions of orange peel particulates as fillers in polymer epoxy composite and studied their mechanical properties, including tensile and flexural strength using a three-point bend test. The study found that orange peel has good thermal and chemical properties, including fixed carbon, adsorption efficiency, ash content, cellulose, hemicellulose, and lignin. The density of the composite increased with particle content, and the increase in filler content led to an increase in the tensile strength of the composite. The maximum tensile strength was achieved at 20% filler loading, while the composite with 20% particle content had the highest flexural strength. The SEM analysis showed that the composite with 20% orange peel content had strong bonding between the matrix and reinforcement, with no debonding, particle chipping out, or crack formation observed. Overall, the study suggests that orange peel can be a promising filler material for polymer composite, and has the potential for use in various engineering applications.

The study by Adeniyi, Iwuozor [5] investigates the production of engineered biochar from orange peel using a one-step chemical activation process. The precursor material was treated with a chemical activator (zinc chloride salt) in a top-lit updraft biomass reactor with retort heating. The study compared the FTIR spectra and chemical composition of the resulting biochar with and without chemical activation. The results showed that the chemical activation process increased the number of oxygenated functional groups in the biochar and decreased its carbon content. The EDS analysis showed that the oxygen content in the biochar increased after chemical activation. The SEM images revealed rough surfaces with heterogeneous surface morphology, and the textural properties analysis showed that the chemical activation process greatly improved the porosity and surface area of the biochar. Overall, the study concludes that the one-step chemical activation process can be used to produce engineered biochar from the orange peel with improved

surface area and porosity, which can be useful for various environmental applications such as the adsorption of pollutants and soil amendment.

The research by Terzioğlu et al. (2021) focused on developing eco-friendly chitosan/PVA composite films for food packaging applications by incorporating orange peel waste. The study investigated the effect of varying orange peel content (0.25-1.25% w/w) on the mechanical, optical, physical, structural, barrier, bioactivity, color, and wettability properties of the films. The orange peel particles were observed to have a heterogeneous size and a rough surface with small pores. SEM micrographs showed no air bubbles, cracks, or pores in the films, and the cross-sectional images showed continuous and compact morphologies. FTIR analysis revealed the presence of polysaccharides in orange peel, which contributed to the C-O-C bond stretching of the chitosan/PVA composite. Overall, the study showed that incorporating orange peel waste into chitosan/PVA composite films could improve their properties for food packaging applications.

The research by Naik and Mishra [17] investigates the abrasive wear behavior of epoxy composites reinforced with orange peel particulates (OPP) as a filler material. The study focuses on the development of lightweight materials that are environmentally friendly and meet new environmental policies. The researchers used the hand layup technique to fabricate the composite material with filler loading varying from 0 to 30%. The abrasive wear behavior of the composite material was analyzed under dry sliding conditions with varying loads at different sliding velocities. The study found that the wear behavior of the neat epoxy material improved significantly with the addition of OPP as a filler material. The incorporation of OPP filler into epoxy decreases the wear rate, indicating improvement in wear resistance. The study also found that the porous structure of the particulate helps in improving the bonding between the filler and the matrix, and the filler weight fraction and normal load are the two important parameters affecting the wear rate of the composite. The surface morphology study of the worn surface concerning wear mechanism indicates plastic deformation and the development of cracks at an optimum filler concentration of 20%. However, at higher filler concentrations (30%), brittle failure of the composite with the formation of more wear debris is found. Overall, the study concludes that OPP filler is a suitable and sustainable option for improving the tribological properties of polymer-based composites.

The study by Adeniyi, Abdulkareem [2] examined the potential applications of biochar obtained from the thermochemical conversion of orange peels (OP) and albedo (OA). The research aimed to evaluate the quality of the biochar product and its potential applications. The biochar samples were characterized using FTIR, SEM-EDS, and BET analysis. The results revealed that both biochar samples possessed polar groups such as alcohol, esters, ketones, aldehydes, carboxylic, ether, and phenols, which make them suitable for applications such as soil amendment and adsorbents for aquatic pollutants. The EDS analysis showed that the OP biochar had a higher carbon content than OA biochar, while the latter contained more inorganic elements, making it more effective in GHG emissions and carbon sequestration applications. SEM analysis revealed that the OP biochar had a smoother surface than the highly convoluted surface of OA biochar. BET analysis showed that the surface area of OP biochar was slightly lower than that of OA biochar, but it was more porous. Overall, the study concluded that the biochar product obtained from orange residues is of high quality and has potential applications in various environmental engineering areas.

The study by Victor et al., (2013), investigated the use of orange peel particles as a reinforcing material and high-density polyethylene (HDPE) as a matrix to produce eco-friendly composites. The composites were produced by compounding and compressive molding, varying the orange peel particles from 5-25wt%. The mechanical and microstructural properties of the composites were studied, and it was observed that the orange peel particles were fairly uniformly distributed in the microstructure of the HDPE composites, leading to an improvement in the mechanical properties. The results showed that the orange peel waste

could be used as biodegradable eco-friendly reinforcement, with the tensile and bending strengths of the composite increased with an increasing percentage of the orange peel particles. The study concluded that orange peel waste could be an environmentally friendly alternative to synthetic fillers in particle-reinforced materials.

In the study titled "Production of useful composite particleboard from waste orange peel", Tasdemir et al., (2019) produced polymeric composite particleboard using waste orange peel as a filler and a urea-formaldehyde and phenol-formaldehyde mixture as a binder. They evaluated the effect of the binder/filler ratio on the tensile strength, limit oxygen index (LOI), and water absorption capacity of the particleboard. The highest tensile strength of 15 MPa was obtained at an equal polymer/filler ratio, and both mechanical strength and LOI values increased with increasing polymeric binder amount. Water absorption capacity decreased as the polymeric binder amount increased. The study suggests that orange peel waste can be used as a filler in place of wood-based materials in the production of particleboard.

5. Potential Applications and Future Outlook

The biochar derived from orange peel (ORPB) and its composites with pure synthetic resin (PSR) have demonstrated promising properties, including enhanced hardness and the presence of functional groups suitable for reinforcement.

- i. The composites could be incorporated into the production of sustainable building components such as composite panels, boards, or structural elements. Their improved mechanical properties could make them valuable for construction applications to manufacture lightweight yet durable components. These components could include interior panels, door trims e.t.c
- ii. The composite materials could be employed in automotive interiors e.g dashboards.

While the existing studies have explored various valorization techniques for orange peel, including biochar production and its potential applications, as well as the use of orange peel as a filler in different composite materials, there appears to be a lack of comprehensive research specifically focused on the utilization of biochar derived from orange peel as a filler in polystyrene composite. Specifically, there is a gap in the literature concerning the combined utilization of orange peel biochar and as fillers in polystyrene composites, and the comprehensive analysis of the composition, properties, and nature in relation to the resulting composite's properties.

Conclusions

The usage of orange residue as fillers in various plastic and epoxy matrixes is highlighted, along with their properties and limitations. It is found that less usage of polystyrene wastes has been deployed in the development of orange residues filled composite development. These composite holds potential for various applications, within construction industry and automotives. Furthermore, this composite material can serve a vital role in interior design components, such as countertops and doors, by providing essential functions like enhancing building insulation.

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**SN26 PHYSIOCHEMICAL, BIOLOGICAL PARAMETERS AND HEAVY METALS CONTENT
OF SUG UNDERGRADUATE MALE HOSTEL MANUAL BOREHOLE WATER,
FCE KONTAGORA FOR ENVIRONMENTAL SUSTAINABILITY.**

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ABSTRACT

Standard method of analysis was used to determine the physiochemical, biological parameters and heavy metals content of female hostel L and K manual borehole water located at FCE Kontagora. These were carried out in order to ascertain its portability, palatability and safety. Water is the source of life, and it nurtures and sustains livelihoods and civilization. Therefore, secure and sustainable access to safe water is an essential element of national security. The results of the analysis show that the two samples are safe for drinking even though that of hostel K show higher values than that of hostel L. The iron content of sample K (3.06mg/l) is above the WHO and NSDWQ 2015 standard limit of 1 and maximum permissible limit of 0.3mg/l but that does not make it a bad for drinking. When water is scarce, it becomes more difficult for community to produce food, prevent the spread of diseases. Water stress contributes to regional instability, derives mass migration and can lead to broader conflict.

KEY WORDS; Physiochemical, Biological, Heavy metals, WHO, NSDWQ

INTRODUCTION

Water is a transparent fluid which forms the world's streams, lakes, oceans rain, and is the major constituent of fluids of living things. As a chemical compound, water molecule contains one oxygen atom and two hydrogen atoms that are connected by covalent bonds. Water is a liquid at standard ambient temperature and pressure, but it often coexists on earth with its solid state, ice; and gaseous state, steam (water vapor). It also exists as snow. The composition of surface and groundwater is dependent of natural factors (geological, topographical, meteorological hydrological and biological in the drainage basin and varies with seasonal difference in runoff volumes, weather conditions and water levels. Safe drinking water is essential to humans and other life forms even though it provides no calories or organic nutrients.

According to WHO (2006), about 1.1billion people lack access to improve waters supply. In most cities, towns and villages in Nigeria, times are spent on seeking and fetching water, often of doubtful quality from distance sources. Ground water is an increasingly essential to resource all over the world. Groundwater is generally less susceptible to contamination and pollution when compared to surface water bodies. Importantly, groundwater can also be contaminated by naturally occurring sources. Soil and geologic formation containing high level of heavy metals can leach those metals into groundwater. Pollution of groundwater due to industrial effluents and municipal waste in water bodies is another major concern in many cities and industrial clusters in Nigeria. It is estimated by the World Health Organization (WHO) that about 80% of all sickness and diseases in the world are associated with water e.g, cholera and typhoid.

QUALITY OF BOREHOLE WATER ASSESSMENT

Ground water is an essential source of raw water, virtual it exists everywhere, and it's -virtually connected, to surface water resources, Contamination of ground water is a serious problem, industrial sources of contaminants, and agricultural activities are major source of contaminants but households are equally important sources. Ground water moves so slowly that problem takes a longtime to appear. Because of this, and because it is so expensive to cleanup a contaminated aquifer (if it can be done at all), it is preferable by far to prevent contamination from happening in the first place (Bradley, D.J, 1977). Water quality is determined by assessing three classes of attributes, Biological chemical and physical. There are standards of water quality set aside for each of these three Classes of attributes. The "World Health Organization (WHO) developed these Standards in year 2000. All public water supplies must be measured against these standards. Some attributes are considered of Primary importance to the quality of drinking water, while others are of secondary importance. Primary drinking water standard regulates organic and inorganic chemicals, microbial pathogens and radioactive elements that may affect that state of drinking water. Secondary drinking water standards regulate chloride, color, copper, corrosively foaming agents, iron margarines, odor, pH total dissolved solid etc. all of which may affect qualities of drinking water. To safeguard the health of people and to reduce to the barest minimum of ugly experiences of drinking and/or using of low-quality water, it is necessary that the quality of water should be monitored with the view to finding lasting solution to health problems associated with the use and drinking of low-quality water. The quality of borehole water however, principally depends on the world health organization(WHO)has set a quality guideline for drinking water and recommends that the properties of every drinking water should fall within the acceptable limit set by it (Umara et-al 2007)

Below is the standard by world health organization (WHO)

Table A. WHO Standards

Parameter	High desirable level	Maximum permissible (l)
Total solid	500	1500
Taste	Unobjectionable	-
Odour	Unobjectionable	-

Turbidity (NTU)	5	25
Chloride	200	600
Iron	0.1	1
Manganese	0.05	0.5
Copper	0.05	1.5
Zinc	5	15
Calcium	75	200
Magnesium	30	15-
Sulphate	200	400
Total hardness	100	500
Nitrate	45	500
Ammonium	-	-
PH (Unit)	7-8	Min 6.5 Max 9.2

STUDY AREA

Kontagora 1s a local government area in Niger State located at northwest Niger State. It has area of 78.31 km* and a population of 5,555,200 at the (2016) census the worlds enclose in the local government include Arewa, central, Gabar, Kudu, Madara, Magajiya, Masuga, and Nagwamalse, out of this listed ward FCE Kontagora is in Madara ward.

TABLE B

S/N	Sample	Area
1	SUG	F.C.E (Male Hostel) Kontagora
2	Undergraduate	F.C.E (Male Hostel A) Kontagora

METHODOLOGY

WATER SAMPLING/PRESERVATION

The steps to be followed in sampling from a borehole or Pump outlet are described in sequence below:

CLEANING THE BOREHOLE

Any attachments that may cause splashing are removed from the borehole. A clean cloth, was used to wipe the outlet in order to remove dirt, and then your hands should be washed. Leaking boreholes must be repaired before sampling.

OPENING THE BOREHOLE

The borehole is pump at a maximum flow rate and the water was allow for 1-5minutes in other to clear the service line.

OPENING THE BOREHOLE PRIOR TO SAMPLING

The borehole was carefully pump on and allow to flow for 1-5 minutes at normal flow rate before taking the water sample.

SAMPLE COLLECTION

While holding the bottle, cover was loose and erase the bottle before taking the sample, the bottle was immediately hold under the water jet and filled as small space should be left to facilitate shaking at the time of inoculation prior to analysis. Bacteria prefer to attack themselves to surface or particles in order to spread the bacteria evenly, shaker the bottle vigorously to detach them from the side

CAPPING THE BOTTLE

The bottle was cap after the filling of the bottle with sample of borehole water, a label was place on the bottle with making tape and return to the laboratory immediately.

TEST METHOD PROCEDURE

Determination of PH (Radojevic et. al. 1999)

Method Potentiometric (Radojevic et. al. 1999)

Determination of Electrical conductivity (EC)

Method; Conductivity meter (Radojevic et. al. 1999)

Determination of Temperature ('C)

Method; mercury method (Radojevic et. al. 1999)

Determination of Dissolve Oxygen (DO)

Method Vinklerazide modification titrimetric (Radojevic et. al. 1999)

Determination of Biochemical Oxygen Demand {BOD}

Method bottle incubation for 3days at 27° C (Radojevic et. al. 1999)

Determination of Chemical Oxygen Demand (COD)

Method open reflux (Radojevic et. al. 1999)

Determination of Total Alkalinity (TA)

Method titrimetrie to PH = 4.5 (methyloorange) (Radojevic et. al. 1999)

Determination of Total Hardness.(TA)

Method EDTA titrimetric (Radojevic et. al. 1999)

Determination of Chloride (Cl)

Method Argentometric titration (Radojevic et. al. 1999)

Determination of Phosphorus, Ortho Phosphate (PO₄)

Method Ascorbic acid, spectrophotometric (Radojevic et. al. 1999)

Determination of Sulphate (SO₄)

Method Nephelometry (Radojevic et. al. 1999)

Determination of Nitrogen Nitrate (NO₃)

Method (Radojevic et. al. 1999)

Determination of Total Dissolve Solid (TDS)

Method Granmetric after filteration (Radojevic et. al. 1999)

Determination of Calcium (CA)

Method EDTA Titrimetric (Radojevic et. al. 1999)

Determination of Magnesium (MG) (Radojevic et. al. 1999)

Method of calculation from total hardness and calcium (Radojevic et. al. 1999)

other procedure involve in some heavy metal are as follows

Determination of Iron (Fe)

Method phenanthroline spectrophotometric (Radojevic et. al. 1999)

Determination of Manganese (Mn)

Method;persulphate spectrophotometric (Radojevic et. al. 1999)

RESULT AND DISCUSSION

The results of the laboratory analysis of the borehole water samples from all the sample points the two hostels are presented below.

Table 1. Result of the Physiochemical parameters

NAM E OF SAM PLE	PH VA LUE	TEMPER ATURE (OC)	ELECTRI CAL CONDUCTI VITY (S/M)	DISSO LVED OXYGEN (S/M)	CHLO RINE CONT ENT (CI)	TOTA L HARD NESS	TOTAL ALKAL INITY	BIOL OCAL OXYGEN DEMAND (BOD)	CHEM ICAL OXYGEN DEMAND (COD)
HOS TEL A	6.84	30	225	8.60	5.84	80.0	54.0	2.20	5.28
HOS TEL B	5.87	32	56	6.80	25.44	14.5	10.0	3.00	5.54
NSD WQ 2015	6.5- 8.5	31	1000	-	250	150	-	-	-
WH O	7.8	31	1000	1500	600	500	100	4.8	4.9

NOTE: NSDWQ- Nigeria Standard for Drinking Water Quality, At Maximum Permitted Level

pH VALUE

This is the value used to express the acidity or alkalinity of a solution. pH of 7.0 indicates neutrality. PH below 7.0 indicates acidity while PH above 7.0 indicates the degree of hydrogen ion concentration (H) in a given Sample, An acceptably PH value for drinking water is between 6.5 and 8.5 recommended by NSDWQ and World Health Organization (WHO). From table 1 the pH value of hostel A was 6.84 and the pH value obtained hostel B was 5.87. Therefore, the result shows that hostel A samples is more of alkaline while that of hostel B is slightly acidic by comparing the pH value obtained from table 1 above with NSDWQ and WHO standards.

TEMPERATURE

Temperature is an important characteristic of water it is the measure of the degree of hotness or coldness of a substance. High temperature cause more rapid chemical reaction rate and reduce solubility of minerals. It also reduces water hardness if the hardness is due to presences of bi-carbonate. Increase in temperature makes condition unfavorable for the development of pathogenic organism that may be present in water. The normal temperature of aesthetically portable water is 31°C. From table 1 above, the temperature obtained for hostel A was found to be 30°C and the temperature obtained for hostel B was found to be 32°C. Therefore, by comparing the temperature of the sample with the NSDWQ and WHO, desirable limit (31°C) and maximum permissible limit (30°C) respectively, the result shows that the temperature of the sample B is above the standard limit set by NSDWQ and WHO while that of sample A is within the range of the standard limit.

ELECTRICAL CONDUCTIVITY (EC)

Conductivity is the ability of a materials (in this case water) to carry electric current. The determination of electric conductivity in a water sample provides a rapid and convenient means of estimating the concentration of electrolytes in water to be used for public supply. Therefore, from the table below the conductivity obtained for the hostel A and Bare 225 and 56 respectively. Therefore, the result show that the conductivity of the samples are within the range of standard limit of NSDWQ and WHO of 1000

DISSOLVED OXYGEN (DO)

The term solids refer to matter suspended or dissolved in water or wastewater. These solids adversely affect the quality of water or effluent.

Water with high dissolved solid is generally of inferior palatability and induces unfavorable physiological reactions in the consumer. For drinking waters dissolved solid of 500 mg/l is desirable waters with high suspended solid value may be esthetically unsatisfactory for bathing.

From the result obtained from analysis the total dissolved solid for hostel A and B are 8.6 and 6.80mg/l respectively, therefore the sample are within the range of permissible total dissolved solid for potable water because the highest desirable 'is. 500 and the maximum permissible is 1500 as standard by WHO.

CHLORIDE CONTENT

Chloride in the form of chloride ions is one of the major inorganic anions in water and waste water. The chloride concentration is higher in the waste water then the raw water because of sodium chloride (NaCl) is a common ingredient of diet and passes unchanged through the digestive system. At the sea coast, chloride may be present in high concentration because of the leakage of salt, water in to the sewage system. It may also increase by industrial process. High chloride content may harm metal pipes and structures as well as, growing plants. From the result obtained from the analysis, the chloride .content of hostel A and hostel B samples are 5.84mg/l and 25.44mg/ They are within the range of permissible chloride content for potable water because the highest desirable is 250 and 600mg/l for NSDWQ and WHO respectively.

HARDNESS (TH)

Water hardness was understood to be a measure of the capacity of water to precipitate soap. Soap is precipitated mainly by calcium and magnesium ions present in the water which is in complex forms, frequently with organic constitute and their role in water is very minimal and difficult to define. Comparing the result obtained from the analysis with the NSDWQand WHO standards, we can observe that the result of hostel A is 80.0 and hostel B IS 14.5 in table 1. The value of hardness in the two samples are within the permissible limit of NSDWQand WHO standard of 150 and 500mg/l respectively.

TOTAL ALKALINITY(TA)

Alkalinity of a water is its acid neutralizing capacity and thus it is the sum of all titrable based in the water it comprises the sum of the bicarbonates, carbonates and hydroxides of calcium, magnesium, sodium and potassium alkalinity is expressed in terms of CaCO_3 , From table 1, hostel A has alkalinity of 54.0mg/l and hostel B has alkalinity of 10.0mg/1 Therefore, by comparing the alkalinity of the samples obtained from the table1 above with the WHO standard (100mg/l), it shows that the alkalinity of the samples is within the range.

Biological Oxygen Demand (BOD)

Biological oxygen demand was carried out in an experiment of a giving sample to determine the biological properties and to compared the result with the WHO standard value from the table 1, the BOD of hostel A is 2.20 and that of hostel B is 3.0mg/l so therefore, the BOD result show that it is within the range of WHO permissible limit.

Chemical Oxygen demand

Chemical oxygen demand test was carried out in the two samples. The chemical oxygen demand of the samples was found to be 2.20 minimum and the maximum found to be 3.00 in table 1. Therefore the COS result show that the values of the two samples are within the permissible range of NSDWQ and WHO

Table 2. Acidity parameters includes (PO₄, SO₄, and NO₃)

NAME OF SAMPLE	PHOSPHATE (PO ₄)	SULPHATE (SO ₄)	NITRATE (NO ₃)	CALCIUM (Ca)	MAGNESIUM (Mg)	TOTAL DISSOLVED SOLID (TDS)
HOSTEL A	1.82	5.36	1.82	16.76	9.14	16.34
HOSTEL B	3.74	7.50	3.74	3.22	1.36	3.75
NSDWQ 2015	-	100	50	-	20	500
WHO	0.05	400	500	200	15	1500

NOTE: NSDWQ- NIGERIA STANDARD FOR DRINKING WATER QUALITY, AT MAXIMUM PERMITTED LEVEL.

Table 2 show result of acidity parameters (PO₄, SO₄, and NO₃) carried out on the samples indicated that the water is not harmful for consumption. The values are far lower than the NSDWQ and that of the WHO. Even though the Calcium, magnesium and total dissolved solid content of sample from hostel A is higher than that of hostel B.

Heavy Metal Analysis

Some heavy metals analysis was carried out in the two water samples the following heavy metals Zn, Cd, Fe, Cu, Ni, Pb, Mn, Cr were analyzed

Table 3; Heavy metal analysis result

NAME OF SAMPLES	Zn	Cd	Fe	Cu	Ni	Pb	Mn	Cr
	Mg/l	Mg/l	Mg/l	Mg/l	Mg/l	Mg/l	Mg/l	Mg/l

Hostel A	0.42	0.00	0.18	0.01	0.00	0	0.01	0.00
Hostel B	0.02	0.00	0.07	0.01	0.00	0.00	0.02	0.00
NSDWQ 2015	3.0	0.003	0.3	1.0	0.02	0.01	0.2	0.05
WHO	15	0.02	1	1.5	10	0.2	0.5	1.30

NOTE: NSDWQ- NGERIA STANDARD FOR DRINKING WATER QUALITY, AT MAXIMUM PERMITTED LEVEL

The above data shows the result of the heavy metals identified from the analysis carried out on the two samples, the data were compared with the Ngeria Standard for Drinking Water Quality, At Maximum Permitted Level. The results of the analysis on the sample show that the water is safe for drinking because the heavy metals (Zn, Cd, Fe, Cu, Ni, Pb, Mn and Cr) content are within the accepted value of NSDWQ as shown in table 3

CONCLUSIONS

Considering the results obtained from the two manual boreholes samples located at female hostel **A** and **B** at FCE Kontagora, Kontagora Local Government Area. Conclusions were drawn as follows;

1. Physical parameters: Based on the mean results of the experiments (temperature=23°C, Turbidity=1.0 NTU, Electrical Conductivity=1.4 µS/cm, Total Dissolved Solid=51.1 mg/L) the borehole water from the two hostels are safe for human consumption when the results are compared to World Health Organization (WHO) standard for drinking water.
2. Chemical parameters: Based on the mean results of the experiments (pH=7.4, Hardness=483.2 mg/L, Alkalinity=71 mg/L Chloride Content=63.8 mg/L) the borehole water from the two hostels are safe for human consumption when the results are compared to World Health Organization (WHO) standard for drinking water, except for hardness which is above WHO standard.
3. Biological parameters: Based on the results of the analysis (coli-form Bacteria=absent) the borehole water from the two hostels are safe for human consumption.

The iron content of sample K (3.06 mg/l) is above the WHO and NSDWQ 2015 standard limit of 1 and maximum permissible limit of 0.3 mg/l but that does not make it a bad for drinking. When water is scarce, it becomes more difficult for community to produce food, prevent the spread of diseases. Water stress contributes to regional instability, derives mass migration and can lead to broader conflict.

RECOMMENDATIONS

- Federal Government should facilitate water cooperation and water management across the country through developmental programs in order to give quality water to its citizens
- Secure and sustainable access to safe water is an essential element of national security, therefore, the government should make it as its topmost priority to its citizenry.

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**SN 27 COMPARATIVE INVESTIGATION OF COMPOST AND EFFLUENT FROM
VEGETABLE WASTES FOR OPTIMUM PLANT PRODUCTIVITY**

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ABSTRACT

This study investigated the effect of amended compost (from vegetable wastes) and its effluent on agricultural soils using *Phaseolous Vulgaris .L.* (Bean seed). Essential parameters such as pH, Electrical Conductivity, Moisture content, Ash content, Volatile matter, Organic Matter, Total organic carbon, Total Nitrogen, Phosphorus and Potassium were analyzed to determine the quality of the compost and effluent. Results revealed that values of pH, Moisture content, Ash content, Potassium and Carbon/Nitrogen ratio were higher in the compost effluent while Electrical Conductivity, Organic Matter, Total Organic Carbon, Total Nitrogen and Phosphorous was higher in the compost. Nutrient values such as Nitrogen and Phosphorus (2723.67 Mg/Kg and 1.53Mg/L respectively) were higher in the compost while Potassium (223.43Mg/L) was higher in the compost effluent. The compost and its effluent demonstrate robust soil enrichment potentials which are essential for chlorophyll production, root development and healthy plant growth.

Keywords: Compost, Compost Effluent, Vegetable wastes, Plant growth, Soil enrichment.

INTRODUCTION

Agricultural practices and waste management play a pivotal role in achieving sustainable development goals. Proper disposal and handling of organic waste, particularly vegetable waste, are crucial for mitigating environmental pollution and enhancing soil health. Potential strategies for managing vegetable waste include composting and wastewater treatment, yielding compost and effluent as valuable end products. Understanding the impact of compost and effluent on plant productivity is vital for optimizing their application in agriculture and ensuring sustainable waste management practices.

Vegetable wastes, encompassing peels, stems, leaves, and unused vegetables, are a substantial by-product of agriculture, food processing, and consumption. Inadequate management of vegetable waste can result in greenhouse gas emissions and environmental pollution. Nonetheless, such wastes present opportunity for recycling and resource recovery (Roy and Mishra, 2017). Composting, a natural process, transforms organic waste into nutrient-rich compost, serving as valuable organic fertilizer. Microorganisms facilitate the breakdown of organic matter during composting, converting it into stable humus-like material rich in crucial nutrients such as nitrogen, phosphorus, potassium, and micronutrients (Rekha and Prasad, 2020). Compost enhances soil structure, water retention, and nutrient availability, promoting plant growth and bolstering soil health.

The management of vegetable wastes can also involve wastewater treatment, yielding effluent containing dissolved nutrients, organic matter, and other compounds. Effluent can be generated through various processes, including leaching, compost leachate, or wastewater from vegetable washing and processing units (Baralet *al.*, 2017). Nevertheless, untreated effluent discharge can lead to water pollution, eutrophication, and environmental degradation if not handled properly. Effluent from vegetable wastes

contains vital plant growth nutrients like nitrogen and phosphorus (Zebarth and Kucey, 1999). However, elevated nutrient concentrations in effluent can harm water bodies, causing excessive algal growth and oxygen depletion, effective effluent treatment is imperative to mitigate its environmental impact and ensure safe disposal or reuse. Though both compost and effluent from vegetable wastes can influence plant productivity and soil health, there is a knowledge gap regarding their comparative effects. Gaining insights into how compost and effluent impact plant growth, nutrient uptake, and overall productivity is critical for informed decision-making concerning their use in agriculture (Anti *et al.*, 2018).

This study aims to bridge this knowledge gap by conducting a comparative analysis of the effects of compost and effluent from vegetable waste on plant productivity. Through a thorough examination of plant growth parameters, nutrient content, and soil properties in both treatments, the study aims to provide valuable insights into the suitability of compost and effluent as organic fertilizers for sustainable agriculture and waste management. Comparing the effects of compost and effluent from vegetable wastes on plant productivity is essential for optimizing their use in agriculture and waste management practices. By offering scientific evidence on the advantages and limitations of each approach, this study strives to contribute to sustainable agricultural practices and environmental conservation. The findings from this study can guide farmers, waste managers, and policymakers in making well-informed decisions to ensure efficient resource utilization and minimize environmental impacts.

MATERIALS AND METHOD

Preparation of composting raw materials

The Fresh kitchen wastes were sourced from commercial and domestic kitchens around Ugbowo, Egor Local Government Area. Cow bones and corn cobs were obtained from abattoirs and corn mill in New Benin, the corn cob was sourced from corn mills in New Benin, Benin City while palm oil sludge was obtained from palm oil mills at Adolor. The kitchen wastes (including fruit and vegetable peels), and palm oil sludge were used as amendment materials. The composting process was carried out in an airtight container to create oxygen-free conditions, allowing anaerobic microorganisms to decompose the organic waste.

The experiment started by layering the airtight container with kitchen waste at the bottom to provide aeration and prevent compaction. Corn cob was added on top of the kitchen waste, providing a source of nitrogen for the anaerobic composting microbes. Palm oil sludge mixed with the cow bones was then spread over the kitchen waste and corn cob layer, contributing additional organic matter and nutrients. Moisture levels in the anaerobic composting container were carefully monitored and adjusted by constantly sprinkling water every two days to maintain optimal conditions for microbial activity. Over the course of approximately 2 weeks, the anaerobic composting process took place, during which the waste materials gradually decomposed into nutrient-rich compost. Regular monitoring was performed to ensure that the composting process was proceeding efficiently.

After the compost has attained maturity and stability, the compost and its effluent were collected and analysed following standard analytical methods.

Analysis of compost and compost effluent samples

a. DETERMINATION OF pH& EC

4g of composting samples were weighed and transferred into a 40ml beaker, and 10ml of distilled water was added to the samples. The samples were mixed thoroughly with glass rod and allowed to stand for one hour with intermittent stirring. The pH meter was calibrated with known pH of buffer solutions 4.0 and 9.0. The pH meter electrode was immersed into the samples and the reading was taken (Rodger *et al.*, 2017). The EC electrode was immersed into the samples and the readings was taken.

b. MOISTURE CONTENT DETERMINATION

3g of the sample was weighed into a well labeled crucible that has been oven dried and weighed. The crucible and the content were transferred into the oven at 110°C for about 2 hours. The crucibles were then cooled in desiccators for one hour. Then the weight of the crucible and sample record (ASTM D2974–(2014)).

c. VOLATILE MATTER AND ASH CONTENT DETERMINATION

The muffle furnace was heated to 950°C and the crucible with the sample from the moisture content determination was placed with lid into the muffle furnace for one hour. The weight loss after one hour was determined by measuring the final weight with an analytical balance (ASTM D2974– (2014).

d. DETERMINATION OF PHOSPHORUS

1ml of digest was mixed with 8ml of distilled water and then 1ml of the colour solution was added along with 0.5ml of ascorbic acid. Spectrophotometer reading was taken at 660nm (Nagorny, 2013).

e. DETERMINATION OF POTASSIUM

The sample were finely ground after drying for 12 hours at 80°C, 1g of the samples was weighed into a high form porcelain crucible; the samples were ashed in a muffle furnace at 500°C for 4 hours. The sample ash was cool and dissolved in 5ml of 20% (2M) HCl, and filtered through an acid washed filter paper into a 50ml volumetric flask. The filtrate was read with flame photometer at 766.5nm (Anderson and Ingran, 1993).

f. DETERMINATION OF TOTAL ORGANIC CARBON AND ORGANIC MATTER

0.05g of sample (cow bone) air-dry was weighed into a 500ml beaker. 10ml 1N potassium dichromate solution using a pipette was added, and 10ml concentrated H₂SO₄ was added using a dispenser, and the beaker was swirl to mix the suspension, while allowed to stand for 30 minutes. 100ml of distilled water was added and 5ml concentrated H₃PO₄ was added using dispenser, and allowed to cool. 10 to 15 drops of diphenylamine indicator was added, and a Teflon – coated magnetic stirring bar was added, and the beaker was placed on a magnetic stirrer. 0.5M ferrous ammonium sulfate solution was used to titrate, until the colour change was observed from violet blue to green. Two blank were prepared containing the entire reagent except the compost sample, and was treated exactly the same way as the sample's suspension (Nagorny, 2013).

Table 1: Result of the Analysis the compost and compost effluent

s/n	Parameter	Units	Palm oil sludge	Kitchen waste	Corn cob	Cow bone
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1	pH		7.54 ± 0.01	3.31 ± 0.01	7.84 ± 0.04	6.40 ± 0.06
2	Electrical conductivity	mS/cm	4.60 ± 0.01	2.68 ± 0.02	134.80 ± 0.30	130.8 ± 0.20
3	Moisture content	%	81.23 ± 0.30	91.50 ± 0.10	52.89 ± 4.03	8.43 ± 1.20
4	Ash content	%	97.43 ± 0.40	99.00 ± 0.00	95.46 ± 0.09	96.76 ± 1.30
5	Volatile matter content	%	2.56 ± 0.40	0.70 ± 0.02	4.40 ± 0.28	3.24 ± 1.30
6	Organic matter	%	36.47 ± 0.01	38.48 ± 0.01	16.50 ± 0.02	22.49 ± 0.20
7	Total organic carbon	%	21.21 ± 0.01	22.22 ± 0.01	9.62 ± 0.02	13.08 ± 0.12
8	Total nitrogen	Mg/kg	15426.21 ± 0.10	1702.57 ± 0.31	5766.77 ± 0.20	1305 ± 0.60
9	Phosphorus	Mg/L	0.21 ± 0.00	0.21 ± 0.00	0.52 ± 0.00	1.81 ± 0.00
10	Potassium	Mg/L	12.73 ± 0.40	0.43 ± 0.06	2.53 ± 0.12	2.00 ± 0.26

Table 2: Result of the Pot experiment using compost

		75% compost		45% compost		20% compost		450g soil (control)	
Duration	Bean seedling	Length of plant (inch)	Amount of leaves	Length of plant (inch)	Amount of leaves	Length of plant (inch)	Amount of leaves	Length of plant (inch)	Amount of leaves
Day 5		4 inches	3 leaves	3 inches	2 leaves	5.1 inches	2 leaves	6 inches	3 leaves
Day 10		5.5 inches	6leaves (3 wide & 3 tiny leaves)	6 inches	2 leaves (wide leaves)	6.5inches	3 leaves (wide leaves)	4.7 inches	3 leaves
Day 15		4.7 inches	6 leaves (3 wide & 3 tiny leaves)	7.5 inches	5 leaves (2 wide & 3 tiny leaves)	6.8 inches	5 leaves (2 wide & 3 tiny leaves)	5inches	3 leaves

Table 3: Result of the Pot experiment using effluent

		150g soil + 2ml effluent		250g soil + 4ml effluent		350g soil + 6ml effluent		450g soil + 8ml effluent	
Duration	Beans seedling	Length of plant (inch)	Amount of leaves	Length of plant (inch)	Amount of leaves	Length of plant (inch)	Amount of leaves	Length of plant (inch)	Amount of leaves
Day 5		SPROUTING	NO GROWTH	4 inches	2 leaves	4.5 inches	3 leaves	5 inches	2 leaves
Day 10		NO GROWTH	NO GROWTH	4.3 inches	3 leaves	5.5 inches	3 leaves	5.5 inches	2 leaves
Day 15		NO GROWTH	NO GROWTH	3.2 inches	3 leaves	3.5inches	3 leaves	6.1 inches	2 leaves

DISCUSSION

Table 1 shows the physiochemical analysis of the compost and compost effluent. They both had pH between the range of 6-8 which is the ideal range for a compost and effluent. The electrical conductivity of the

compost was 1.40mS/cm. The range often considered ideal for most crops is between 0.5 - 2.0mS/cm. The extremely high electrical conductivity of the compost effluent (3.13mS/cm) may be due to its alkaline pH. The pH can increase the ionization of salts and other substances dissolved in the solution. The Nitrogen and Phosphorus content play pivotal roles in plant growth. They help with stem and leaf development, promote root growth and flower production. The potassium helps with the overall plant health and regulation of water and nutrient uptake. High-nitrogen compost tends to decompose faster than compost with lower nitrogen levels. Carbon-rich materials are essential because they help create a balanced carbon-to-nitrogen ratio. This is critical for efficient decomposition and the prevention of foul odors in anaerobic conditions.

The compost and its effluent were infused into soil to monitor the length of the plant and amount of leaves of bean seedlings.

Table 2 shows the results of the pot experiment using compost. The outcome of the pot experiments with 45% and 20% compost outperformed the one with the 75% compost. This may be attributed to the following factors:

1. Nutrient levels: Excessive compost can lead to nutrient imbalance thereby affecting plant growth.
2. Water retention: Compost improves soil's water-holding capacity but too much compost can lead to excessive water retention, potentially causing water-logged conditions that hinder plant growth.
3. Salinity: High salt levels may be detrimental to many plants.
4. Microbial activity: A lower compost content might have better supported microbial activity in the soil promoting nutrient availability to plants.
5. Aeration: Adequate aeration is crucial for root health. Higher compost content can sometimes lead to compacted soil and reduced aeration, negatively impacting root development.

Table 3 shows the results of the pot experiment using compost effluent.

Growth remained limited as no growth was observed in the 150g soil + 2ml effluent. Environmental conditions such as light, temperature and humidity can influence plant growth. The 2ml of effluent did not provide enough nutrient needed by the bean plant. Adequate moisture is crucial for plant growth and the 2ml of effluent may not have supplied the right quantity needed by the soil. There was a notable decrease in plant length from 4.3 inches to 3.2 inches for the pot experiment of 250g soil + 4ml effluent and from 5.5 inches to 3.5 inches for the pot experiment of 350g soil + 6ml effluent. These reductions in the length of the plant could be attributed to the excessive nutrient level which could stress or damage the plant, Over-fertilization which could hinder root development, inadequate or excessive watering which could lead to over-saturation and environmental factors such as light and temperature. The 450g soil + 8ml effluent had an increased plant length from 5 inches to 6.1 inches at the end of the experiment.

Compost provides a slow-release, long term benefit to soil health while compost effluent offers quick nutrient availability making it suitable for specific growth requirements and stages. Adjustment of the amount and frequency of compost effluent application, Monitoring soil moisture levels, Ensuring a balanced nutrient supply and watering practices, Using a healthy plant material and Providing the appropriate environmental conditions for plant growth are essential for optimum plant productivity.

CONCLUSION

The analysis of composting materials revealed their distinct qualities and how they influence composting effectiveness. Comparison between the compost and its effluent highlighted differences in the parameters analysed (such as pH, electrical conductivity, moisture content, ash content, volatile matter, organic matter, nitrogen, phosphorus, potassium and C/N ratio). The compost demonstrated robust soil enrichment potential, offering ample total nitrogen (2723.67Mg/Kg), phosphorus (1.53Mg/L) and potassium (10.17Mg/L). Conversely, the compost effluent contained nitrogen (1571.42Mg/Kg), phosphorus (0.20Mg/L) and notably higher potassium (23.43Mg/L) but lacked the concentrations required for robust plant growth compared to the compost. Thus, the compost effluent potassium level necessitates additional nutrient supplementation for comprehensive soil fertility. The compost was a better fertilizer than its effluent due to its higher Nitrogen and Phosphorus content

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