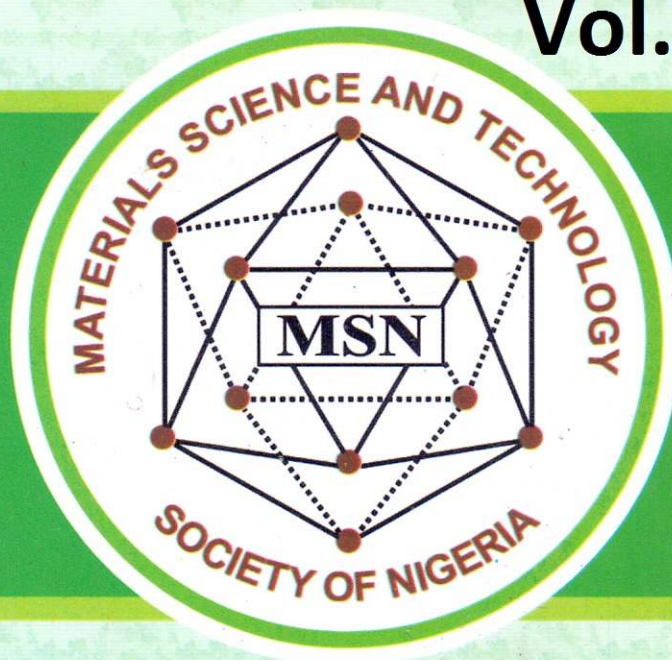


Book of Proceedings

OF THE

15TH ANNUAL INTERNATIONAL CONFERENCE/ NIGERIAN MATERIALS CONGRESS (NIMACON 2016)

Vol. II



21st - 25th November, 2016

Held at



**Ahmadu Bello University, Zaria,
Kaduna State - NIGERIA.**

COLLABORATORS



PROCEEDINGS

of the

NIGERIAN MATERIALS CONGRESS

(NIMACON-2016)

VOLUME II

Published by

Materials Science and Technology Society of Nigeria (MSN)

National Headquarters

Engineering Materials Development Institute,

Km 4 Ondo Road,

PMB 611, Akure, Nigeria.

www.msn-ng.org

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ISBN 978-060-609-21

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FROM THE EDITORS'S DESK

The Materials Science and Technology Society of Nigeria (MSN) in conjunction with Ahmadu Bello University, Zaria hosted the 2016 Nigerian Materials Congress tagged NIMACON2016 which was held between 21st and 25th November, 2016 at ABU Hotels, Kongo, Zaria.

The main objective of the conference is to bring experts/researchers on materials science and technology in Nigeria and the rest of the world to interact and exchange ideas on the diversification of the national economy through the development of engineering materials from solid minerals in the country. Keynote and plenary papers were presented by experts on the conference theme: **Engineering Materials and Solid Minerals Development: Panacea to the National Economic Diversification**. Particular attention was given to the potential utilization of solid minerals in the country for the production of important engineering materials used in many industrial applications.

We are very delighted to present this 2016 Book of Proceedings (Volume I and II) containing a compendium of well researched articles spanning across all areas of Materials Science and Technology disciplines.

We sincerely appreciate the immense contributions of our participants, collaborators and sponsors, particularly Ahmadu Bello University, Zaria, the Kaduna State Government and the Raw Materials Research Development Council. Others are Federal Ministry of Science and Technology, Federal Ministry of Solid Minerals Development, National Agency for Science and Engineering Infrastructure (NASENI), Energy Commission Abuja; Engineering Materials Development Institute (EMDI), Akure; Kaduna State Ministry of Education, Science and Technology, Pan African Materials Institute (PAMI), Abuja; National Research Institute for Chemical Technology (NARICT), Basawa, Zaria, University of Ilorin, Ilorin, Kwara State, Nigeria Institute of Leather and Science Technology (NILEST) Zaria.

We have made some effort in editing the papers to ensure conformity and uniformity to some extent. However, on our own part, any error or omission is highly regretted but author(s) are solely responsible for the content and the correctness of their published work.

Finally, we thank you all for the interest shown in Materials Science and Technology Society of Nigeria.

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BUILDING HOUSES WITH LOCALLY AVAILABLE MATERIALS IN EDO STATE, NIGERIA: COST, BENEFITS, AND PROBLEMS

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ABSTRACT

Housing is one of the basic necessities of life after food and clothing. The high cost of building materials in Nigeria is making the stakeholders to look for alternative sources of building materials locally. Therefore, the purpose of this paper was to empirically examine the cost, major benefits, and problems associated with houses constructed with local materials in a developing country. Relevant texts, journals, personal interviews, past cost data and administered questionnaire were used to obtain data from the randomly sampled population. The study was a cross sectional survey of 70 questionnaire administered to respondents using structured questionnaire. Only 55 questionnaire were returned and accepted for analysis. The questionnaire were administered to Architects, Engineers, Quantity Surveyors, Builders, selected clients, and contractors. The percentile grading and mean score techniques were used to analyze the data. From the findings, promotion of cultural heritage, abundance of materials in the locality, provision of cool room temperature, enhance technological advancement, create employment, source of conserving foreign exchange, bring down the price of foreign materials, availability and affordability of some local building materials were the major benefits of houses built with locally available materials. Others were reduction in energy usage, cut down CO₂ emissions, and minimize generated wastes. The study identified the significant problems associated with building houses with locally available materials as: low strength, frequent maintenance, lack of standards and specifications, legal acceptability, social acceptability, requirement of increased labour work, and easily wearing of erosion of the materials as the most significant. Others were technology to handle the setting, uncertainty of the cost, double standard in the part of the government, problem of mass production, and uncertainty about the demand and strength of materials. Also, findings revealed that very few of these local materials were expensive at low quantities, example was stabilized earth blocks. Based on the findings, the study recommended among others that professional Institutions in the built environment should collaborate and put up an executive bill that will enhance and encourage entrepreneur in developing local building materials through the Federal Ministry of Power, Works and Housing to the National Assembly. Also, the joint Institutes should ensure that the proposed Construction Bank come to reality that would encourage investors access fund easily with a view to improving local building materials. Government should fund Nigeria Building and Road Institute (NBRI) very well with a view to meeting up with the mandate.

Keywords: Building Materials, Cost of Building, Houses, Local Materials.

INTRODUCTION

Housing is one of the basic necessities of life after food and clothing. The high cost of building materials in Nigeria is making the stakeholders to look for alternative sources of building materials locally. Researchers have shown that more than half of the world's 6.6 billion people live in urban areas, crowded into 3 percent of the earth's land area (In UNCHS's study as cited in Fadairo & Olotuah, 2013). The population of Nigeria is over 180 million and has an estimated housing deficit of over 17 million units (National Bureau of Statistics, 2014). Nigeria's urban housing problems manifest in overcrowding, slum housing and the development of shanties in virtually every major Nigerian city, cities in Edo State not exempted.

The housing problem vary from inadequate quantity and quality of housing to the attendant impact on the psychological, social, environmental, and cultural aspects of housing. Building houses are capital-intensive; perhaps, the cost of adequate housing is beyond the reach of most Nigerians (Ebekozi, 2012; Olotuah, 2012). In Nigeria, over 7 out of every 10 persons live below the minimum poverty level and 9 of every 10 are in the low income group (Fadairo & Ganiyu, 2010). It is obvious that these people cannot provide housing for themselves. All attempt by previous and present government to provide housing through various policies regarding housing delivery to the general public has failed as a result of poor implementation to meet up with the high magnitude of housing units needed (Adedeji, 2011; Fadairo, 2008).

Therefore, building houses with locally available materials with a view to meet the housing requirements cannot be over-emphasized. Although the National Housing Policy of February 1991 paid due recognition to local building materials in its chapter six, but implementation has totally failed. The term local building material has generated many arguments in housing study and in the construction industries today. Inability to define what is local has been a great issue. For instance, when does a material become local? Is it where it is produced, is it the technology/invention process involved in the use or arrangement of it, is it the methods of production or is it when it crosses an international or refuses to cross an international boundary? Would one be right to refer to building materials coming from Cameroun, Niger, Benin Republic and other surrounding African countries as local or non-local building materials? When for instance, a firm in Nigeria buys a tile making machine from Germany and uses the machine for the production of exactly the same stuff of tiles they produce in China or Spain, is such product still local? These are the worries of experts in housing and building industries and these issues need further classifications.

However, in Omole's study as cited in Omole & Bako (2013) defined the term local building materials as "those materials used in building construction, got around us, with less stress and with less or no further processing". Based on this definition, the term "local" when used with building materials is a relative term. Therefore, for instance goods/building materials produce in Spain, Italy, Germany, e.t.c. are local products at home, but become imported to

other countries that import them. Examples of local building materials include the following: literate; sandcrete; stabilized earth; burnt clay; clay brick; bamboo; raffia leaves; palms-kernel shell; crushed coconut shell (for floor and terrazzo material); dung; coarse and fine aggregate; timber work (hardwood and softwood); plywood; cement; paints; sanitary appliances and fittings; electrical installations (wiring cables, conduct pipes and accessories).

According to Ajayi's study as cited in Taiwo and Adeboye (2013), opines and encourage the use of non-conventional materials such as sawdust, palm kernel, mud, just to mention a few, being cost effective and environmental friendly replacements/complements for stone dust, coarse aggregate and sandcrete. Also, Omole and Bako (2013) identified high cost of building materials as one of the major factors militating against housing delivery system. The authors are of the opinion that this reason gave the thought to developers and experts in housing industries to fashion out an alternative ways of solving these problems. Perhaps the alternative way out is the use of local building materials.

The benefits associated with usage of local building materials for houses cannot be over-emphasized. Danso (2013); Omole and Bako (2013) highlight them as follows:

- i. It cut down or reduces prices in a relative term
- ii. The source can easily be visited and this makes it reliable
- iii. Adaptation and the use of local building materials will make the imported ones relatively cheaper
- iv. Most of the local building materials requires less or no further processing and thus make them very economical
- v. Production of local building materials definitely creates employment for the labour market
- vi. The adaptation and use of them led to the development of local technology
- vii. It is a good measure of conserving foreign exchange
- viii. It fosters the custom and cultural heritage of the people

Omole and Bako (2013) highlighted some of the criticisms against the use of local building materials as follows:

- i. Legal acceptability
- ii. Social acceptability
- iii. Durability as doubtful
- iv. Technology to handle the setting
- v. Uncertainty of the cost
- vi. Double standards on the part of the government
- vii. Lack of standards and specification
- viii. Lack of organizational / institutional framework
- ix. Problem of mass production
- x. Uncertainty about the demand
- xi. Uncertainty about the strength of material when compared with their imported counterparts.

Similarly, Danso (2013) identified the following as the criticisms:

- i. Low strength
- ii. Requires frequent maintenance
- iii. Requires a lot of labour work
- iv. Materials wear or erode easily
- v. Materials are easily attacked by rodents/pests

In view of the above, the main question of this paper is that, 'what are the cost implication, benefits, and problems associated with houses built with locally available materials in Edo State, Nigeria'? The purpose of this study, therefore, is to empirically examine and analyze the cost implication,

major benefits, and problems with houses constructed with local materials in the context of Nigerian construction industry. The objectives of the study are:

- i. Evaluate the cost implication associated with houses constructed with local materials in Edo State, Nigeria
- ii. Assess the major benefits associated with houses constructed with local materials in Edo State, Nigeria.
- iii. Evaluate the major problems associated with houses constructed with local materials in Edo State, Nigeria.

METHODOLOGY

This study is descriptive, designed to obtain views from selected clients, contractors, construction professional consultants in regard to cost implication, major benefits, and problems associated with houses constructed with local materials in Edo State. Relevant texts, journals, personal interviews, past cost data and administered questionnaire were used to obtain data from the randomly sampled population. The study was a cross-sectional survey of 70 questionnaire administered to respondents using structured questionnaire. Only 55 questionnaire were returned and accepted for analysis. The questionnaire were administered to Architects, Engineers, Quantity Surveyors, Builders, selected clients, and contractors respectively. A snowball sampling technique was adopted to identify respondents who have been directly or indirectly involved in building houses with locally available materials within Edo State, Nigeria, to seek their opinion. This is because according to Ofori and Dampson (2011), with this approach to sampling, the researcher makes initial contact with a small group of respondents who are relevant to the research topic and uses these to establish contact with others.

The data were analyzed using descriptive statistics to evaluate the cost implication, major benefits, and problems associated with houses built with available local materials. The first objective was percentage while the second and third objective respectively for each item was computed with SPSS version 16.0. Thereafter, the computed mean ratings were compared with the theoretical mean rating (assuming normal distribution of responses above neutral) of 4.0 to evaluate the major benefits and problems of houses built with available local materials. Any computed mean of an item relating to the benefits and problems of houses built with available local materials equal or exceeding 4.0 indicated expression of benefits or problems of houses built with available local materials, while values below 4.0 indicated expression of minor benefits and problems of houses built with local materials

RESULTS AND DISCUSSION

Table 1 reveals the summary of major demographic profile of respondents. In terms of stakeholders, 63.6% of the respondents consultants, 18.2% of the respondents were clients and contractors respectively. From Table 1, it shows that at least 81.8% of the respondents have at least 10 years minimum experience. Also, all the respondents have a minimum of HND/PGD/B.Sc/B.Tech. In terms of preference for locally available materials for building houses, 81.8% preferred soil/earth, 12.7% preferred agricultural waste while 5.5% preferred industrial waste. This implies that most of the respondents preferred the use of soil/earth as a local material for building houses.

Table 2 shows that about 67.3% of the respondents agree that local materials usage for building houses is cheap as against the 21.8% who agree it is on expensive side, while 10.9% of

the respondents could not decided whether expensive or cheap. It is therefore evidence that respondents are well aware of the cost effectiveness of the use of local materials even through the use of some of these local materials e.g sandcrete block for construction is still very much in vogue. During the oral interview, most of the respondents agree that although few of the local materials are expensive eg Nigerian electric cables, they (respondents) are of the opinion that the usage of locally made building materials cannot be overemphasized because its cheap and has economic value to the economy.

Table 1: Summary of Demographic Profile of Respondents (n= 55)

Category	Number of Respondents	Percentage (%)
Stakeholders		
Consultants	35	63.6
Clients	10	18.2
Contractors	10	18.2
Total	55	100
Years of Experience		
10 years	10	18.2
10-19 years	15	27.2
20- 29 years	20	36.4
= 30 years	10	18.2
Total	55	100
Academic Qualification		
HND/BSC/PGD/B.Tech	30	54.5
MSC/M.Tech/M.Phi	21	38.2
PhD	4	7.3
Total	55	100
Reference for local materials		
Soil/Earth	45	81.8
Agricultural waste	7	12.7
Industrial/chemical waste	3	5.5
Total	55	100

Table 2: Cost Implication Associated with Using Local Materials for Building Houses

S/Nos	Cost	Frequency	Percentage
1	Very Expensive	5	9.1
2	Expensive	7	12.7
3	Undecided	6	10.9
4	Fairly Cheap	15	27.3
5	Cheap	22	40.0
	Total	55	100

With reference to Table 3, the respondents ranked increase technological advancement at first (1st) position as the major benefits of houses built with local available materials with a mean score of 4.75, followed by job creation which was ranked second (2nd) position with mean rating of 4.69. Conservation of foreign currency was ranked (3rd) with a mean rating of 4.60, and the fourth (4th) ranked position was provision of cultural heritage with mean rating of 4.51. Others were: affordability of materials, environmental friendly, provision of cool room temperature, availability of materials, reduction in processing, and fire resistance characteristics. The last three benefits were rated below 4.00 and there referred to as minor benefits of building houses with locally available materials. This finding deviated from Danso (2013) that ranked promotion of cultural heritage as 1st position. Apart from the above benefits, during the oral interview, a larger percentage of the respondents believe that

some of the locally building materials are medicinal and could increase the immunity of the human body system. This could be subject to research.

Table 3: Identified Benefits Associated with Houses Constructed with Local Materials

Identified Benefits	Mean Score	Rank
Increase technological advancement (industrialization)	4.75	1
Job creation (Employment/wealth creation)	4.69	2
Conservation of foreign currency (Naira get stronger)	4.60	3
Promotion of cultural heritage (Tourism)	4.51	4
Affordability of materials	4.47	5
Provision of cool room temperature	4.40	6
Environmental friendliness	4.40	6
Availability of materials	4.34	8
Burning down prices of foreign materials	3.71	9
Reduction in processing	3.65	10
Fire resistance characteristics	3.34	11

Table 4: Identified Problems Associated with Houses Constructed with Local Materials

Identified Problem	Mean Score	Rank
Have low strength	4.81	1
Requires frequent maintenance	4.69	2
Lack of standard and specifications	4.62	3
Materials ware or erode easily	4.43	4
Easily attacked by rodents/pests	4.43	4
Problem of mass production	4.31	6
Double standard on the part of government	4.22	7
Lack of organizational institutional framework	4.22	7
Technology to handily the setting	4.07	9
Legal and social acceptability	3.75	10
Uncertainty about the demand	3.51	11

The result as presented in Table 4 indicates that houses constructed with local materials have low strength was ranked first (1st) as the major problem associated with houses built with locally available materials with a mean rating of 4.81 followed by requires frequency maintenance which was ranked second (2nd) position with a mean rating of 4.69. The third identified problem associated with houses constructed with local materials was lack of standard and specification with a mean rating of 4.62. Other problems associated with houses constructed with local materials were: materials ware or erode easily, easily attacked by rodents/pest, problem of mass production, double standard on the part of government, and lack organizational/institutional framework. Although the major problems identified in this finding do not deviate from Danso (2013) findings, but Danso (2013) identified only five (5) problems while this study identified eleven (11) problems. According to the respondents during the oral interview, even with these problems, locally made building materials are still better than foreign/imported building materials, if only the government can create the enabling environment for the advancement of these locally made materials.

CONCLUSION AND RECOMMENDATIONS

The purpose of this study was to empirically examine and analyze the cost implication, major benefits, and problems associated with houses constructed with local materials in an emerging country context. The study revealed increased

technological advancement, job creation, conservation of foreign currency and promotion of cultural heritage as the major benefits of houses constructed with locally available materials in Edo State, Nigeria. Also the study agreed that these local materials are available and affordable, that means, cheap in respect of cost. On the other hand, low strength, frequent maintenance, and lack of standard and specification were found to be the major problems associated with houses built with locally available materials in Edo State, Nigeria.

It is therefore recommended among others that encouragement of the use of local building materials should be a collective responsibility of the government, individual and private organization. Government should ban or place restriction on same imported building materials with a view to allow our local industries to grow and encourage people in using the available locally produced building materials. Also the joint Institutes within the built environment should ensure that the proposed Construction Bank come to reality that would encourage investors access funding easily with a view to improving local building materials. Government should fund Nigeria Building Research and Road Institute (NBRRI) very well with a view to meeting up with the mandate.

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INTERFACIAL AND CORROSION-INHIBITING EFFECT OF *TAPINANTHUS DODONEIFOLIUS* LEAVES EXTRACT ON COPPER (CU131729) CORROSION IN CHLORIDE SOLUTIONS

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ABSTRACT

Inhibition effect of *Tapinanthus dodoneifolius* (TD) leaves extract on corrosion of copper in 2 M HCl and 3.5% NaCl solution has been investigated by weight loss, polarization technique and quantum chemical calculations. Surface morphology and elemental analysis was carried out on the corroded specimen using SEM/EDS to compliment results obtained. The weight loss results showed that the corrosion inhibition potentials of TD as temperature-concentration dependent. Polarization studies showed that TD suppressed both the cathodic and anodic processes by acting as mixed-type inhibitor without altering the corrosion mechanism. Calculated thermodynamic parameters (ΔH_{ads}^* , ΔS_{ads}^*) showed that adsorption process is spontaneous with electrostatic interactions which indicates physical adsorption. DFT studies confirmed the corrosion inhibiting potential of TD molecular composition with adsorption energy computed via molecular dynamic. The SEM/EDS data show the presence of TD leave extract molecules on the specimen surface indicating its adsorption on Cu surface which resulted in reduced corrosion rate.

Key words: Corrosion inhibition, Copper, *Tapinanthus dodoneifolius*, molecular dynamic

Introduction

Due to excellent thermal conductivity of copper, high ductility and reasonable level of corrosion resistance makes it useful engineering material suitable for applications in marine environments, heat exchangers, beverage industry, oil refineries, nuclear plants, electrical and electronic industry among others. These properties of copper deteriorate when deployed in aqueous service environment through corrosion processes. Corrosion of copper and its inhibition in various media have attracted the attention of many researchers particularly the media that contain chloride ions [1-3]. The use of inhibitors is generally accepted as a proficient way to contain metal corrosion economically and the development of organic based corrosion inhibitors have gained acceptance in several applications on account of their practical usefulness. Although most organic based inhibitors used for copper corrosion exhibit a number of environmental acceptability, most azole-molecule inhibitors are susceptible to degradation by oxidizing biocides but a major limitation arises from aromacity. The effectiveness of these heterocyclic molecules is based on their ability to form a polymer like film, which prevents copper corrosion [4-7]. However, several studies have been carried out on copper corrosion inhibition using azole-based compounds due to their molecular structure is found to exert a major influence on the degree of inhibition [8]. The relation between the efficiency and structural properties of inhibitor molecules have been reported using experimental techniques alongside theoretical methods [9-11]. The patent organic compounds of commercial interest have relative molecular structures that are obtainable in biomass extracts' composition and several applications with dominant bioactivity such as the agricultural and medical industries engage the use of biomass extracts. This gives biomass extracts an edge over conventional organic inhibitors. The researches on material corrosion inhibition have taken towards developing cheap and effective compounds with low or zero environmental impact. Biomass extracts apart from being readily available and nontoxic, it contains broad spectrum of organic compounds which includes heterocyclics that incorporates nitrogen, oxygen, sulphur and several functional groups.

The multi-component composition of biomass extracts is the basis for investigations on its corrosion protection effect on metals/alloys in different media, but little is known of the detailed function because of the complexity of the process. Quantum chemical calculations have been successfully used to study reaction mechanisms and also to interpret the

experimental results by solving chemical ambiguities [12,13]. Though, it is important to note that ambiguities still exist regarding the inhibition contribution of individual molecule within the multi-molecular composition of biomass extracts.

This study reports the possible role of *Tapinanthus dodoneifolius* (TD leaves extract) as corrosion inhibition for CU131729 surface in aqueous acidic and near neutral solution using weight loss, electrochemical technique and quantum chemical calculations. Surface morphology and elemental analysis was carried out on the corroded specimen using SEM/EDS to compliment results obtained while the effect of temperature gave thermodynamic parameters such as ΔH_{ads} , ΔS_{ads} and ΔG . Quantum chemical calculations performed to elucidate individual molecular reactivity of TD leaves extract composition was used to estimate their binding energy on Cu(110) surface and hence the adsorption configuration.

Material preparation

Copper (CU131729) sheets of 99.9% purity used for this study was procured commercially from Advent research materials Ltd, Eynsham Oxford England OX29 4JA with the following typical analysis ppm: Ag < 500, Bi < 10, Pb < 50, O < 400, others < 300, Cu balance. The sheet was press-cut into suitable dimensions with a hole of 1mm drilled at the middle of the upper edge of the specimen and then abraded with metallographic emery paper of fineness of 1200 grits. The specimen was degreased in absolute ethanol, dried in acetone, further dried with hot air and stored in moisture-free desiccator prior usage. Dried leaves of TD leaves extract were blended to powder; 50 g of powdered leaves was refluxed in 500 ml ethanol, allowed to cool for 3 h and filtered. The filtrate was concentrated using rotary evaporator and stored in an oven at 40 °C. From the concentrate, inhibitor test solutions were prepared in concentrations of 10, 100 and 1000 mg/L. Part of the concentrate was taken for chromatogram analysis using a GCMS-QP2010 PLUS Shimadzu, Japan. All test solutions were freshly prepared from analytical grade chemical reagent using bidistilled water. Data analyses were carried out using Origin Pro 8 Data analysis station & graphing workspace.

Weight loss

In weight loss experiments, CU131729 specimens (4.0 x 4.0 x 1.0 mm) were weighed before total immersion in a 250ml beaker containing 200 ml test solutions, being suspended by suitable hooks at 1 cm below the solution surface. The beakers were placed in a freely aerated thermostated water bath

maintained at constant temperature at 303, 313, 323 and 333 $\pm$ 0.5 K. The specimens were retrieved after 3 hours, scrubbed with brush under running bidistilled water, dried and weighed [14]. The difference in weight before and after immersion of the specimen in different test solution was taken as the weight loss and used to calculate corrosion rate in millimeter penetration per year ($\text{mm} \cdot \text{y}^{-1}$) using equation 1 [15]

$$K_{CR} = \frac{k\Delta W}{\rho A} \quad 1$$

where k = unit of corrosion rate constant ($8.76 \times 10^4 \text{ mm} \cdot \text{y}^{-1}$), ΔW is weight loss in mg, ρ is density of metal, T is exposure time in hours, A is area of working electrode. Inhibition efficiency ($IE\%$) was calculated using the following expression

$$IE\% = \left(1 - \frac{K_{CR(inh)}}{K_{CR(blank)}}\right) \times 100 \quad 2$$

where $CR_{(inh)}$ and $CR_{(blank)}$ are the corrosion rate in the presence and absence of leaf extracts respectively.

Electrochemical technique

The potentiodynamic polarization studies were carried out using Potentiostat/Galvanostat model 263 using Power Suite software. Data were taken after the copper specimen with an exposed area of 1 cm^2 was immersed for 1800 seconds in aerated relevant test solutions at open circuit potential. The polarization scan curves were obtained by applying a potential of -0.25 V to 1.6 V vs. SCE at a scan rate of 0.333 mV/s to the copper specimen. The value of E_{corr} and i_{corr} was obtained from Tafel extrapolation of the curves while the protection efficiency was determined using equation 3 [16]

$$E_i\% = \frac{i_{corr}^0 - i_{corr}}{i_{corr}^0} \quad 3$$

Where i_{corr} and i_{corr}^0 is corrosion current densities for inhibited and uninhibited solutions respectively.

Computations

All stimulations were done using MS Modeling 4.0 software workstation. The geometry optimization process was carried out for inhibitor molecules and the Cu surface by means of the DFT electronic structure program, DMol3 using a Mulliken population analysis as well as a Hirshfeld numerical integration procedure. Electronic parameters for the simulation include unrestricted spin polarization using the DNP basis set and local potential Perdew and Wang (PWC) exchange-correlation potential functional [16]. DFT Semi-core Pseudopotentials (DSPP) was used as the core treatment which replaces core electrons by a single effective potential. $2 \times 2 \times 1$ mesh parameters was set as k point with custom grid for the metal surface and density mixing charge was set to default using Direct Inversion in an Iterative Subspace (DIIS) with 0.14 eV thermal smearing applied to the orbital occupation to speed up convergence alongside convergence tolerance maximum force at $0.05 \text{ eV/\AA}$. Molecular dynamics (MD) simulation of the interaction between single inhibitor molecule and Cu(110) surface was performed using Forcite quench molecular dynamics [17] to sample several different low energy configurations and identify

the low-energy minima. The Cu surface was first relaxed via minimizing its energy by geometry optimization and then cleaved along the (110) plane. The symmetry was increased and its periodicity changed by constructing a supercell 12×10 with a vacuum height of $20 \text{ \AA}$. This serves as a representative part of the interface that is devoid of arbitrary boundary effects. Calculations were carried out, using the COMPASS (condensed-phase optimized molecular potentials for atomistic simulation studies) force field and the Smart algorithm, in a simulation box $29.79 \text{ \AA} \times 24.82 \text{ \AA} \times 26.08 \text{ \AA}$ with periodic boundary conditions. Stimulation conditions include fixed energy (NVE ensemble) with initial temperature of 303 K at time step of 0.1 fs was employed while the system was quenched every 250 steps with convergence tolerance energy at $1.0^{-4} \text{ kcal/mol}$ and displacement of $5.0 \times 10^{-5} \text{ \AA}$. The adsorption energy (E_{Bind}) was calculated using the relationship in equation 4 [18];

$$E_{Bind} = E_{Cu-inhibitor} - (E_{inh} + E_{Cu}) \quad 4$$

Results and discussions

Weight loss: The dissolution rate of CU131729 specimen in 2 M HCl and $3.5\% \text{ NaCl}$ solution as a function of temperature in the absence and presence of TD leaves extract is shown in Fig. 1 & 2. As can be seen from these figures, the test inhibitor inhibited corrosion of pure copper in 2 M HCl and $3.5\% \text{ NaCl}$ solutions. The inhibition efficiency and thermodynamic activation parameters of *Tapinanthus dodoneifolius* leaves extract adsorption on CU131729 specimens as functions of temperature and concentration are listed in Table 1. It is clear from these data that corrosion inhibition of CU131729 specimen in both media increased with increasing inhibitor concentration but decreases as temperature is increased. The observed inhibition efficiency is attributed to adsorption of TD leaves extract at corrosion active sites along CU131729 surface but the adsorption strength weakened with temperature thereby resulting in shortened time lag between adsorption and desorption at the metal interface. The observed trend could be attributed to increased rate of ionization and diffusion of active species in the bulk solution [19]. The optimum temperature for both solutions was found at $303 \text{ }^\circ\text{K}$ which could be an indication that the stability of corrosion product formed and/or adsorption of inhibitor at higher surface coverage area on CU131729 surface. The increased temperature undermined the corrosion resistivity of CU131729 surface and that of TD leaves extract adsorption strength; probably due to the fact that an increase in temperature decreases the rate of adsorption for physically adsorbed species as a result of the weakening of Vander Waal's forces of attraction and constant bombardment of constituent molecules. This assertion is supported by Ekpe *et al* (2001) [20]. This is an indication that TD leaves extract adsorbs at CU131729 surface via physical adsorption. Corrosion inhibition of CU131729 surface with TD leaves extract was found to be more pronounced in the 2 M HCl solution than $3.5\% \text{ NaCl}$ solution. This might be due to the nature of TD leaves extract composition and any change with time and/or electrode potential as a consequence of reduction reactions and/or formation of surface products in the different media.

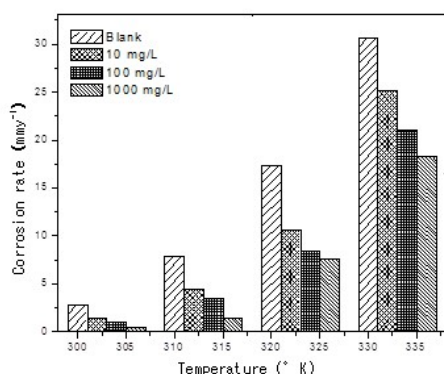


Fig. 1: Corrosion rate of CU131729 specimen in 2 M HCl solution containing different concentrations of *Tapinanthus dodoneifolius* leaves extract as a function of varying temperature.

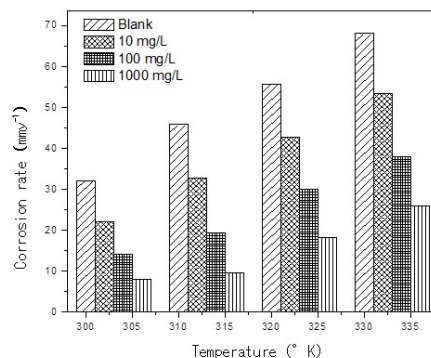


Fig. 2: Corrosion rate of CU131729 specimen in 3.5 % NaCl solution containing different concentrations of *Tapinanthus dodoneifolius* leaves extract as a function of varying temperature

Table 1: Thermodynamic activation parameters of *Tapinanthus dodoneifolius* leaves extract adsorption on CU131729 specimens with inhibition efficiency at 303 °K

Sample	2 M HCl				3.5 % NaCl			
	$\Delta S^*_{ads} (\times 10^{18})$ J.mol ⁻¹ .K	$\Delta H^*_{ads} (\times 10^{21})$ J.mol ⁻¹	r^2	IE% (303 °K)	$\Delta S^*_{ads} (\times 10^{19})$ J.mol ⁻¹ .K	$\Delta H^*_{ads} (\times 10^{20})$ J.mol ⁻¹	r^2	IE% (303 °K)
Blank	-7.85	1.82	0.9823	--	-1.16	5.04	0.9673	--
10 mg/L	-6.89	2.16	0.9975	48.1	-1.14	6.16	0.9778	31.4
100 mg/L	-6.61	2.27	0.9945	62.9	-1.11	7.31	0.9826	56.1
1000 mg/L	-4.78	2.88	0.9819	82.5	-1.06	9.13	0.9194	75.4

The effect of temperature gave invaluable information about the inhibition process from which thermodynamic parameters were calculated for the adsorption of TD leaves extract on Cu surface as recorded in Table 1. Transition state theory plot shown in Fig. 3 gave the values of the activated enthalpy and entropy of adsorption via the slope and intercept [16]. The positive values of ΔH^*_{ads} indicate physical adsorption mechanism. The result indicated of that the tested compounds acted as inhibitors through adsorption on copper surface, which resulted in formation of a barrier to mass and charge transfer. The values of ΔH^*_{ads} reflect the strong adsorption of these compounds on copper surface. The negative signs of ΔS^*_{ads} for all inhibitor concentrations are related to the substitutional process, which can be attributed to an increase in water desorption entropy [21]. The values of ΔS^*_{ads} show that the inhibitor concentration with highest ΔS^*_{ads} value has higher efficiency. In other word, it can be claimed the molecule which adsorbs at surface with higher order produces higher protection against corrosion. Most interestingly, the association was found to produce a net increase in the entropy of the system, suggesting a decrease, upon aggregation, in the ordering of the water molecules that were originally adsorbed on the metal surface [22]. The values of ΔS^*_{ads} are large indicating that the activated complex in the rate determining step represents an association rather than dissociation step. This means that the activated inhibitor composition were in a higher order state than that at the initial state.

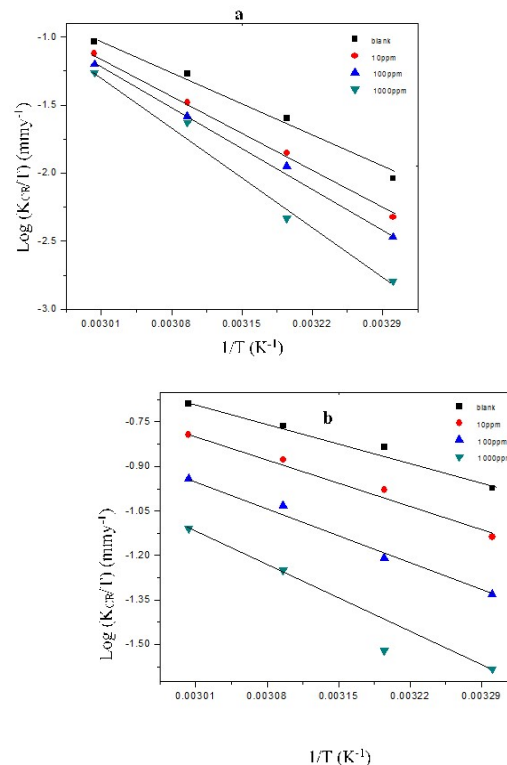


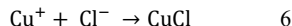
Fig. 3: Transition state theory plot of TD leaves extracts on CU131729 specimen in (a) 2 M HCl and (b) 3.5 % NaCl at different temperatures

Electrochemical technique

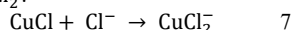
Polarization plots were obtained for CU131729 specimen in the chloride solutions without and with different concentrations of TD leaves extract are shown in Fig. 4 & 5 while calculated values of inhibition efficiencies ($E_i\%$) and associated electrochemical parameters; E_{corr} and I_{corr} determined by extrapolation of Tafel lines to corrosion potential are listed in Table 2. The electrochemical reduction corrosion process occurring at the copper-chloride solutions interface is well known to be of three distinct regions [23-26]; (i) a region of increasing current from the Tafel region at lower overpotentials, which extends to the peak current density due to the dissolution of copper metal to copper ion (Eq. 5)



(ii) a region of decreasing currents until a minimum is reached due to the formation of CuCl (Eq. 6) which retards further oxidation of the metal.



(iii) a region of sudden increase in current density leading to a limiting value as a result of CuCl_2^- formation which is responsible for the copper dissolution (Eq. 7) via the oxidation of CuCl to CuCl_2^- .



It is obvious from Fig. 3 that both anodic and cathodic polarization curves for observed in the chloride solutions with the presence of inhibitor are similar to anodic and cathodic plot for the free solution but a noticeable decrease in both E_{corr} and I_{corr} was observed with increasing inhibitor concentration. This suggests that TD leaves extract reduced the corrosion reaction without altering the corrosion mechanism. The shift in E_{corr} with increasing inhibitor concentration could be due to the fact that the inhibitor had a strong influence on the oxygen reduction than the copper dissolution [27]. Some authors reports that in dilute chloride solutions Cu_2O film is formed on the copper surface. In a scenario where CuCl is trapped, the protective layer is damaged with initiation of pits [1,7]. In the present study, it is proposed that the formation of cuprous oxide may be favoured over chloride complexes formation as a result of the surface films that diminish the aggressive chloride ions attack. The corrosion current density was found to decrease with the introduction of TD leaves extract and further decreased with increasing inhibitor concentration thus, increasing inhibition efficiency. This decrease in i_{corr} is attributed to the delayed formation of CuCl_2^- which dissolute into the bulk solution [3] and/or undergoes further oxidation to cupric ions. Both the cathodic current and anodic current density decreased in presence of inhibitors suggesting that TD leaves extract acts as a mixed type inhibitor for copper corrosion [28]. This indicates that TD leaves extract first gets adsorbed onto copper

surface and impedes by merely blocking the reaction sites of CU131729 surface without affecting the cathodic and anodic reaction mechanism. By considering the collective observations on the change in the Tafel slopes, change in current density, and the direction of change in corrosion potentials, the inhibition process appeared to be mixed type in nature with pronounced effects.

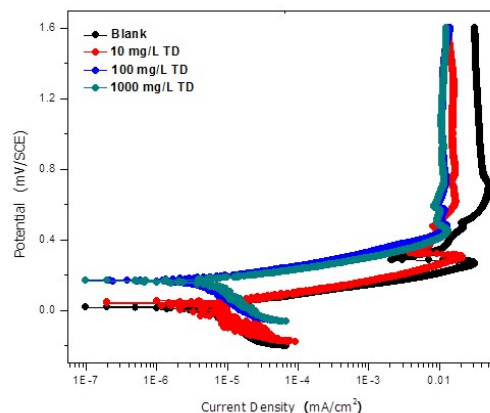


Fig. 4: Potentiodynamic polarization plot for CU131729 specimen in aerated solution of 2 M HCl solution in the absence and presence of *Tapinanthus dodoneifolius* leaves extract.

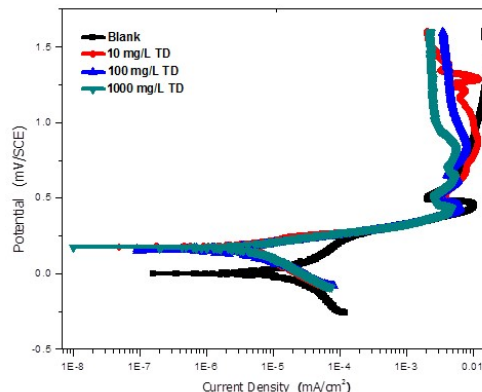


Fig. 5: Potentiodynamic polarization plot for CU131729 specimen in aerated solution of 3.5 % NaCl solution in the absence and presence of *Tapinanthus dodoneifolius* leaves extract.

Table 2: Corrosion parameters obtained from potentiodynamic polarization scan for CU131729 in chloride solutions without and with the presence of *Tapinanthus dodoneifolius* leaves extract.

Sample	2 M HCl				3.5 % NaCl			
	i_{corr}	E_{corr}	θ	$E_i\%$	i_{corr}	E_{corr}	θ	$E_i\%$
Blank	2588.01	16.022	--	--	137.4	-0.323	--	--
10 mg/L	1627.03	33.117	0.3713	37.13	23.44	175.11	0.8294	82.94
100 mg/L	6.479	166.22	0.9975	99.75	29.34	154.28	0.7865	78.65
1000 mg/L	7.726	163.91	0.9970	99.70	7.842	162.37	0.9429	94.29

Computations

Quantum chemical calculations give insight on the geometric and electronic properties of the compound; an important consideration on the choice of corrosion inhibitors. The compound geometry has an influence on its adsorption behaviour on metal surfaces as it predicts the optimal orientation by which the compound might cover the metal surface. Compounds with planar geometry have been reported to exhibit higher inhibition efficiency than corresponding compounds with less planar geometry [29]. Electronic parameters of compound provide insight about the reaction

tendency via donation/backdonation of electrons between the compound and metal surface. Regions in the compound with high electron density would preferably undergo electron transfer with partially filled or vacant d orbital of the metal surface resulting in a donor-acceptor bond. According to Frontier Molecular Orbital theory (FMO), low lying LUMO induces a backdonation of electron from the metal to the molecule whereas high E_{HOMO} facilitates adsorption by influencing the transport process through the adsorbed layer [16]. Chemical calculations on E_{HOMO} , E_{LUMO} , energy gap (ΔE), and Binding energy (E_{Bind}) for some TD leaves extract

molecular composition are presented in Table 3 while Fig. 6 shows the optimized geometry for HOMO and LUMO plots. Literature has shown that excellent corrosion inhibitors are usually molecules that not only offer electrons to unoccupied orbital of the metal but also accept free electrons from the metal using their anti-bond orbital to form stable chelates. Analyzing the HOMO orbital of the inhibitor molecules revealed that the HOMO and LUMO orbital plots were mostly found around the same region. This kind of orbital distribution could be ascribed to p- π conjugation effect, consideration the lone pair electrons and unsaturated bonds, which enhances formation of a donor/acceptor bond with the metal surface, however, considering the E_{LUMO} values in Table 3, the low value obtained showed the molecules to be of more electron acceptor. Hence, the formation of adsorbed layer due to electrostatic interaction at the metal/electrolyte interface which essentially blocks cathodic reaction and reduced anodic dissolution of the metal [30]. This is in agreement with the weight loss and potentiodynamic polarization results. In order to examine the most suitable adsorption modes between each molecule and Cu(110) surface, the adsorption energy (E_{Bind}) was calculated using the relationship in Eq. 3. The obtained values are shown in Table 3 with negative values suggesting that there was propensity towards spontaneous adsorption. The high values of binding energy could be attributed to the planar geometry and low energy gap (ΔE) values. The unshared electron pairs and the p- π conjugation system found within the stimulated molecules result in dissociative adsorption which is favourable to crack the intramolecular bond of the adsorbate molecule, enhancing electrostatic interaction with the metal surface.

Surface morphology

The obtained micrographs for the representative areas of corroded CU131729 surface after 150 hours of immersion in 2 M HCl and 3.5% NaCl solution without and with the presence of TD leaves extract are shown in Fig. 7 & 8. The micrographs for in 2 M HCl solution without the inhibitor was severely corroded and is seen to have high density pits due to formation of cuprous chloride and oxychloride complexes while that of 3.5% NaCl solution had spherical pits over the surface. This is attributed to the action of the Cl^- ions undermining the cuprite surface film formed but the introduction of the leaves extract mitigated such process to a great extent and suppresses the adsorption of Cl^- ions on the passivating film and/or slowing down of their access to it. This process enhances stability and compactness of the passive films on CU131729 surface [31]. Several reports have shown that chlorine actually influence the stability of cuprite film based on replacement of O^{2-} ions in the cuprite film which balances up the charge in p-Cu₂O structure as Cu^+ ions migrate towards the oxide/electrolyte interface and Cl^- ions then diffuses underneath the oxide film [32]. However,

when the O₂ content of the surface film is reduced, there is disruption of the structural order which enhances breakdown of the oxide film [33]. Further inspection revealed that TD leaves extract allowed few swallow pits along grain boundaries on CU131729 surface and holiday regions that were not corroded indicating a strong adsorption on CU131729 surface. This is attributed to the complex (Cu-TD)_{ads} formed on the copper surface suppress copper dissolution and prevented cuprous chloride formation. The corrosion inhibition process is associated with formation and growth of insoluble stable film on the metal surface through the process of complexation of the organic molecules [33-35]. The leave extract was incorporated into the cuprite surface film and enhanced the compactness which in turn mitigated the formation of CuCl. Starosvetsky *et al.*, (2006) reported that copper activation occurs only after a certain incubation period, during which a thin layer of CuCl is formed, which further facilitates the rapid dissolution of copper. This could be explained by the incorporation of chloride into the Cu₂O film and the possible formation of CuCl.

Energy dispersive X-ray analysis gave additional information about the inhibition mechanism of the leaves extract. It is widely accepted that the process of inhibiting corrosion is associated with formation and growth of insoluble stable film on metal surface through the process of complexation of the inhibitor molecules. EDS analysis of the specimen surfaces after the immersion test was performed on the surface film and corrosion deposits. The results obtained are as shown in Fig. 9 - 12. The elemental analysis for CU131729 in 2 M HCl solution revealed the presence of oxygen, nitrogen and sulphur as well as minor amount of chlorine atoms, an indication that the leave extracts interact with CU131729 via coordination bonds through these atoms. The spectra confirmed that the corrosion product that developed was possibly CuO with traces of (N-Cu-S)_{ads} and (Cu-Cl-TD)_{ads} while the spectra for 3.5% NaCl solution revealed traces of silicon and sodium atoms which is expected to be from NaCl precipitates. The possibility of these atoms also forming weak bonds with the metal surface is not ruled out. Moreover, the low peaks for chlorine atoms could only mean that the inhibitor molecules replaced Cl^- ions on the surface of the metal thereby reducing the attack on the metal surface [35]. These EDS results prove that the protective film composed of strongly adhered inhibitor molecules on the metal surface via forming complex chelating ligands and Cl-complex deposits. The presence oxygen as well as minor amount of nitrogen, sulphur and fluorine was disclosed by EDS spectra an indication of the formation of metal-oxides and traces of complex chelating ligands of the inhibitor molecules on the metal surface.

Table 3: EHOMO, ELUMO, energy gap (ΔE), and Binding energy (E_{Bind}) from the molecular dynamic simulations for *Tapinanthus dodoneifolius* leaves extract molecular compositions

	EHOMO (Ha)	ELUMO (Ha)	ΔE (Ha)	E_{Bind} (kcal/mol)
1,6-Anhydro-beta-talopyranose	-0.1898	-0.0587	0.1311	-42.67
1,2-15,16-diepoxyhexadecane	-0.2263	0.0364	0.2627	-78.5
2,4-hexadiyne-1,6-diol	-0.2211	-0.0746	0.1465	-78.5
3,7-Dimethyl-1-octyl methylphosphonofluoridate	-0.2639	-0.0192	0.2447	-61.84
Methyl 2-butyl-2-cyclopropene-1-carboxylate	-0.2187	-0.0468	0.1719	-61.15
Cyclohexyl heptyl	-0.1807	0.0035	0.1842	-64.92

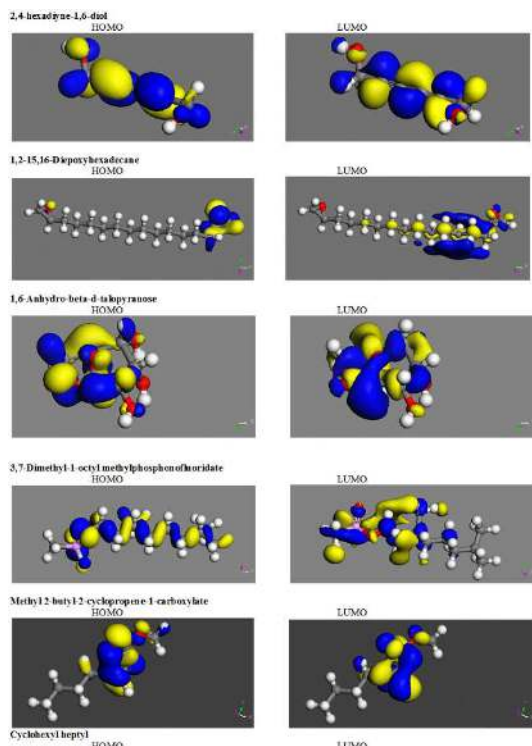


Fig. 6: Charge density plot of some TD leave extract molecules showing HOMO and LUMO

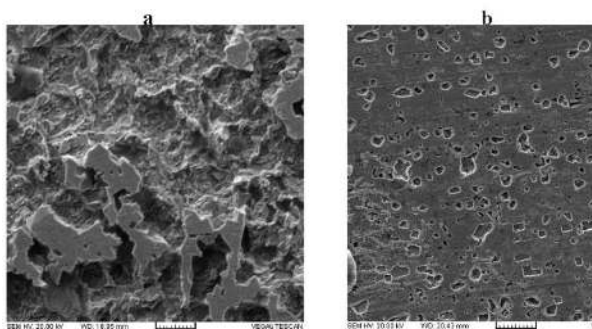


Fig. 7: SEM micrographs of CU131729 surface after immersion for 150 h in (a) 2 M HCl (b) 3.5% NaCl solutions without inhibitor

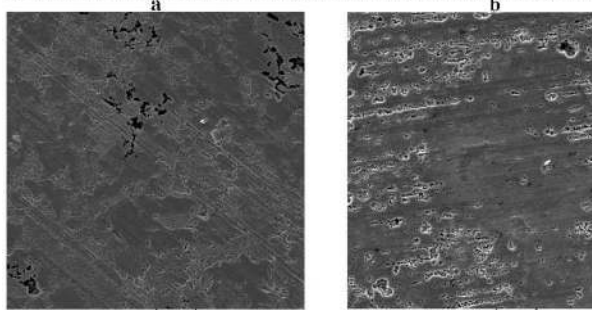
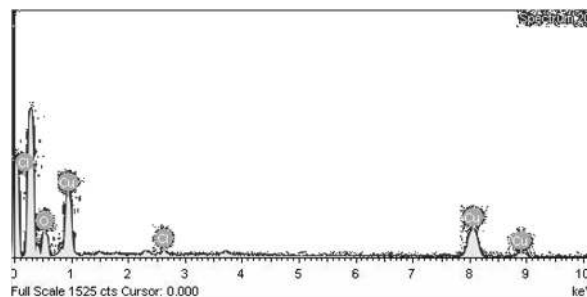
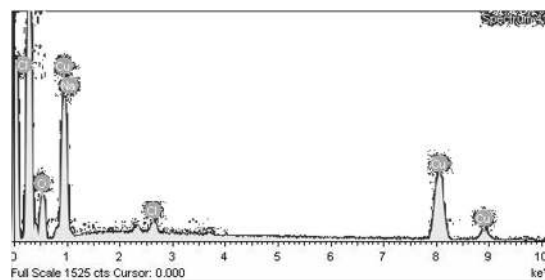


Fig. 8: SEM micrographs of CU131729 surface after immersion for 150 h in (a) 2 M HCl (b) 3.5% NaCl solutions with as inhibitor



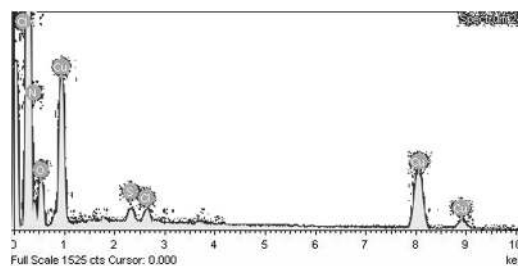
Element	Weight%	Atomic%
O	21.06	51.05
Cl	1.58	1.73
Cu	77.36	47.22
Totals	100.00	

Fig. 9: EDS analysis of the corrosion product film on CU131729 surface in 2 M HCl solution without inhibitor



Element	Weight%	Atomic%
O	17.08	43.61
Na	1.62	2.89
Cl	2.43	2.80
Cu	78.86	50.70
Totals	100.00	

Fig. 10: EDS analysis of the corrosion product film on CU131729 surface in 3.5% NaCl solution without inhibitor



Element	Weight%	Atomic%
N	8.41	19.52
O	20.69	42.03
S	2.34	2.37
Cl	2.50	2.29
Cu	66.06	33.79
Totals	100.00	

Fig. 11: EDS analysis of the corrosion product film on CU131729 surface in 2 M HCl solution in the presence of TD leave extract

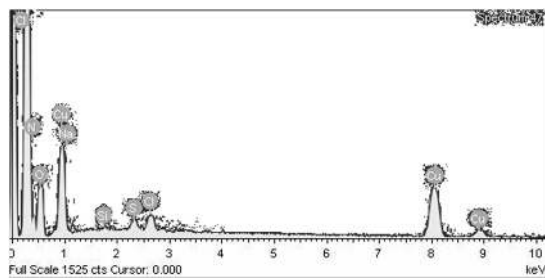


Fig. 12: EDS analysis of the corrosion product film on CU131729 surface in 3.5% NaCl solution in the presence of TD leave extract

Conclusion

This study examined the corrosion inhibition capability of TD leaves extract on CU131729 specimen in chloride solutions. The ability of the molecular composition of the leaves extract to adsorb on the metal surface depends on the electrostatic interaction between the metal surface and the inhibitor. On the other hand, the strength of adsorption depends on the size, functional groups and orientation of the inhibitor molecules on the metal surface. Weight loss data reveal that inhibition efficiencies increased with increasing inhibitor concentration and decreased with increase in temperature. The obtained thermodynamic parameter for the inhibited solutions is suggestive of physical adsorption mechanism. The calculated activated enthalpy and entropy values were found to be higher in 2 M HCl solution than those for 3.5% NaCl solution. The potentiodynamic polarization study revealed that the introduction of inhibitor to the chloride solutions shifted E_{corr} values to the positive and decreased i_{corr} values. The increasing values of E_i obtained with increasing inhibitor concentration is attributed to greater adsorption of inhibitor molecules at active sites on the metal surface which prevented formation of chloride complexes on the passive film and further strengthened the compactness of the passive film on the metal surface. The data obtained from quantum calculations for individual molecules of TD leaves extract show that individual molecules interacted with the metal surface through lone electron pairs donors, heterocyclic rings and unsaturated bonds. The calculated interaction energy between single inhibitor molecule and metal surface is nonspecific and engaged high binding energy. Surface exam with SEM has shown that inhibitor addition leads formation of strong inhibiting film which could passivate the metal with very less passivity current densities value. As demonstrated by the results from EDS investigations, chlorine was systematically detected on the representative area of the metal surfaces that were locally attacked. The low amounts of chlorine detected on the metal surfaces in the presence of the inhibitors suggests that the inhibitor molecules displaced Cl^- ions from the metal surface and further blocked its activity on the metal surface. It is evident that the inhibitor molecules bonded on the metal surface and recued the corrosion rate. The EDS results is in agreement with the weight loss, potentiodynamic polarization and SEM data obtained from this study.

Acknowledgements

The author wishes to acknowledge the support of Dr. A.M. Kolo, U.F. Hassan, H.U. Gende and U.I. Tafida of the Chemistry Dept. A.T.B.U. Bauchi and also Prof. Emeka E. Oguzie of Federal University of Technology Owerri for his mentorship.

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THE STEEL INDUSTRY: A STIMULUS TO NATIONAL DEVELOPMENT

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ABSTRACT

The Steel Industry will continue to serve as stimulus to national development and economy booster to industrial development of a country. The industry will serve as the backbone of industrialization of our great country, Nigeria if all the necessary parameters are put in place. The benefits of having a functional steel industry will translate to a functional country. It should also be noted that steel industry will contribute to all the facets of the economy, including the important role steel plays in economic development and growth. In this presentation, the paper will highlight on the multiplier effects in the development and sustenance of agriculture, health care and virtually every other sector of the economy. The role of steel in defence was also identified. Discussion and emphases were place on the efforts made in the development of Steel Industry in Nigeria with a view to discussing the potentials that could be accrued for operating the industry. The paper also seek the concept of Government through this process of advocacies by requesting the Nigerian Government to complete the steel industry like Ajaokuta Steel Company Limited located at Ajaokuta in Kogi State. It should be noted that the steel industry was conceptualized as far back as 1958, because of the vital and strategic role of the steel industry in the transformation and reformation of the economy. If Nigeria ever desires to drop the toga of “underdeveloped economy” for that of “industrialized economy” catalyst and economy booster the industry must be completed and make operational. If the steel industry had been completed, commissioned and effectively operated thirty-four years ago as conceptualized in the vision of the initiators, Nigeria would have been a different country in terms of industrial and economic development today.

Key words: Steel, Industry, Stimulus, National and Development

1.0 Introduction

In its annual report of 1985, the United Nations Industrial Development Organization stated thus: “whether a developing country should develop its own iron and steel industry depends upon various factors. Undoubtedly, it is advantageous for a country to develop its own iron and steel industry if the necessary raw materials are available” (Technological Perspectives In Machine – Tools Industry and their Implication for developing countries, UNIDO, 1985). Over time, Nigerians have been worried over the deplorable state of the steel industry in the country; and many have felt sorry for our dear country, Nigeria.

2.0 Steel in National Economy

It is generally known that present material civilization has been largely due to man’s knowledge and application of metals. Without metals, there would be no railways, aero- planes, automobiles, ships, turbines, electric motors and generally no electrical power. There will be no modern bridges or massive oil rigs and the little but important things of life from simple razor blades to knives and forks and the printed newspaper would be essentially lacking, perhaps, a few of these could be fashioned from wood, but they couldn’t go very far. It is also widely recognized that central to all these metallic inventions, innovations and motive power, is the particular class of metal known as “STEEL”.

Primary steel sector industries are fundamentally different from other industrial establishments in many respects. They are basically strategic industries that serve the long term industrial needs of a nation through their unique role as feeder channels to myriads of other key establishments. No serious programme of industrialization can be contemplated without a strong steel base, at least a steel base that would grow with the visualized scope of general industrialization over a set period. Looking at some of the few successful economies of the developing nations such as South Korea, Brazil, and Taiwan and to some extent India had their success stories largely from well-articulated steel development programmes leading to innumerable ancillary, downstream and spin –off industries.

The apprehension of sections of the Nigerian elite, over the huge resources committed to the steel companies in the country is of course understandable. However, it must realistically be appreciated that the economic viability of steel company cannot be measured by the traditional indices of measurement because of their strategic nature. Very few, in fact less than 20 per cent of the steel companies the world over do break even. All the same, large business interests and government agencies sustain the steel company.

It was during the year following the World war II that steel became fully utilized in building the industrial society that has achieved so much prosperity in the industrialized world. The World’s output of crude steel between 1871 and 1980 totalled 18.71 Billion tonnes and almost 70 percent of this total was produced in the 34 years between 1946 and 1980, which positively emphasized the impact of steel on the moulding of an industrial economy.

3.0 Steel as an Index of Power

Since the Second World War, the nations of the world have come to appreciate the unique role of steel as the base for rapid technological progress and STEEL has become an index of National Power. Steel had enabled Britain to launch the first industrial Revolution and Western Europe to colonize most of the World. Germany overran Europe while Japan suddenly leapt to the forefront of modern technology. Similarly, the United States became a supreme post –war global power as it systematically boosted its steel capacity to excel the entire output of continental Europe.

About 1780, over two centuries ago, the greatest amount of iron produced in the world was less than 20,000 tonnes a year! Today the size of the furnace in Ajaokuta Steel Company can produce this quantity in under a quarter of an hour. By 1840, the figure was about 1.25 million tones and by 1900 it was 9 million tones. Today, Iron and Steel production has become phenomenal giant nations like United States, the former USSR and Japan produced 326 million tonnes of steel in 1970 and over 405 million tonnes in 1974, the peak year in world steel output.

In 1980 the total world output was estimated at 900 million tonnes of raw steel. It is not surprising therefore, that Nigeria's emergence as latest debutant on the steel scene was widely acclaimed locally and generated understandable euphoria throughout the country. Steel being the necessary and almost sufficient condition for a nation's power base, it is wise that our great country Nigeria should join the club.

4.0 Steel as Economic Nerve Trigger.

The great importance of steelmaking to national economy is not restricted to its immediate or direct application. For its smelting alone, it triggers off a series of economic activities for its input raw materials and energy such as:

- (a) Iron ore: Mining, transportation, beneficiation, preparation;
- (b) Coke: Coal mining, sizing and preparation, coking in coke ovens;
- (c) Lime stone: Quarrying and calcining;
- (d) Oxygen: Manufacture of oxygen and lances for steel refining;
- (e) Bricks: Clay preparation and firing;
- (f) Additives; Manufacture of nozzles;
- (g) Air and fuel: Pre-heating and atomizing of oil and gas;
- (h) Energy: Power construction, generation and distribution, services, etc.

Added to these large scale economics and industrial activities associated with the raw materials used for steel making, are ancillary downstream foundry, machining, fabricating and processing industries, as well as extensive services such as transportation and supplies which are given a big boost.

Statistical evidence indicates that the production of raw steel is attended to by over twenty types of ancillary industries and associated economic activities: These do not include continuing research into the further development, utilization and adoption of raw materials resources and technology.

5.0 Steel and Industrialization

In the advanced or developed economies such as, USA, Japan, Germany, France, U.K., etc, industrialization has been associated with ability to produce consumer and capital goods which enhance domestic self-sufficiency and reduce foreign exchange drainage; and ability to promote employment generation and local manpower development and hence increase in per capital income, purchasing power and potential to invest.

The role of the Iron and Steel Industry in national industrialization is pre-eminent. This is because steel remains the basic raw material for a host of manufacturing activities and hence the material backbone for national economic development in general. Malaysia exports 75% of its steel products to other countries.

6.0 Steel as a Strategic Industry.

The steel industry is the bedrock of the industrial growth of any nation. It is so vital to the development of any nation that every country attempts to acquire and take control of the sector even in cases where the raw materials are not available locally. For instance, Japan and South Korea, who are among the largest producers of steel in the world today, do not have the raw materials for steel production locally. The giant technological stride that they have experienced over the years is attributable to the development of their steel industries.

Today, over 80% of the world's industrial goods and infrastructure are steel based. Furthermore, products of integrated Steel Company sustain spare parts and components of the industries that produce these goods. Such industries will provide the base for Nigeria's industrial take-off. The

abandonment of the company has contributed to the economy woes of the Nation.

7.0 Foreign Exchange Earner.

The amount of foreign exchange being expended on the importation of steel today runs into billions of dollars. This colossal amount of money is an unacceptable waste of our meager resources and could have been diverted to other vital sectors of the economy. On the other hand, it is expected that the Ajaokuta Steel Company Limited when completed will generate enormous foreign exchange through export. It is also envisaged that the products of company would be exported to the West African sub-region and other African countries.

During the short period of Global Infrastructure Holding Limited (GIHL) a statement was credited to the Management (Ajasteel 2006:6) that Ajaokuta steel company limited generated \$74m in foreign exchange for the sales of 128,000 metric tonnes of rolled products.

According to the report, ribbed bars were exported to four West African countries as follows: 3,800 metric tonnes to Mauritania, 3,400 metric tonnes to Cote d'Ivoire, 1,050 metric tonnes to Benin Republic and 600 metric tonnes to Mali. In the same vein The Ajaokuta steel company limited supplied Power Holding Company of Nigeria (PHCN) with 65MW of Electricity. Other beneficiaries of the company's 85MW of electricity generated from the Independent Thermal Power Plant (TPP) include, Lokoja, Okene as well as Benin city and its environs.

In another report (Ajasteel 2006:7), 50,000 megawatts have been exported from the Ajaokuta Steel Company Catchment Power Company to Power Holding Company of Nigeria (PHCN) to service electrical strength in Okene, Lokoja, Itakpe and Ajaokuta Villages since 2005 to 2007. Further a concessionary agreement process had commenced between Ajaokuta Steel Company limited Management and the Management of Obajana Cement Factory to export 147,000 megawatts of electricity to the cement industry to enable it go into production when completed.

8.0 Availability of Raw Materials

Unlike some countries that are major producers of Steel in the world, Nigeria is blessed with virtually all the raw materials that are necessary for the production of steel. For instance, we possess a large reservoir of iron ore deposits in Itakpe, which is the primary source of raw material to Ajaokuta Steel Company Limited.

There are iron ore deposits in several other locations within Kogi state and other parts of the country. The country is also blessed in abundance with other relevant raw materials such as Dolomite, Clay and Limestone required for Steel production. Even the coking coal that is to be imported has been discovered in some locations like Lafia/Obi in Nasarawa State and Enugu in Enugu State. This will surely reduce our dependence on imported coking coal.

11.0 Availability of Skilled Labour.

Nigeria possesses the skilled manpower and technical know-how to run the company efficiently. Also, thousands of professionals have been trained both locally and internationally in anticipation of the take-off of the Steel Company.

In addition, the Federal Government has set up institutions such as the Metallurgical Training Institutes in Onitsha, Ajaokuta and several other locations for training the future manpower needs of Ajaokuta Steel and other related Steel Industries.

9.0 The Multiplier Effects on the Economy.

The Steel Company is envisaged to have multiplier effects that will permeate all sectors of the Nigerian economy

such as the industrial, agricultural, transport and construction sectors. For instance, when the company is completed and commissioned, Nigeria would become a major producer in industrial machineries, auto-electrical spare-parts, shipbuilding, railways and carriages.

Ajaokuta alone is expected to attract over a hundred downstream industries. Thus the gains of having the steel industry far outweigh whatever considerations being used for its delayed take-off or abandonment.

10.0 Technology Transfer

There is no doubt that actualization of the Steel company will bring about technology transfer to the country. This will open a new vista for our technological take-off. It is expected that when the Steel Company becomes functional, foreign investors would be attracted to participate in the steel development. Indeed, nothing can expedite and actualize the much talked about technology transfer to developing countries especially Nigeria like the take-off of the Ajaokuta Steel Company Limited and other steel industries.

12.0 Steel as Industrial Raw Material

Steel has contributed immensely to the development of nations and from this view; steel has also attracted raw materials processing industries afore-mentioned, such as mining, beneficiation, and coking, calcining and refractory manufacture. Steel, in its various crude or primary forms, together with its by-products, is an essential input raw material for a host of other industrial activities or works. Many allied industries which would be activated or receive stimulus from raw steel production.

(i) Mild or Low-carbon steel (billets) - Rolling mills - Rounds production rods and bars-rolled from ingots or billets for civil works, construction and building industry and general engineering fabrication including furniture.

(ii) Medium-to High carbon steel (billets, slab and bloom)- Pipe manufacture and tubes made by extrusion or piercing also used in construction and furniture. Channels and angles for heavy works construction, derricks, etc. Also strip mills for flats, plates and sheets rolled from slabs, construction and fabrication of vessels, tanks and reservoirs, truck bodies and trailer trays; silos, drums and various containers; cabinets and general furniture; railway rolling stock; cold strip mills for cold rolling of sheets for cabinets and higher quality vessels and containers.

(i) Low carbon alloy steel (slab bloom): - Flat sheets usually cold-rolled from slab and bloom for the construction and fabrication of reactor vessels, car bodies and high quality silos, and various domestic utensils

(ii) High-carbon alloy and special Alloy steel (Slab): - Quality (Special) steel manufacture: Stainless steels for laboratory and hospital instruments, high quality goods and anti-corrosion and heat-resisting vessels and parts; austenitic steels for petrochemical company and equipment, manganese steels for rails and cables and other parts of rolling stock. Tungsten and vanadium steels for special ordinance equipment and tools and nuclear reactor vessels; chromium, molybdenum steels for oil drilling.

(iii) Scrap and Foundry Steel (Ingots, Billets): Steel Foundries for making castings and forgings leading to the manufacture of implements, automotive and machine parts and household items. Machine tools manufacture from heavy castings whence fabrication of agricultural implements, appliances, company machinery and parts and major ordinance equipment.

(iv) By-Products: (a) Coke Ovens - Application to industry as from-coke; also tar and tar felt for insulation, benzol, pitch, naphthalene, ammonia, sulphur; highway and macadam.

(v) Slag: Application to fertilizers; clinker for cement industry and highway 'macadam'

13.0 Steel and Food Production

The role of the steel industry in transformation of the agricultural sector from the mere production of raw materials to the conversion of the raw materials to intermediate or finished products for export has already been identified. The general decline in the agricultural sector is arguably due to the absence of a viable steel industry.

There are three broad levels of agricultural mechanization technology, namely: the Hand Tool Technology (HTT) Draught Animal Technology (DAT) and Engine-Power Technology (EPT). All three levels are applied in the agricultural sector of Nigeria. However, studies have revealed that 86% of tillage land preparation is done by HTT, 4% by DAT and 10% by EPT (Mrema and Mrema, 1993).

It must be noted that, whatever level of agricultural mechanization is desired, the role of steel is pre-eminent because a large percentage of the implements are either steel or steel based. Therefore any Action Plan for the revolutionizing of the agricultural sector must be hinged on the development of the steel industry like the Ajaokuta steel company limited.

Let us look at this case study, where Nigerians Lament as reported in one of Nigerian daily Newspapers, The Sunday Sun (April 13, 2008:49) "RISE AND RISE OF RICE PRICE" - The global escalation of the price of rice, which has a ripple effect on the country, and affected prices of other stuffs, has created fears in the minds of Nigerians who are worried about the consequences the shortfall might have on the poor.

According to Oghenekvwe Laba, a random check in the market across Lagos metro - police indicates that the situation is real and hard biting. The angry outburst of Austin Jeffiam, Bukateria operator in Lagos Island, best sums it up: "where do we go from here?" Imagine a cup of rice selling for ₦ 160 instead of ₦ 100. Three weeks ago, a bag of rice was selling for ₦ 10,500 instead of ₦ 6,500. The way things are, if the prices of food items continue to rise the way they are going, the poor in this country will starve to death.

The question is what do we do to curb the imminent crisis staring us in the face? A rice farmer, Mrs Olufunke Mudashiru wondered why the Government should import rice to the tune of ₦80 billion when Nigeria have large fertile land suitable for growing rice, She said, "I do not see reason why we are importing rice because this country is blessed with vast area that are favourable to massive production of rice". We have areas we can grow such rice as Ofada rice in Ogun state, there is also Abakaliki in Ebonyi state and some areas in the North".

Just as she stressed the need for Government to provide necessary agricultural equipment for farmers to enable them cultivate enough rice for the country, the actualization of the Ajaokuta Steel Company Limited becomes very necessary to ensure availability of equipment for the production of abundant food for the populace.

As an industry and wealth creator for the nation metallurgical industry is supposed to be second to farming. The company should be responsible for the production of different types of metals and alloys for usage in various sectors of the economy including agriculture. The company can handle different types of farm implements, spare parts and machinery for farming processes.

The availability of these metals at a cheap rate will greatly contribute to the development of agric-mechanization in the country. The metal produced from the steel company would be used to fabricate different types of farm machinery

and spare parts that could be used in agric-mechanization. The production of these metals is possible only if the steel company is well established and allowed to meet the demand.

The non-completion of the steel company will mean that the plan for agric-mechanization will only end up in our imaginations. It should be made known that we need to create and develop indigenous technology in order to use the facilities of the steel company to fabricate our farm machinery. In the absence of indigenous technology, the next alternative would be to embark upon the importation of farm machinery. This would result to costing the Government huge sums of money due to foreign exchange. For this reason, there is great need to complete the steel company, and sustain it in contributing towards the development of agric-mechanization nationwide.

14.0 Steel and Transportation

Transportation is one of the very important linkages of the steel industry. For instance a 1.3 million tonnes/annum capacity steel company will require the movement of over 5 million tonnes of raw materials and products. This certainly poses an important annual transportation challenge. This will require the development of road, rails and waterways. It will lead directly and indirectly to the employment of thousands and thousands of people.

Also to be noted is that 70 – 75% of automobiles are made up of steel (Hogan, 1993, Ilori, 1996). The percentage for railway tracks and cabins is even higher. Therefore, if Nigeria ever hopes to be able to meet her transportation facilities requirements, without having to depend indefinitely on foreign suppliers, the company must be completed and allow to operate on a full scale.

16.0 Steel and Health Care

It can be observed that many health care delivery equipment and facilities are steel based. For example, scissors, bowls and dishes, trolleys, beds, chairs and some operating and diagnostic tools are steel based.

This is another important reason why attention must be paid to the Ajaokuta Steel Company Limited for the realization of these objectives.

17.0 Steel in Defence (Armaments)

Defending a country's territorial integrity against external aggression is one of the most important functions of the present day nation state. Modern military armaments and ammunition are all based on steel. Military armaments may be imported from other countries willing to sell. However, two very important observations must be made:

- (i) No country will supply armaments that are sufficiently advanced to another country. Only second or third-rate armaments, which the supplier country is phasing out, are supplied to the buying country.
- (ii) At the first sign of problems, the advanced and supplying countries get together and "impose an arms embargo" on the target country or countries. The European Union imposed an arms embargo on Nigeria from 1996 till 1999.

It is very clear that in order to be truly independent, Nigeria must acquire the capability to manufacture her own military hardware and this translates directly to a compulsory development of the company because of the benefits that could be derived in terms of manufacturing her own armaments, nuclear weapons and other war equipment. Today India, Pakistan and North Korea have nuclear capabilities. India successfully tested a long-range ballistic missile and today North Korea is threatening South Korea, America and some part of the World because of their breakthrough in armaments creations. All these would not have been possible without a virile steel industry.

In his paper titled "Steel in Defence" Major S.K. Oni, of the National Institute of Policy and Strategic Studies, stated,

among others, that "At present, Nigeria relies on overseas purchases to equip her armed forces and other security forces. The disadvantages of this are many. It is obvious that any further delay in the completion of Ajaokuta Steel Company will not be in the overall interest of our defence policy in view of the strategic role of steel in defence" (Oni, 1988).

Let us draw from this lesson on the invasion of Iraq by the Americans and the British Governments and their inability to cope with the challenges of the North Korea, or even to easily run over Iraq, that unless a country produces and uses the armaments needed to defend its people, territory, resources and sovereignty, it shall be subjugated and enslaved.

The core of this modern technological base is an Iron and Steel industry like the Company and for company to serve the purpose for which it is established, ownership and control must remain in the hands of the Government and people of our Nation (Nigeria) and not foreigners who whenever it suits them, manipulates the steel company, imposes and effects sanctions.

A lot of money has been sunk into the company. Almost all the past leaders of the Country lack the long term vision and patriotic will to complete the company and operate the steel industry. Some of them have been further confused by the major steel powers and their international collaborators like the International Monetary Funds, the World Bank and World Trade Organization hence there lack-cluster approach to completing the steel company.

For some of them, it is pure unmitigated greed. They simply want to steal the money needed for the company and this company is the necessary backbone for any form of sustainable national development for the country in the immediate and distant future. According to a pioneering Nigerian Economist, the late Dr. Pius Okigbo, in a lecture delivered at Institute Management and Technology, Enugu in 1980, warned that "No country can claim to be industrialized if it does not develop metalworking industries: it must have its own steelmaking as the basis of the ferrous metal industry.

The steel fabricating industries multiply beyond count. The key lies in the establishment of iron and steel industry as the basic unit of any serious industrial development".

20.0 Steel and Employment Opportunities

The steel company has the prospect of employing a large number of the nation's labour force. The Steel company itself is expected to employ more than ten thousand workers directly while it will create employment for millions of Nigerians indirectly through the upstream and downstream industries. This will further help to alleviate the ridiculous unemployment problem of the nation.

As an important element of industrialization, the Ajaokuta steel industry is vital for developing linkages with all other sectors of the economy. Let us consider the setting and operation of a typical iron and steel company. On the one side are sets of inputs that must go into an intricate progression of production processes, ranging from raw materials (Iron ore, coal, refractory clay, limestone, dolomite etc.) through energy and utilities (electrical energy, gaseous and liquid fuels and water) to operating spare parts and consumables. Each of these inputs can generate an upstream activity.

On the other side are sets of outputs, which serve as inputs for other industries and / or applied as finished products. Downstream industries can be set up using these outputs, which include metalworking and forming (forge, fabrication, machining, drawing, stamping, etc) iron and steel foundries, pipe and tube making companies, etc. The products from these works form the major inputs for other bigger industries like automobile, engineering and machine tools, agro-allied, construction and various consumer goods manufacturing industries, etc.

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ABSTRACT

In historical perspective, the need for the establishment of an iron and steel industry in Nigeria was first expressed in 1958. Further action was taken by the immediate post independence government as is evidenced in the 1st National Development Plan (1962 - 1969), which states inter alia that “Substantial progress had been made in plans for a steel complex which will utilize Nigerian raw materials.” From the onset therefore policy formulation as regards the establishment of an iron and steel industry envisaged the availability, locally of at least the major raw materials inputs. In 1967, the Military Government (headed by General Yakubu Gowon) invited the Government of USSR to assist in setting up the steel project based on the availability of iron ores from Agbaja-Koton Karfi deposits. These deposits did not meet the specifications for use in the Ajaokuta blast furnace. As a follow up, the government with the support of USSR sponsored an extensive aeromagnetic survey of over 22% of the whole country. Ground magnetometric surveys and drilling for more suitable ones were subsequently undertaken. Exploration for iron ore was then concentrated at Birnin Gwari and Ayagba (Kaduna State), Ejigbo (Oyo State), Itakpe, Chokochoko, Ajabanoko and Agbado-Okudu (Kogi State). Investigations for coking coal centred on and around Afuze (Edo State), Lafia/Obi (Nasarawa State) and Gombe/Danduya (Gombe State).

Initial results of this joint effort prepared the ground for the signing of contract 1717 (4th November 1970) between Nigeria and V/O Techno-export (USSR) and the subsequent establishment of NSDA in 1971. In collaboration with the technical partners, the Exploration Division of NSDA (now National Steel Raw Materials Exploration Agency) commenced actual detailed and systematic exploration for the ores and other minerals in 1971. It was based on the strength of the recommendations of NSDA following the establishment of proven iron ore reserve at Itakpe and other deposits that Government sited the iron and steel plant at Ajaokuta in 1975. The paper therefore discusses the usage of raw materials for the development of iron and steel in Nigeria. Summary and Recommendations were made with a view to harnessing all the potentials available for iron and steel development in Nigeria.

Key Words: Development, Iron, Steel, Industry and Nigerian Raw Materials

1.0 Raw Materials Development

The availability of raw materials is a key consideration in the establishment of an iron and steel plant since it usually takes some time for steel companies to break even. In this case, the Nigerian authority started early to look for sources of raw materials within the country in order to be able to select the appropriate technologies that could be used and ensure that the industry is viable. The Soviet specialist and NSDA exploration division worked extensively over a large area of the country exploring for deposit of iron ore, cooking coal, limestone, and dolomite and refractory clays. Areas of the country explored in detail included Birni Gwari and Ayangba in Kaduna state, Ejigbo anomaly in Oyo state and Agbado-Okudu in Kwara state for iron ore deposits. In addition, Afuze in Edo state, Danduya and Gombe deposits in Bauchi state were also explored for cooking coal.

However, it was the discovery of the Itakpe iron ore deposit in 1973 by the soviet aero magnetic survey team that catalysed the development of the steel industry in Nigeria. Fairly good iron ore deposits were discovered at Itakpe, Agbaja, Ajabanoko and Chokochoko all in the region around Okene, Kabba and Lokoja in the present Kogi state of the country. British surveyors, who were earlier appointed by the federal government of Nigeria to carry out initial feasibility studies, also found that there were large iron ore deposits at Agbaja near Lokoja and Udi near Enugu. Coal was also discovered in large quantities at Enugu and limestone at Jakura near Lokoja (Tarbunde, 1983:3). Coal deposits from Lafia/Obi were also investigated, but the quality of the coal was impaired by high ash and sulphur contents with the deposits occurring in seams that are difficult to mine. Overall however, Nigerian coal is said to be one of the most bituminous in the world owing to its low sulphure and ash content and therefore the most environmentally-friendly.

There are nearly 3 billion tonnes of proven coal reserve in the country presently (BPE, 2005). In a study carried out by a business consultant, SKOUP and company involving extensive chemical testing of various samples of coal from deposits from the South and North locations, It was found that some Nigerian coal were suitable for cooking using the direct reduction method in steel-making (SKOUP and company Ltd, 2004). The study recommended increasing Nigeria's import substitution in steel manufacturing beyond the planning of projects by establishing a sponge iron mill fired by Nigerian coke. The study further showed that tar and coke could be produced at competitive prices in the country.

Other raw materials required in the industry that were discovered and found suitable included Jakura limestone, Ubo barble, Mfamosing limestone, Burum dolomite, Osara dolomite and Onibode/Oshiele refractory clay (Chukwumerije et. Al 1982). The picture emanating from the successful explorations, especially the Soviet-Nigerian joint efforts, which arose from the Moscow protocol of 1970 proved contrary to the then prevailing view that Nigeria had no iron or ore nor coking coal suitable for steel production.

See table 1.1 below for the location of raw materials and their possible uses in the development of the iron and steel industry in Nigeria.

It is fairly common knowledge that the nature, quality and availability of raw materials dictate the technology type that should be used in the development of a particular steel industry. Nigeria has fairly large deposit of iron ore but closer scrutiny indicates a paucity of good coking coal. The available coal has significant percentages of ash and Sulphur content. The iron ore could be improved upon to meet the requirements of Ajaokuta plant, even as the Delta direct-reduction plant demands high quality iron ore of about 66 per cent ferrous content (Ogbu et. Al 1995:9). The Delta plant uses natural gas for fuel. This resource is so abundant in Nigeria, which is a major oil

producing country that the iron and steel industry will hardly lack for gas as fuel. For the main coal deposits in Nigeria, these are found at the Enugu and Lafia-Obi coal fields. The Lafia-Obi coal has coking properties but is high in ash and sulphur,

and the deposits has structural problems. On the other hands, the Enugu deposit is reasonably free of impurities but is non-coking.

TABLE 1.1
Raw Materials for the Development of the Steel Industry in Nigeria

Raw Materials	Source	Role	Requirements Ajaokuta	10,000t/yr Delta
Iron ore	Itakpe hill, Ajaba Noko, Shoko-shoko, and Agbaja	Sinter; sent to blast furnace to produce pig and molten iron	2,200	1,550
Coal	Enugu, Lafia, and imported	Carbonized in coke ovens; Fuels furnace	1,300	0
Limestone	Jakura, Mfamosing, And Ubo	Used in sintering and Heating iron ore	690	130
Scrap	Recycled and imported	Melted in electric-arc furnace; Used as coolant in the Steel making shop	293	250
Bauxite	Imported	Used to maintain slag fluidity	13	
Dolomite	Osara and Burum	Low grade used as flux in iron Making; high grade used in Brick refractories	250	
Refractory Clay	Onibode, Oshiele and Ozubulu (Imo)	Used to produce bricks in aluminosilicate plant		
Manganese	Imported	Used to control quality of Metal in blast furnace	85	
Water	Widespread	Used for cooking	120	83
Natural gas	Widespread	Powers furnace	3,700	2,000

Source: Osita Ogbu et. Al (1995), Technology Policy and Practice in Africa, Canada, IDRC

The planners in this industry that, initially, it will be necessary to import coking coal, until a better blend is made from the Enugu coal. Research has shown that a 20 per cent shell blend of the Enugu coal is possible, which will contribute significantly to foreign exchange savings on imported coking coal (Ogbu et. Al, 1995).

The National Iron Ore Mining Company (NIOMCO), which was established in 1979 was to supply Ajaokuta Steel Company Limited with about 2.2 million tonnes of super concentrates per annum. The company's name was initially associated ores mining company, but later changed to National Ore Mining Company Limited on the 13th of February 1987 when its activities are streamlined towards exploration, exploration, processing and supply of iron ore concentrates to the country's steel plants at Ajaokuta and Aladja. The industrial processing plant here was designed to supply ore of 63/64 ferrous grade super concentrate to ASCL and 550,000 metric tonnes per annum of 67/68 per cent ferrous grade super concentrate to Delta Steel Company Limited (DSC). The supply of iron ore to DSC started in October 1994, though this was grossly inadequate. As at April 1991, the beneficiation plant which was to produce iron ore concentrates and super concentrate was about 40 per cent ready at the Itakpe mining district (Okorocho, 1991:1). The beneficiation plant was expected to have been completed and commissioned by the end of 1992.

In 1989, about 59,176 tonnes of iron ore was produced by NIOMCO, 359,136 tonnes in 1990 and 245,000 in 1991 (Adeniji, 1991:18). The total iron ore stock piled as at 1991 was about 1.8 million tonnes (CBN, 1991:84). The company was 100 per cent equity owned by the federal government of Nigeria with staff strength of 1,892 until it was acquired by global infrastructural holdings Ltd. (GIHL), in 2005. The company is decisive in determining the ability of Ajaokuta to produce steel in a sustainable manner. GHIL was awarded a long term mining concession to the Itakpe and

Ajabanoko iron ore mines., NIOMCO iron ore mines have an estimated reserve of about 300 metric tonnes together with a 2.7 metric tonne beneficiation plant and possibility for further expansion (Adepoju and Olaleye, 2001).

2.0 AN OVERVIEW OF THE MINERAL AND MATERIALS REQUIREMENT

Indeed, a number of minerals are required to run an iron and steel plant. These include,

2.1 Iron Ores:

Iron is the most important mineral needed in the steel industry and in nature it is second to aluminium in occurrence. It accounts for 4.6% of the earth's crust. The main ores of iron now used in the iron and steel industry are predominantly oxides and hydroxides, though ferrous carbonate (siderite, FeCO₃) is sometimes used. Others, chamosites, pyrites, etc occur in large quantities but are not easily beneficiable for iron and steel making. The main undesirable elements in most iron ores are phosphorous and sulphur. The Ajaokuta steel plant for instance can tolerate iron ores of at least 63% Fe and only about 0.08% phosphorous.

At the planned initial capacity production of 1.3million tonnes, the Ajaokuta steel plant will required an annual supply of 2.135 million tonnes of concentrate of iron ores. The demand will obviously increase as production expands to 5.2 million tonnes per annum.

2.2 Coking Coal

Coking coal provides the heat energy needed to melt down the raw materials and also acts as a reducing agent in the blast furnace. Ranking of coals for productive seams is characterised by variation of carbon content and volatile matter deduced on the relationship between ultimate analysis and other major bulk properties – these parameters include swelling index, Grey-King number,

dilatation and reflectance. Others are moisture content, volatile contents, and mineral matter contents etc. Prime coking coals have volatile contents in the range 20-32% (dmmf). Ajaokuta steel plant for instance will not tolerate more than 18.32% of volatile matter in the coal. The first phase of Ajaokuta steel plant will require the supply of 1.32 million tonnes of coke/annum.

2.3 Fluxes

Fluxes are needed for the removal of gangue/impurities associated with the ores. They are added to the charge to form slag. In addition, they lower the temperature of the molten ores, reduce the specific gravity/viscosity of the melt, and increase the fluidity of the slag. They are classified as basic, acidic and neutral fluxes based on their properties. Examples are, limestone, dolomite, marble, silica, bauxite and fluorspar. The 1st phase of the Ajaokuta steel plant will require about 965,000 tonnes/year of limestone and dolomite for the sinter production, iron making and steel making.

2.4 Refractory Raw Materials

These are heat resistant raw materials which line the walls of the furnace to prevent deformation at the high temperatures of the melt. They are again classified as acidic, basic or neutral. These include the aluminosilicates (fire clays), bauxite, fluorspar, cryolite, kyanite, silimanite and silica. As a rule, refractory raw materials must be free from sulphur and phosphorous.

2.5 Ferro-Alloys

Ferro-alloys are the raw materials added to iron to produce specific types of steel. They include, manganese, chromium, nickel, tungsten, cobalt, molybdenum, titanium, vanadium, niobium, silicon, etc. All these materials have high melting points and most do not occur in their free state but are produced from the reduction of naturally occurring oxides, sulphides etc.

2.6 Foundry Raw Materials

Molten steel from the steel furnace is usually poured into moulds of various shapes and sizes. The moulds are made from silica sands that satisfy the refractory requirements of fitness, bonding strength, permeability, sintering point and durability. Binder, flakers and filters such as bentonite, graphite and diatomite are usually added to bind the mineral grains. Minerals such as chromium and zircon sands are also fast gaining acceptance as mould materials in recent times.

3.0 EXPLORATION ACTIVITIES – AND ON-GOING PROJECTS

3.1 IRON ORE EXPLORATION

The pre-Cambrian iron formations in Nigeria are usually quartzites in banded forms. The ferruginous quartzites of Itakpe and near-by occurrences consist of four distinct varieties:

- (i) Magnetite quartzites – 37.3% of deposit
- (ii) Hematite quartzites – 25.9% of deposit
- (iii) Magnetite – hematite quartzites – 19.7% of deposit
- (iv) Hematite magnetite quartzites – 16.9% of deposit

The successful investigation of Itakpe banded iron ore formation with a proven reserve of 310 million tonnes represents the first major achievement of the Agency. Also geological work on Ajabanoko iron ore deposit yielded about 65 million tonnes (indicated and inferred reserves).

However, with just over 300 million tonnes of reserve the life expectancy of the Itakpe deposits reduces appreciably from 30-40 years (assuming supply to Ajaokuta alone) to 10-15 years (assuming supply to Ajaokuta and Delta

Steel Companies). This underscores the need for more work to increase the reserves. Consequently, further work to prove more reserves is being carried out by the Agency on the Ajabanoko, Agbado-Okudu, Choko-Choko, Tajimi, Toto-Moro and other adjoining deposits within the Okene-Lokoja area.

3.1.1 Oolitic Iron Ores

Initially the idea of iron and steel development in Nigeria centred on the availability of vast reserves of oolitic ironstone in the Agbaja-Koton Karfi-Egeneja area. Minor occurrences were also found within Udi Hills, Bida and Sokoto areas. However, work on the deposits was discontinued on account of high phosphorus and sulphur contents which are deleterious in the iron and steel making process. Work has again resumed on the Agbaja-Koton Karfi-Egeneja oolitic iron ores. This renewed interest is as a result of advances in technology which are making it possible to use a wider range of iron ores and coal quantities in the new emerging iron making plants in Japan and South Africa.

Table 3.1: CHEMICAL CHARACTERISTICS OF THE OOLITIC IRON ORES

	Agbaja	Koton-Karfi	Egeneja
Average thickness (m)	11.82	13.53	10.21
Overburden (m)	5.62	6.73	5.51
Fe-total%	47.35	51.29	48.05
P ₂ O ₅ %	2.11	2.35	2.22
SiO ₂ %	7.05	5.21	6.07
Al ₂ O ₃ %	9.61	6.19	7.85
Ore Reserves in Million tonnes:			
Indicated	962.0	428.0	82.5
Inferred	1250.0	850.0	400.0
Total	2212.0	1278.0	482.5

The preliminary geological studies undertaken jointly by BRGM of France and National Steel Raw Materials Exploration Agency established that more than 3.9 billion tonnes of oolitic iron ores occur at Agbaja, Koton Krfi, Egeneja, and Atte in the Lokoja area of Kogi State. Several millions of tonnes more are reported to occur at Udi Hills, Bida and Sokoto areas.

3.2 COAL EXPLORATION

Iron ore and coal are the two major raw materials inputs in steel making. Having established the availability of iron ore the Agency also has worked on the Obi/Lafia coal from 1973 – 1979. The work undertaken involved the study of 36,000 metres of cores from 138 boreholes and bulk samples from two (2) vertical shafts sunk in the area. Unfortunately, drilling could not provide enough information to ascertain the exact situation with regards to the recoverable coal, and hydrogeological and other mining conditions of the deposit due to the structural complexity of the seams.

The result of the geological investigation put the Obi coal at a total reserve of 128.3 million tonnes. However, only 32 million tonnes of seams 12 and 13 out of the 36 seams encountered can be commercially exploited. The Obi/Lafia coal has been classified as medium coking with high ash (30-50%) a sulphur (1-6%) contents. Based on available information the washability of the coal has been classified as 'Very difficult' to 'formidable'. To reduce the ash content by 50%, the final volume of coal would be 20% of the original bulk.

3.2.1 In-Seam Exploration

In-seam exploration was therefore, recommended to upgrade geological knowledge of the deposit which cannot otherwise be obtained through additional drilling. It would include shafting and tunnelling with all the necessary documentations to be executed by competent contractors. The tendering process has been completed while three contractors have been selected for consideration by the Ministry. The total cost of the project is about N2.0bn. In view of the high cost, the execution of the project is planned to proceed in phases.

Table 3.2 Characteristics of Obi/Lafia Coal

	Specification for Coking Coal	Average values of coals from Lafia-coal deposit seam 12/ seam 13.
Ash content (wf)	6-8%	30-38.2%
Sulphur content (wf)	<1.2%	>2.6% / 3.8%
Free Swelling Index	>4.5	8- 8.5
Caking property index after ROGA	>20	44 – 78
Dilatation	>60 DDPM	187 – 200 DDPM
Gray – king index	>1.00	G9 – G11

3.3 REFRACTORY CLAYS

In the late '70s and early '80s the Agency had worked extensively on the Onibode Clay Deposit. Two hundred

(2002) boreholes were drilled and seven hundred and sixty five (765) samples analysed both locally and overseas. The work established a proven and estimated reserve values of 3.05 and 3.75 million tonnes respectively. The pyrometric Cone Equivalent (PCE) value is 1700°C and the clay is considered to be of low to medium plasticity. However, logistic and other considerations necessitated the search for other refractory clay deposits in Kogi and adjoining States. The result of this effort if the current detailed exploration of the clay deposit at Oza-Nagogo and its environs in Edo/Delta States as well as Ukwu-Nzu clay. In addition work is continuing on Bendel, Oshiele and Miroko-Lisabi clays.

3.3.1 Oza-Nagogo Clay Exploration

The work so far accomplished include:

- (i) Preliminary exploratory pitting, trending and auger drilling up to a dept of 13m.
 - (ii) Topographic Survey on scales of 1:5000 and 1:2000 respectively.
 - (iii) Geophysical profiling including Vertical Electrical Sounding of the deposits areas.
 - (iv) Core drilling of four (4) boreholes at Oza-Nagogo.
 - (v) Determination of the mineralogical and chemical characteristics of the clay using the XRD and XRF.
 - (vi) Determination of the engineering and physical characteristics of the clays.
 - (vii) Determination of the refractories (PCE values) at NMDC Jos and Pettersburg Institute, Moscow.
- The preliminary assessment of the deposit put the reserve at 35 million tonnes. Details of the physical and chemical parameters of the Oza-Nagogo Clay are shown in Tables 3.3, 3.4 and 3.5.

TABLE 3.3 Physical characteristics of Oza-Nagogo Clay

S/N	LOCATION OF SAMPLE	SAMPLE NO.	MOISTURE CONTENT (%)	SPECIFIC GRAVITY	LIQUID LIMIT (%)	PLASTIC LIMIT (%)	PLASTIC INDEX (%)	SHRINKAGE LIMIT (%)
1.	Evebi	ERC-1	24	2.50	70	34	36	13
2.	Evebi	ERC-2	24	2.58	84	32	52	14
3.	Iduleha	IRC-1	21	2.58	76	33	43	15
4.	Iduleha	IRC-2	27	2.58	76	42	34	-
5.	Iduleha	IRC-3	-	2.59	78	42	36	-
6.	Iduleha	IRC-4	33	2.60	71	39	32	-

TABLE 3.4 Chemical Composition of Oza-Nagogo Clay

SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	LOI
46	1.32	38.07	0.78	0.14	0.09	0.07	0.02	13.7

3.3.2 Comparative Analysis of Onibode and Oza-Nagogo Clays

In part, the exploration of Oza-Nagogo Clays was necessitated by the need for a more plastic to blend with Onibode Clay. The Oza-Nagogo clay with limit excess of 76% has a higher plastic index (PI=34-38%). That means the Oza-Nagogo clay can be used without additional binding material. The Quotient, Q – Value calculated without from the Aluminium oxide, Titanium oxide and

Iron Oxide contents shows that Onibode and Oza-Nagogo clays have high purity. Also, the assessment of Al₂O₃, TiO₂ of both deposits classify them as high grade (Category 1) and medium grade (Category 2). The refractoriness values for Oza-Nagogo and Onibode are 1750° C AND 1700°C respectively. The reserves for both Onibode and Oza-Nagogo are high enough, considering that Ajaokuta Steel Plant's annual consumption is put at only 65,000 tonnes.

In general, the thickness of Oza-Nagogo clay deposit is greater than that of Onibode and the proximity to Ajaokuta as well as the Warri – Ajaokuta rail line confers and added advantage.

Table 3.6 Comparative Characteristics of Oza-Nagogo and Onibode Clays

PARAMETER	OZA-NAGOGO CLAY	ONIBODE CLAY
Specific gravity	2.48- 2.60	2.47 – 2.69
Natural moisture content (%)	24 - 35	12 – 21
Plastic rating	High plasticity	Low – Intermediate plasticity
Plastic index (%)	34 – 38	12 – 14
Quotient value (Q)	High purity	High purity
Al ₂ O ₃ + TiO ₂	High and medium grade (Category 1 and 2)	High and medium grade (category 1 and 2)
PCE refractoriness	> 1750°C	1700°C
Nearness to the steel plant	Very near	Rather far
Loading point/Haulage	200km away by rail	500km away by road
Alkali earth metal	Adequate for the steel industry	Adequate for steel industry
Fe ₂ O ₃ in the clay	2.09%. could be smaller below surface sample	0.75% (Low)
Overburden	Laterite (thick)	Laterite (thin)
Underground water	Below the clay unit	Below the clay unit
Thickness of overburden	10 – 20m	2 – 8m

4.5 TSAKASIMTA MAGNESITE

The need for local sourcing of suitable refractory raw materials for the steel industry necessitated the detailed investigation of 1km² magnesite occurrence delineated from 40km² area at Tsakasimta near Garkida in Adamawa State. Detailed geological mapping including cadastral and geophysical survey (scale 1:2000) and core drilling were carried out to assess to deposit. A total of 45 pits were excavated and 8 boreholes drilled. Geotechnical studies including hydrogeological, engineering geological and mining methodology were carried out to assess to deposit. A total of 45 pits were excavated and 8 boreholes drilled. Geotechnical studies including hydrogeological, engineering geological and mining methodology were carried out.

Reserve estimation of Tsakasimta magnesite deposit show proven reserve of over 535,000 metric tonnes with an average of 35.8% MgO, while other characteristics show that it meets Ajaokuta's specification. Further work is continuing in the adjacent areas including Gardemna to increase the proven reserves.

4.6 LIMESTONE AND DOLOMITE (BOLDEN)

There have been tremendous achievements in the exploration of the various fluxing and refractory mineral raw materials. Detailed work has been undertaken by the Agency of the Mfamosing limestone, Osara and Burum dolomites, and the Ubo, Jakura and Itope marble deposits. Information on other deposits such as the Yandev, Ashaka and Nkalagu as well Kalambian limestone deposits are easily available. The data bank on Nigerian limestone/dolomite/marble deposits confirms self

sufficiency and a broad range of quantities to meet various industrial applications including iron and steel making.

Iron ore and coke, which represent the two major mineral raw materials for iron and steel making usually have constituents of gangue (impurities) which of ten have very high melting points. The flux raw materials (limestone etc) not only serve to remove the gangue but also reduces the vitrification temperature. The Ajaokuta Steel Plant alone is planned to consume about 700,000 tonnes of limestone, and 265,000 tonnes of dolomite annually at the 1.3 million tonnes /year of steel production.

4.6.1 Review of Characteristics of some Nigerian Limestone/Dolomite (BOLDEN)

4.6.1.1 Mfamosing Limestone Deposit (Cross River State)

This marginal basin deposit of Cretaceous age occurring 30km NE of Calabar has been explored in detail by the Agency. Over 35 boreholes were drilled which reveal an overburden varying from 0 – 18m and a maximum limestone thickness of 36m.

The studies showed a spartial distribution of silica and magnesium, with the deposit tending to be sulphur rich (1-2%) at the upper layers and sulphur free below. Thus, the upper layer portions of the deposit is considered unsuitable for the steel making shop.

Quantification of the deposit gave a proven reserve value of 26.18 million tonnes. In addition a probable reserve of 20.33 million tonnes of steel grade limestone has been calculated out of which 11.33 million is assured. Calabar Cement Company (CALCEMCO) is presently exploiting the deposit for cement manufacture.

4.6.1.2 JAKURA MARBLE

This is a Precambrian crystalline formation occurring 13km West of Jakura Village, and about 85km from Ajaokuta. Two types of limestone are distinguishable, the pure medium grained greyish variety and the impure sugary textured marble with graphite specks, pyrite and muscovite impurities. Where pegmatite dykes intrude the marble, garnet, fluorite and andradite result from skarn mineralisation. The reserve has been estimated at 46.4 million tonnes with an average overburden thickness of 9.6m.

4.6.1.3 Ubo Marble

This is a Precambrian crystalline deposit in a hilly terrain occurring 8km NNE of Oguda and situated 32km SE of Okene. It outcrops as massive bodies, greyish white considerable variation in texture along strike from coarse to fine grained. The marble is composed mostly of calcite with minor dolomite ex-solutions, specular graphite and plagioclase as impurities.

Work undertaken confirmed a proven reserve of 14.4 million tonnes and an inferred reserve of 21.3million tonnes. A major problem with this marble however is the rather high $\text{SiO}_2 + \text{Al}_2\text{O}_3$ contents which may make it unsuitable for fluxing in steel making.

It should also be noted that this deposit extends northwards to form another major body presently being owned by Ukpilla Cement Company. An estimated reserve of 29.9 million tonnes had earlier been calculated by other workers.

4.6.1.4 Igbetti Marble (Oyo State)

This Precambrian crystalline limestone occurs 3km west of Igbetti in Irepo LGA, about 200km north of Ibadan. The marble outcrops in lensoid shaped bodies traceable for 3-5 km with a total length of 24km. The marble is predominantly dolomitic, whitish and sugary in texture with subordinate greyish varieties. The marble is brittle, jointed, fractured and is associated with silified rocks and fibrous tremolite. It has a general dip of 45-57° and reserves are estimated at 49 million tonnes.

4.6.1.5 Ekpeshi Marble

Both crystalline limestone (marble) and dolomite occur in the basement complex in a rather complex geologic association. Crystalline Limestone and dolomite are selectively quarried/mined for specific use industries from this area. Ajaokuta Steel Company is interested in the dolomite here rather than the associated limestone. Many private miners are actively exploiting this deposit, including Freedom Mines, Charmount etc.

4.6.1.6 Itope Marble

This marble body outcrops 3km east of Itope across the River Niger at Ajaokuta. The Precambrian crystalline marble forms thick bands within meta-sedimentary series of semi-Pelitic gneisses. The thickness of the deposit varies from 4.5m to 54m extending for over 270m long and dipping 50° to 90° in some places. The estimate reserve of this deposit is 806,000 tonnes.

4.6.1.7 Osara Dolomite

Osara dolomite is a lensoid, massive and crystalline body sandwiched between gneisses (situated within Ohuakara) about 4km off Okene – Lokoja road.

Detailed exploration carried out by the Agency confirmed the suitability of the dolomite – assessment of which was made using standard mineralogical, chemical and physical tests for steel plant refractories. Although the large grain size of the dolomite is a disadvantage, this has been overcome by the production of doloma clinker/pellets by a two-phase dead-burning method. Through this method the desired high bulk density (3.19 – 3.21 gm/ml) and low porosity (3.92%) have been achieved. The Osara deposit has an estimated reserves of 1.7million tonnes and the

proximity to Ajaokuta Steel Plant is an added advantage for its use for refractory and fluxing purposes.

4.6.1.8 Burum Dolomite, FCT

Crystalline dolomite occurs in Burum East, Burum West and Takalafia areas of FCT, in a Precambrian terrain underlain by tremolite schist, granites, gneisses, siliceous breccia pegmatite.

The marble is fine to medium grained, and consists of calcite and dolomite. The overburden varies from 4.5m to 7.5m thick. The deposit can be classified into dolomite (57.71%), dolomitic-limestone (15.01%) and silicious-dolomite (27.28%) with a total mineable reserve estimated at 9.5 million tonnes. PW Syndicate is one of the companies exploiting these deposits presently.

4.7 FERRO-ALLOYS EXPLORATION

Following preliminary investigation for chromite and manganese at various locations, more detailed programmes are presently being undertaken. Geological mapping, trenching and pitting have been carried out at Sado, Maikwanaga (Zamfara State) and Jibiya (Katsina State), while a drilling programme at Tunga-Kudaku (near Anka) is on-going.

The chromite occurs as podiform mineralisation in serpentinite and analysis indicate over 35% Cr_2O_3 content in pods.

On the other hand manganese exploration has been carried out at Mallam Ayuba (Kaduna State). Detailed analysis show that the ore is mostly sparsate garnet, an ore from which is difficult to extract. Work has also been undertaken in Fika where modular manganese occur in shells of gypsum. Currently preliminary investigation for manganese has been extended to the Oban Massif (Cross River State) and Derina area (Kebbi State).

5.0 SUMMARY AND RECOMMENDATIONS IN RESPECT OF MATERIALS AND ENERGY FOR THE NATION'S IRON AND STEEL INDUSTRY

(i) Even though iron ores of various grades are in abundant supply in the world, transportation cost of bulky materials account for more than half of the cost of bringing these ores to the market.

(ii) In respect of (1) above, the big advantage of the nearness of Ajaokuta plant to the ore mines (only 60km by rail) offsets the cost disadvantage of beneficiation of the low grade ores.

(iii) The economic reserves of all Nigeria's banded iron ore deposits guarantee self-sufficiency for not only the Ajaokuta plant but also for the needs of Delta Steel Company. The proximity of the latter and rail linkage being an added advantage.

(iv) Modern technological advancement which allows for the use of a wider range of iron ore and cal quality (materials considered unsuitable for conventional Blast Furnace Operation) brings to focus the vast oolitic iron ore deposits of Nigeria. Their use in the future programme for production of non-structural steel is a cheering feasible option.

(v) Refractories and fluxes have been extensively explored in Nigeria and exist in large enough quantities to satisfy the present and future requirements of the two plants. Virtually all of these occur in close proximity to the Steel Plants.

(vi) Nigerian coals presently being mined are of poor metallurgical quantity, with high ash and volatile contents. In the medium term, it is hoped that coke production at Ajaokuta can be achieved from blending prime coking foreign coals, moderately coking Obi/Lafia coal and the non-coking local coals in the ratio 60:30:10.

Increasing shortage of coking coal from the traditional sources of supply are likely to be met to a considerable extent, by new deposits being opened up in Canada, Queensland Australia and Siberia (Russia). There is, nevertheless, considerable doubt that the world will be able to satisfy the growing demand for coking coal with satisfactory quality in terms of sulphur and ash content to meet the increase strict BF standards. This is because countries with reserves of cooking coal may not wish to continue exporting the raw materials, preferring to use them in their own expanding industries.

Although coking coal cannot be entirely replaced by alternative fuels in conventional process, development of new routes to iron and steel making and modification of the old methods to improve blast furnace practice would help in removing total dependence on prime coking coals.

(vii) New thrust in mineral exploration by the Agency if geared towards proving more iron ore deposits and the search for more coals in the Benue trough. In addition, the exploration for ferro-alloys at the Oban Massif and other locations will be intensified.

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HARNESSING LOCAL RAW MATERIALS FOR ENGINEERING AND TECHNOLOGICAL DEVELOPMENT IN NIGERIA

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ABSTRACT

It has been said that no meaningful industrialisation can take place in a nation without Iron and Steel. In fact, the Iron and Steel is the bedrock of Nigeria's industrialisation and ultimate factor in the realisation of our industrialisation efforts. Most of the Steel industries have been constructed and erected and they have to go into full operation in view of the huge money already sunk into these projects and the relative irreversibility of investment. Harnessing the local raw materials for engineering and technological development in Nigeria. The development of the economy could therefore be vibrated if the available local raw materials are harnessed. Metallurgical Research and Development have been carried out which have assisted the industry to discover the use of locally sourced raw materials for the operation of these industries. Apparently, most of the imported raw materials are expensive and some time difficult to import them due to bureaucratic process and challenges faced at this present stage of steel development in Nigeria. The need for sustained availability of the raw materials for these steel industries calls for drastic reduction in the imported raw materials and this paper will therefore focus on availability of local raw materials which could be harnessed and translate to engineering and technological development in Nigeria. The paper further highlights the local raw materials needed for steel industry; processes for metallurgical coke and of refractory clay were reviewed. Local deposits of these materials were mentioned. The future of metallurgical research and development were brought to the fore and finally some suggestions and recommendations were given which will assist Government, stakeholders and those that are involved in the practice of steel operations and other engineering processes but with emphasis to the steel industries.

Key Words: Harnessing, Local, Raw, Materials, Engineering and Technology

1.0 INTRODUCTION

There can be no national industrial and technological advancement without functional steel sector. It is also very strategic for effective technology acquisition. However, steel industries cannot grow sustainably without drawing the bulk of its materials need locally.

Thus, import substitution in terms of raw materials and spare parts in an indispensable strategy in developing steel industries. Metallurgical research and development therefore is a necessity in achieving import substitution as the example of steel development in most of the developed countries. The locally available raw materials should therefore be harnessed. The development of raw materials required for most of the metal-based industries, for iron and steel making in actual fact begin with exploration as shown below.

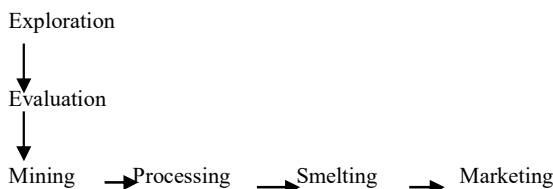


Figure: 1 Activities of the Mineral Industry

Research and development programs of Metallurgical interest have been executed in some institution of higher learning, research centres and industries, especially since independence in Nigeria. The most significant of these projects on record have recounted – the contributions of metallurgical research and development to national economy. It is conclusively advocated that an increased – research and development activities in the metallurgical industry is the self – reliant industrialization and economic development of Nigeria as we face this present global economy meltdown.

Several of the minerals resources known to occur in Nigeria (including iron ore, coal, gypsum, clay, salt etc.) could be described as relatively low grade, but they are considered so

only in the context of currently commercialized production processes and technologies. With more intensive research and development, it should be possible to develop processing techniques that are peculiarly appropriate to the local resource. A case in point relates to the local iron and steel industry for which iron ore and metallurgical coals are essential but currently import raw materials.

Unfortunately, Nigeria's largest iron ore reserve on the Agbaja' largest plateau in Kogi State (with over one billion ton of ore) is known to contain unacceptably high levels of phosphorus, an element that is difficult to eliminate in convectional ore beneficiation and iron and steel furnace processes, in addition to being deleterious to the properties of the un finished steel product, similarly, the coal resources of Anambra, Benue and Plateau States a new non –coking and therefore unsuitable for direct use in the blast furnaces.

In both of these cases, local research and development efforts geared to the characteristic of these local resources could result in their economical utilization by the local steel industry, thus saving larger sums in foreign exchange that could have been spent on importation, while enhancing Nigeria's security of supplies of critical raw materials.

Despite the growing competitions from some non – ferrous metal like Aluminum with its alloys, and non- metallic materials, notably plastics, in the country, the supremacy of steel is rather secure. Consequently the buck of metallurgical research relevant to the current global economic meltdown will provide the necessary impetus to develop the metallurgical industries in Nigeria in the areas of iron and steel making and heat treatment processes with a view of overcoming the present global economic meltdown.

2.0 RAW MATERIALS FOR STEEL PRODUCTION

It may interest you to note that during the short period of production at the Ajaokuta Steel Company Limited and Iron ore mining Corporation at Itakpe both in Kogi state, the Delta Steel Company Limited (DSC) Aladja produced steel which were made into billets (ranging from low to medium carbon

steel) for use at Ajaokuta Steel Company Limited, without necessarily depending on imported ores because the vast proven local ore reserves that are largely available have been improved upon and the qualities upgraded.

Consequently, the beneficiation of these local ores has attracted a lot of metallurgical research. In the past, the Metallurgical Research and Test Division of the National Steel Council had been able to upgrade samples of huge reserve of sedimentary magnetite – hematite ore deposit at Itakpe from 38-40 % as mined to 65 % Fe by the gravity method (Anagbo & Udevi) ⁽³⁾

This concentrated quality would satisfy the 63% Fe requirement for the production of iron in Ajaokuta Steel Company Limited through the use of the blast furnace whenever the furnace is operational, it is also determined that provided that the silicon content could further be minimized. A super concentrate of 68% Fe was produced by a second stage flotation process, providing a possible raw material even for the direct – reduction steel plant (as being practiced at DSC), especially with the intrinsic low sulphur and phosphorus contents of the deposit. The research got to a stage where a pilot plant scale was developed for the beneficiation flow sheet involving Reichert Cone, the Humphrey Spiral and the Magnetic Separator ⁽⁴⁾

The Tuto –Buro fine –grained hematite ores have similarly be upgraded from 32% also by the gravity method while the Ajabanoko ores (Kogi State) was improved by magnetite separation from 39 % Fe to 63% Fe -Anagbo ⁽⁵⁾ From the research carried out, it implies that the ore from these two deposits could also be processed for the blast furnace feed. The vast deposit of over a billion tonnes of Oolitic sedimentary ore at Agbaja is unfortunately associated with very high phosphorus content (Anagbo & Udevi) ⁽⁶⁾

It has only been possible to upgrade the ores from 52-56% Fe to 60% Fe. In this state it could be blended with richer ores to feed the blast furnace at the Ajaokuta Steel Company Limited, provided the phosphorus content could be attenuated.

It was estimated that at full capacity the Delta Steel Company Limited will require 1.55 million tonnes of iron ore while the first phase of Ajaokuta Steel Company Limited would gulp up to 2 million tonnes per year ⁽⁷⁾

In the early 80s the cost of per tonne of ore was put at \$45, a whopping sum of \$159.75 million per year would have been needed for investment in iron ore alone when both industries become fully operational. A substantial part of this sum could be saved if the momentum of local ore beneficiation is maintained to curb importations.

2.1 ITAKPE IRON ORE

Research and Development work carried out on Itakpe iron ore by NMDC Jos, established that the supply of the required specifications of concentrates to Ajaokuta Steel works is never in doubt. In the research work NMDC, Jos collaborated with NIOMP and DSC Warri have proved through research that the handling problems associated with abundant fines in the super-concentrates transported from NIOMP to DSC can be solved. It is on record that the Itakpe super – concentrates produced by Froth Flotation using feeds of sizes 0- 180 μ m (> 80% < 90 μ m) and 0-90 μ m (> 705 < 63 μ m) meet the requirements of DSC in terms of physical and chemical characteristics in Fe > 66%, gauge of < 3.5% and sieve size of - 45 μ m < 30 % ⁽⁸⁾ G. Usman (2002)

3.0 REVIEW OF METALLURGICAL COKE

In the production of steel, the next but important raw material is the metallurgical coking coal. The use of these coking coals is via the blast furnace route. In the 80s, it was established that about 401 million tonnes of coals in Nigeria were intrinsically deficient for the direct application to steel making. The issue of coke-able coals has therefore also

attracted considerable metallurgical research, Adigwe discovered that it is possible to reduce the objection of the medium – rank Lafia – Obi (coking coal) high sulphur content, moisture content and ash content from 44 % to only 10% ⁽⁹⁾

Further work was set in motion to control the sulphur content as being investigated by Afonja; He further showed that Enugu coal estimated at 64.3 million tonnes reserves, characteristically of the low ash content can be upgraded to 30% in convection modern preparation with imported high rank coal. The drive would be to blend the imported coals with upgraded Lafia coal.

Since its inception in 1979, the Research Centre of NMDC, Jos has been conducting applied research to ensure the inclusion of an appreciable percentage of locally available coals in metallurgical coke making at the Ajaokuta Steel Plant. Samples from Enugu, Okaba and Lafia coal deposits were extensively investigated and their results documented.

3.1 Coal chemical Composition (Coal Grade)

Coals are selected by grade, which takes cognizance of the chemical quality in respect of ash, sulphur, phosphorus, alkali and chloride contents.

In any chemical parameter of a particular coal exceeds limits specified at a coke plant, the coal may still be satisfactory for specific use if it is possible to formulate a blend with other coals or materials such that the final charge lies within the limits specified. It should be noted that alkalis cause coke breakdown, scabs and other operating problems in the blast furnace. Consequently, the alkali content in a coal charge for coke making is always kept as low as possible. It is restricted to a maximum of 1.95% in the case of Ajaokuta Steel Company Limited ⁽¹⁰⁾. Also chlorides pass into by –product section and require considerable water to remove from the tar recovered in the By-product plant. Because of its corrosive nature, chlorides also cause maintenance problems in the coal handling and coke oven plant

In April 1993, at Vukhim pilot plant Russia, a number of coals were used to compose coking coal blend for the operation of Ajaokuta Coke Oven Plant. Six coals from Australia, United State of America and Great Britain were subjected to a series of tests after which eight-charge variants were shot listed ⁽¹¹⁾ and also some time in 1993, direct blending test of imported and Enugu coal was carried out on a 250 Kg pilot Oven at NMDC, Jos.

3.2 Coal Blend Studies

Lafia and Enugu coals have been co-carbonized and also co-carbonized with a prime coking foreign coal – Ogmores coal from U.K. The effects of coking modifiers such as pitch have also been determined for the carbonization of Lafia and Enugu coals. Ashland A240 petroleum pitch was used. The resulting coke products were subjected to optical microscopy, micro strength tests and reactivity tests.

As present research conducted by NMDC, Jos, the state of test, research and development of relevant local materials and their preparedness for use in the steel industry was brought to the limelight. Apart from the fact that Lafia / Obi coals would be blended with other imported coals, the Atito Akpuneje coal (Nasarawa state) shows promising characteristics (Ash 14.9, Fixed carbon 53.5) ⁽¹²⁾

Improved quality of coke was produced at a pilot scale from blend of Okaba and an imported coal (Agro- allied, supplied by ASP 1993), employing the pre-heating coking improvement technique. The pre- heated blend between Agro- allied coal (medium coking) and 5% Okaba coal almost satisfy ASP's M10 ($\leq 9\%$ as against obtained value of 9.5%) and M40 ($\geq 78\%$ as against obtained value of 76.2%) requirements despite that Agro- allied low Free Swelling Index (FSI) of only 2.5 Consequently, primer coking coal with an FSI of 6, blended with Okaba coal and an additive of bitumen, would no doubt

result in far more than 5% Okaba blend in the imported coal.⁽¹³⁾

The execution of these would bring saving for the country to about \$632 million per year as estimated for use in the first phase of Ajaokuta Steel Company Limited. Other basic raw materials that are important to steel making which has drawn the attention of researchers in the metallurgical / metal based industries is clay.

4.0 REVIEW OF REFRACTORY CLAY AND DEPOSITS

Based on research carried out, where a pilot plant was designed to upgrade the products of a Nigeria industry based in Ukpok / Ozubulu belt (Anambra) and offshore, to determine and find out the requirements of refractory as needed in making iron and steel in terms of plasticity.

Among the clay, vast deposits of identified Kaolinite exist in Oza- Nogogo, Ukwuazu, Okhuo and Iguorasi (Edo state). Refractory clays have also been reported in abundance in Onibode and Oshiele (Ogun), Ogbete and Ekulu (Enugu) as well as Giru (Sokoto), Nsu (Imo) and Barkin Ladi (Plateau). High quality bricks clays occur in many parts of the country including Umuahia (Imo), Abeokuta (Ogun) and Abakaliki (Ebonyi).

A good number of studies were carried out on local clay deposit in Nigeria, the result-oriented showed that they satisfy the chemical and physical requirements for manufacture of refractory brick. Critical parameter with alumina (Al_2O_3) that ranges between 31.24 % and 38.50 % and their refractoriness are from 1660°C to 1750°C. However, initial investigation into Oza- Nogogo clay deposit show that it is plastic with Alumina content of 31.08% and a refractoriness of over 1600°C.

A laboratory test was carried on Jakura limestone and the result indicated that it has pure chemical composition of about 55% CaO and low silica value of 0.80%. The Osara dolomite which is about the best so far studied gave a 54.80% CaO, 42.82 MgO (Calcined) and a refractoriness of 1710°C.

Table 4: shows clay deposit in Nigeria

5.0 HARNESSING THE LOCAL RAW MATERIALS FOR ENGINEERING AND TECHNOLOGICAL

Two distinct patterns are readily identified from the few metallurgical research and development projects enumerated above. Firstly we notice that the bulk of result-oriented research and development projects are associated with the premier steel industry.

It is clearly indicative of an urge, perhaps borne out of necessity, to indigenize what is essentially an imported technology. It is for this reason that some of us have contended that no transfer of technology is possible which side tracks the 'Philosophical approach'. In ensuring that any imported technology process is adequately matched with 'indigenizing' research, development and raw materials sourcing in this present time a fundamental pattern, must be adopted which will drive the desire technology and development.

Secondly it must be admitted that most of the local result-oriented metallurgical research have been unduly restricted by infrastructure and definitely funds. Yet it has been demonstrated that a reasonable investment in research investment and development can bring rewarding returns and is in any case mandatory for speedy technological and economic empowerment and development.

The often-quoted rapid technological growth of Japan since World War II is a case in point. For instance, in 1973, Japan invested an equivalent of N1Billion (by first tier rate of N1= Y180.272) in technological research and development and 200 out of every 10000 Japanese was involved in research work, spending at an average rate of 40 %

per annum to sustain what we observe from as far as the Japanese feat.

The point being made here is that Nigeria should plan for accelerated economic empowerment and development program by deliberating encouraging research and development, since the steel industry is a spring determinant of our economic stability by way of producing the essential industrial raw materials, the funding of Metallurgical Research and Development must receive priority consideration.

From the National Metallurgical Development Centre (NMDC) Jos, Nigerian's point of view and experience, it is very obvious that a lot of result-oriented metallurgical research would be necessary to all metallurgical industries, like the Ajaokuta Steel Company Limited, Delta Steel company Limited and other related industries.

This will also assist to indigenize the imported technology as much as possible and therefore improve the chance of these metal-based industries for surviving.

6.0 SUGGESTIONS/ RECOMMENDATIONS

Finally, as a way of harnessing the local raw materials for engineering and technological development in Nigeria, it is suggested that metallurgical industries, stakeholders and government should do the followings:

(a) That now declare there should be a legal frame work to legalize the use of local raw materials by enforcing the local content principle.

(b) Funds should be made available to ensure that the huge profits made by selling scarce and essential commodities at inflated prices, should be made to contribute 15- 20% compulsorily to a Research and Development Fund (RDF).

(b) The Research and Development Fund should be organized along the lines of the Industrial Training Fund (ITF) and would help in the harnessing the local raw materials for the industries to increase their productivities at much reduced cost.

(c) Proper utilization of resources by research centres should be enforced by the Government with a view to harnessing the local raw materials in order to achieve optimal performance in engineering and technological development.

(d) The Government should consider establishing Research and Development centres in each Geo-political Zones in Nigeria, where newly graduated Nigerians could be involved in research and developmental works with a view to carrying out useful research works that will assist the nation to determine the quality and quantity of the locally available raw materials rather than allowing them to roam the street in search of employment.

(e) Government should encourage the participation of private investors in building centres and funding research works / programs with a view of identifying such local raw materials as could be used for engineering and technological development of our nation.

(f) Most of the metallurgical-based industries should make it as a point of duty to develop a data base centre where all the information generated could be used for industrial growth and development through the process of converting such raw materials for useful purposes.

(g) The Management of the steel industries and research centres should update and upgrade their equipment and pay more attention on how to harness those locally available raw materials for engineering activities.

(h) The concept and ideology of an industrialized nation like Nigeria, which has been based on the policy of import substitutions, needs must be reversed. Researches in the steel industry with the use of these locally sourced raw materials should be our major focus.

(i) An industrialized nation should not be structured in such a way that it has to depend on foreign raw materials, imported components, spare parts and expatriate skill for sustained engineering and technological development.

(j) To achieve the desirable object of substituting imported raw materials with locally sourced ones, a lot of funds will be spent on research and development.

(k) The Metallurgical Training Institute in Onitsha should be encouraged to develop a research centre, where findings from these works are documented and use same as aiding teaching tool for students.

(l) A Nation that wants to be self – reliant, self sufficient and strong economically should not build on mass importation of raw materials but rather source for these raw materials locally.

8.0 CONCLUSION

The economic impact of Research and Development (R&D) on local raw materials to develop the steel industry and later for expansion and improvement cannot be over-emphasized. As a security in case of international supply problems in the future, R&D on all types of relevant deposits has to be conducted continuously ahead of production.

Consequently, all the Metallurgical base industries requires adequate funding to provide consumables, replace obsolete equipment and other specialized equipment to facilitate aggressive research for determining the availability of local raw materials for engineering and technological development.

All institutions of learning , research centres should join in this crusade; they should therefore work in conjunction with the steel industries, so that they could jointly proffer solutions to importation problem of raw materials by harnessing those that are readily tested and certified good for engineering and technological development , expatriates skill and technology techniques needed for substituting them with locally sourced raw materials should be encouraged .

Finally, Today's neglect of harnessing the local raw materials is tomorrow's regret of engineering and technological breaks through, for Nigeria Government to meet up with the need of the industrial transformation in the face of this current economy crisis and to realize the aims and objectives of establishing the steel and materials development , we must therefore join hand to set up all the necessary machineries to ensure that the local raw materials are harnessed

for the growth and development of engineering and technological transformation in our country Nigeria.

The only way out of this quagmire is to have effective policy and legislative laws that will enforce the principle and practice associated to harnessing the local raw materials for development there by overcoming the effect of materials and steel development at the epileptic status in Nigeria.

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Table: 1 Coal Reserves And Resources in Nigeria

State	Location	Indicated in Site Reserve Million T	Inferred Resources Million T	Overall Resources Million T
Benue	Orukpa Okaba Ogboyoga	57	73	
		73	250	
		107	320	
Delta	Asaba (lignite)	250	Unknown	
Enugu	Enugu Area Ezimo	54	200	
		56	60	
Plateau	Inyi Lafia – Obi (Coking Coal)	20	Unknown	
		15	Unknown	

Source form: Selection of coals for Making High Quality Metallurgical Coke at Ajaokuta

Table 2: Results of Proximate Analysis and coking Properties Determination of Nigerian coals

S/N	Origin of the Coal Sample	Proximate Analysis				Sulphur slot a.d	Crusible Swelling Numble (CSN)	Gray King Coke type
		Mad	Aad	Vad	Vdat			
1	Enugu (washed)	8.2	12.54	34.5	42.5	0.7	0	A
2	Onyema	3.4	13.80	40.40	48.9	0.5	0	A
3	Okaba	9.4	11.60	35.30	44.70	0.50	0	A
4	Akpunuje	8.5	7.0	26.90	31.90	0.60	0	A
5	Lafia (original)	1.5	25.60	22.60	32.20	2.30	6	G
6	Lafia after beneficiation H.M.S. of 1.4g/CM ³	1.6	11.30	22.10	30.0	Sulphur intact	8	G3

Note: ad – as determined, daf – dried ash free, tot – total

SOURCE FROM: The Development of Steel Industry from Nigerian Raw Materials

Table 3: Petrographic Composition of Nigerian Coals

(V – Vitrinite, E – Exinite, M – Micrinite, F – Fusinite, MS – Mineral Substance)

Coal Sample	Maceral Analysis					Maceral Composition
	V	E	M	F	MS	
Enugu	58.6	18.1	1.0	16	5.7	Vitrinite: Collinite Exinite: Spores and cuticles Fascinate: 50% F + 50 % SF Pyrite in mineral substance
Okaba	55.5	19.5	1.5	18.5	5.0	Vitrinite: Collinite and telinite Exinite: Spores and cuticles Fusinite: Fusinite and semi-Fusinite, Scleronite
Lafia	47.5	25.0	1.0	7.5	19	Vitrinite: Collinite Exinite: Spores, cuticles, Low-Reflectance. Fusinite: Fusinite (60%) and Semi-fusinitie (40%) Pyrite in mineral sub-Stance

Note: The Leitz photometer then used is now broken down and obsolete.

SOURCE FROM: The Development of Steel Industry from Nigerian Raw Materials

Table 4 DATA BANK ON SOME CLAY DEPOSITS IN NIGERIA

S/N	DEPOSIT	CHEMICAL COMPOSITION (%)								PHYSICAL PROPERTIES	
		Al ₂ O ₃	SiO ₂	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	L.O.I	Plasticity Index	Refractoriness
1	GIRU (Kebbi State)	38.50	43.63	0.67	0.02	0.10	0.03	0.04	14.16	0.42	1750
2	KANKARA (Katsina State)	36.40	46.48	1.09	0.79	0.87	0.08	0.10	14.31	3.19	1700
3	NSU (Imo State)	31.24	49.57	1.72	0.61	0.43	0.06	0.09	11.79	6.03	1710
4	KWI (Plateau State)	31.69	37.63	14.48	0.025	0.12	0.06	0.12	12.40	0.68	1660
5	ONIBODE (Ogun State)	35.00	48.00	1.70	0.2	0.3	0.12	0.05	13.1	6.5	1730
6	OZUBULU (Anambra State)	34.10	47.21	1.85	0.61	0.48	0.07	0.12	11.03	5.71	1727

SOURCE FROM: The Development of Steel Industry from Nigerian Raw Materials

MULTISTAGE ALKALINE LEACHING DE-MINERALIZATION OF A MEDIUM COAKING COAL

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Abstract

Coal is a fossil fuel created from the remains of plants that lived and died about 100 to 400 million years ago when parts of the Earth were covered with huge swampy forests. Coke is produced from high grade coking coal which must have ash and sulphur content below 12% and 0.8% respectively. Nigerian Chikila coal was collected at a depth of about 4.5 m, air dried, crushed and pulverised. Fractions of -425+300 μm and -75 μm were preliminary leached with KOH, NaOH, Na_2CO_3 and NH_4OH . Based on result, NH_4OH was selected for comprehensive leaching of the coal using 2^4 factorial variables combination. Multistage leaching was carried out. Analyses using UV spectrophotometer and particle induced X-ray emission (PIXE) were done for the filtrates and coal concentrate obtained respectively. The as-received sample gave proximate analysis of 4.70 % moisture, 42.12 % volatile matter, 12.60 % ash, 1.68 % sulphur and 40.58 % fixed carbon. The multistage leaching of -425+300 μm fraction using H_2O - NH_4OH - H_2O sequence produced a coal concentrate with 3.96 % moisture, 36.63 % volatile matter, 8.79 % ash, 1.11 % sulphur and 49.51 % fixed carbon. The alkaline leaching resulted in a decrease of 30.23 % in ash, 33.93 % in sulphur and 13.03 % volatile matter. Also an increase in carbon content of 22.01 %. A successful upgrade of the leaching to pilot scale will make the coal available as a blend component for economical industrial cokemaking.

Keywords: Alkaline, Coking, coal, leaching, multistage, concentrate

1.0 INTRODUCTION

Coal is classified as a non-renewable energy source because it takes millions of years to form. Coal usually contains significant quantities (normally more than 10%) of different impurities such as sulphur, silicates, carbonates and many others (Bolat *et al.*, 1998). The coal reserves of Nigeria are estimated at 2.75 billion tonnes, with occurrences spreading over 13 states of the country (Fatoye and Gideon, 2013). Chikila coal is located in Guyuk Local Government area of Adamawa state and the reserve is not yet determined Adeleke *et al.*, (2007). The world is in short supply of Prime grade coking coal. Hence, there is a need to upgrade low grade coals by reducing their ash and sulphur contents. Physical, chemical and biological methods are used to upgrade coals with low ash, low sulphur and improved thermoplastic properties. The chemical leaching methods which include molten caustic leaching, agitation caustic leaching and mineral acid leaching have been successfully applied to coals (Adeleke *et al.*, 2013). It has been established that mineral acids are effective leaching agents for ions of ash constituents found in coal. These ions include Ca^{2+} , Fe^{3+} , K^+ , Mg^{2+} , Na^+ , Al^{3+} and Mn^{2+} (Neupane and Donahoe, 2013)

The aim of this study is to evaluate the multistage leaching process of the high ash and high sulphur medium caking Chikila coal at normal atmospheric pressure.

2.0 MATERIALS AND METHODS

2.1 Materials

2.1.1 Sample Collection

Chikila coal Samples from Guyuk local government in Adamawa state, Nigeria was used for this research. Two tons of the coal was collected by the National Metallurgical

Development Centre (NMDC) Jos, at a depth of about 4.5 m. About 8.6 kg was obtained from the bulk sample and 4 kg of these was used for the work.

2.1.2 Sample preparation

The coal was air dried, crushed and 4 kg sample was pulverized using Pascal Engineering 18862 primary crusher to obtain the experimental samples. A representative quantity of 500 g sample of the coal was taken by coning and quartering method, which was prepared for sieve analysis.

2.2 Methods

2.2.1 Experimental design

Preliminary leaching was carried out on the coal samples using the selected aqueous alkaline solutions. This enabled the selection of the alkaline that was most suitable to leach the coal sample. This preliminary leaching test was done using the high levels of the variables, which are; -425+300 μm size sample, 75 min leaching time, 90°C temperature and 1 molar concentration of each of the acid and alkaline selected for the leaching.

The single stage leaching was conducted using 2^4 factorial design. The experimental variables were; alkaline concentration (denoted by C), time of leaching (denoted by t), temperature of leaching (denoted by T) and coal particle size (denoted by S). The basis of the experimental design was that each of the four variables was used at 'high' levels (denoted by H) and 'low' level (denoted by L). The experimental variables are used as subscript as either low (L) or high (H). The number of experiment in the design was 2^4 (i.e. 16). Using the above nomenclature, the various interacting combination among the variable used in the design were;

$L_T L_C L_t L_s$ (I) $H_T L_C L_t L_s$ (II) $L_T H_C L_t L_s$ (III) $H_T H_C L_t L_s$ (IV)
 $L_T L_C H_t L_s$ (V) $H_T L_C H_t L_s$ (VI) $L_T H_C H_t L_s$ (VII) $H_T H_C H_t L_s$ (VIII)
 $L_T L_C L_t H_s$ (IX) $H_T L_C L_t H_s$ (X) $L_T H_C L_t H_s$ (XI) $H_T H_C L_t H_s$ (XII)
 $L_T L_C H_t H_s$ (XIII) $H_T L_C H_t H_s$ (XIV) $L_T H_C H_t H_s$ (XV) $H_T H_C H_t H_s$ (XVI)
 The values used for each variables at low and high level is presented in Table 1.

Table1: High and low variables

Levels	Temperature (T, °C)	Concentration (C, M)	Time (t, Min)	Particle Size (S, μm)
Low	30	0.2	20	-75 μM
High	90	1	75	-425 +300

2.2.2 Proximate analysis

Proximate analysis was done to determine the percentage by weight of the Fixed Carbon, Volatiles matter, Ash, and Moisture Content in the coal using modified forms of methods described in ASTM D 3175-89 and Francis and Peters (1980).

2.2.3 Single stage leaching

Preliminary leaching was carried out on the coal samples using potassium hydroxide, sodium hydroxide, ammonium hydroxide and sodium carbonate. About 1 g of -425+300 μm coal fraction was weighed into a 250 ml beaker containing 30 ml of 1 molar solution of potassium hydroxide and carefully homogenized by stirring for about Two minutes. The slurry was then placed in a Gallenkamp 7B 16590 oven maintained at 90 °C for 75 min. The leached slurry was filtered into a conical flask using a XingXing filter paper. The residue was collected, oven dried at about 80°C and then re-weighed. The difference in weight was noted for determining the fraction of coal that has been dissolved. This procedure was repeated for sodium hydroxide, ammonium hydroxide and sodium carbonate. The ammonium hydroxide gave the highest weight loss and was then selected and used for the 2⁴ factorial single stage leaching. The single stage leaching was carried out following the design given in section 2.2.1 and the levels in Table 1. The first leaching involved L_T L_c L_s. 1 g of the -75 μm fraction was leached and filtered as described for potassium hydroxide in the preliminary leaching stage but with 0.2 M NH₄OH at 30 °C for 20 min and in duplicates. The procedure was again repeated for other experimental designs in section 2.2.1.

2.2.4 Multistage leaching

The three-stage multistage leaching was carried out in three sequences that involved alkaline and water, that is: NH₄OH-H₂O -H₂O, H₂O- NH₄OH -H₂O and H₂O-H₂O- NH₄OH. The first stage leaching and filtration in the NH₄OH -H₂O-H₂O sequence was carried out as in the preliminary leaching stage using 1 M NH₄OH for the 1 g -425+300 μm fraction sample at 30 °C in 75 minutes contact time. The procedure was repeated on the residue concentrate obtained using H₂O. The latter water cleaning stage was again repeated as the third stage of the NH₄OH -H₂O-H₂O sequence. The other two sequences were carried out following the description above but in order H₂O-NH₄OH -H₂O and H₂O - H₂O - NH₄OH. The sequence that gave the highest weight loss was noted. The filtrate and dried leached coal from this stage were taken for spectrophotometry and PIXE analysis.

2.2.5 UV Spectrophotometric analysis

The selected filtrates obtained were analyzed for sulphur using a UV-visible spectrophotometer (CECIL model no CE2502 2000 series). The calibration samples were prepared and the quartz cuvettes were rinsed with deionized water several times. 3 ml of sample were placed into cuvette using a pipette. The cuvette was wiped with very fine paper to remove any water droplets or dust and was then placed into the spectrophotometer and reading was taken (Woolins, 2010).

2.2.7 Particle induced X-ray emission analysis

The best multistage leached and as-received coal samples were subjected to particle induced X-ray emission analysis using 1.7MV Pelletron Tandem Accelerator model 5SDH, for sulphur. For each case, about 100 mg of the sample was ground into fine powder using a mortar and pestle. The powder was

then compacted to 29-mm diameter pellets using hydraulic press equipped with a case-hardened stainless steel die at 130 atm for 1 minute. Binding agent was added to the powder before pressing to make the pellet durable. The pellet was then mounted directly onto the target frame for irradiation. The X-ray spectrum was initiated by irradiating sample with a proton beam produced from pure Hydrogen by, in this case, 1.7 MeV protons. The readings were shown on the display unit and printed.

3.0 RESULTS AND DISCUSSION

3.1 Proximate Analysis of Chikila Coal

The proximate analysis of the coal is shown in Figure 1. The moisture content in the as-received sample is 4.70%. This value of moisture content is high and would result in a decreased plant capacity and an increase in operating costs with consequent decrease in the calorific value of the coal Jauro *et al.*, (2008). However, the best leached sample gave a lower moisture content of 3.96 % indicating an improvement in the coal. But when compared to the moisture content required for good coking coal which is 1.5 %, the moisture content value is still high (Obaje, 1997). The required moisture content of coal to be used for metallurgical cokemaking is however expected to be between 1 % and 6 % Leonard *et al.*, (1996). This shows that Chikila coal can still be used for metallurgical cokemaking. High and variable moisture contents affect both the coke rate and the balances within the blast furnace Leonard *et al.*, (1996).

The volatile matter present in the as-received sample is 42.12 %. This implies that there is high presence of methane, hydrocarbons, hydrogen, carbon monoxide and incombustible gases like carbon dioxide and nitrogen in the coal. The effect of this high value of volatile matter includes among others, proportionately increase in flame length and easier ignition of coal Khan *et al.*,

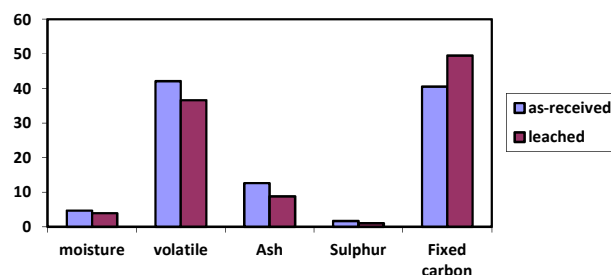


Fig. 1: Proximate analysis of Chikila Coal (as-received and as-leached multistage)

(2003). However, the best leached sample gave a lower volatile matter content of 36.63 %. The reduction suggests that the volume originally occupied by volatile matter has been replaced by carbon thereby increasing the carbon content. The increase in carbon content is an indication of improvement in the coal quality. This is because it is a significant constituent of the coal required for coke making Adeleke *et al.*, (2013). The Figure also shows the ash content of the as-received coal to be about 12.60%, which exceeds the allowable limit of 12% for coals to be carbonized to produce metallurgical grade coke Leonard *et al.*, (1996). The coke ash is a nonproductive part of coke which increases slag volume and increase heat energy input for ironmaking. Industrial experience indicates that a 1 wt. % increase of ash in the coke reduces metal production by 2 or 3 wt. %. Ash content values higher than 10 wt. % can be satisfactory but only if the ash chemistry is acceptable Leonard *et al.*, (1996). Other implications of high ash content in Chikila coal include reduction in handling and burning capacity,

increase in handling costs, reduction in combustion and boiler efficiency, clinking and excessive slagging (Poos, 1992). However, the best leached coal sample was found to have an ash content of 8.79 % making it suitable for appreciable inclusion in blends for cokemaking.

The as-received sample of Chikila coal has a fixed carbon of 40.58 %. The fixed carbon content of coal is used as an indication of the yield of coke in a coking system. The 40.58 % value of fixed carbon content in Chikila coal shows that the as-received sample of the coal will not yield a good coke because the value is very low Nasirudeen and Jauro, (2011). However, the best leached sample has a higher fixed carbon content of 49.51 %. This shows that the leaching has brought a significant increase to the fixed carbon content of the coal. The fixed carbon content of the leached Chikila coal is however lower than that of leached Lafia-Obi coal which is about 60% Adeleke *et al.*, (2011).

3.2 Single Stage Leaching of Chikila Coal Using 2⁴ Factorial

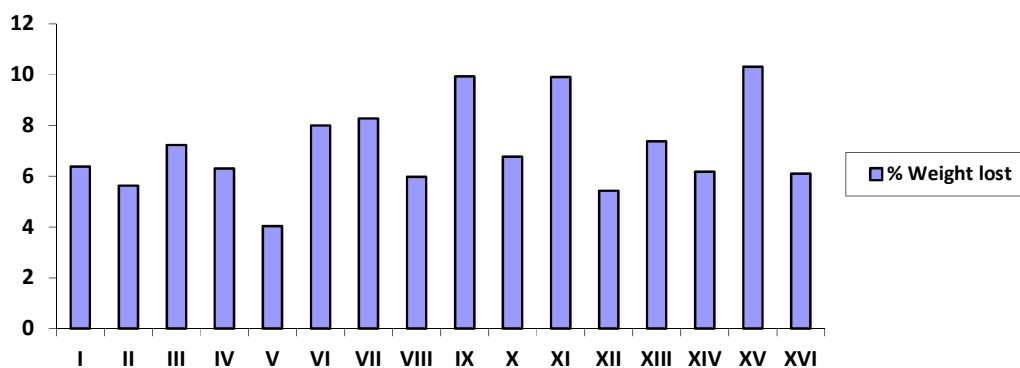


Fig. 2: Chikila coal single stage leaching using ammonium hydroxide

3.3 Multistage Leaching

Results obtained from multistage leaching are presented in Figure 3. The best yield for the multistage leaching was obtained with the combination of water and alkaline in the order; water-alkaline-water. The result shows that 12.63 % of the coal was leached out when the sequence was in the order H₂O-NH₄OH-H₂O (W-A-W). This gives the greatest yield for the entire multistage leaching and single stage leaching. This observation agrees with the conclusion of Adeleke *et al.* (2011; 2013) that the H₂O-Na₂CO₃-H₂O leaching sequence gave higher ash and sulphur reductions in Lafia-Obi coal than the Na₂CO₃-H₂O-H₂O leaching sequence.

The reason for the higher leaching potency of the H₂O-NH₄OH-H₂O sequence may be because in the route, the preliminary water washing might have prepared the coal matrix for the subsequent alkaline leaching, making it more efficient and the last water washing might have helped in dissolving some of the soluble product of the alkaline leaching. Dilute alkaline leaching has been shown to be an efficient method Wu *et al.*, (2011). The multistage leaching thus gave a much higher weight loss than the 10.30% obtained for the alkaline single stage leaching.

The results obtained from 2⁴ Factorial single stage leaching with variables as prepared in section 2.2.1 is presented in Figure 2. It is observed that the highest weight loss of 10.30 % was obtained when the leaching temperature is low, 30 °C, the molar concentration of alkaline is high, 1 molar, the particle size of coal is high, -425+300 µm and the leaching time is high, 75 min. This shows that alkaline leaching has the greatest effect on Chikila coal when it is done at high alkaline concentration, low temperature and a relatively coarse particle size of coal. The leaching was more potent at low concentration of alkaline because at low concentration of alkaline, few OH⁻ was required to be available at the reaction surface with the oxides. Furthermore, the low temperature of 30 °C was enough to give the required kinetics for the leaching process. The best leaching yield was obtained with a particle size of -425+300 µm. This is a relatively coarse particle size and the surface area available for the leaching reaction is optimum at this level. The explanation for this is that as the particle size decreases, the surface area of coal increases and the reaction rate definitely increases Seferinoglu *et al.*, (2003).

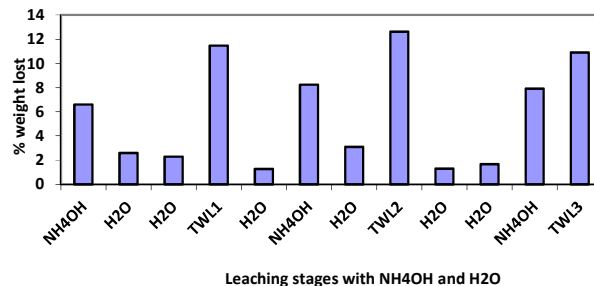


Fig. 3: Multistage leaching using NH₄OH and H₂O in various sequences (TWL1, TWL2 and TWL3 are total weight loss for sequences 1,2 And 3 respectively).

3.4 Filtrate spectrophotometry analysis

The spectrophotometry analysis of the filtrates carried out for sulphur and presented in Table 3, indicates that the filtrate obtained from the multistage leaching process that involves H₂O – NH₄OH – H₂O, contains highest amount of sulphur which is measured as 0.04 mg/g. This is considerably large in comparison to the ones obtained for other leachings presented in the table. This indicates that more sulphur was leached out of the coal through the multistage leaching of using the water-alkaline-water order of leaching.

Table 2: Filtrate spectrophotometry analysis

Sample	Sulphur conc. in milligram per gram of coal (mg/g)
Best NH ₄ OH leached, Single Stage	0.010
H ₂ O – NH ₄ OH – H ₂ O	0.036
H ₂ O – H ₂ O – NH ₄ OH	0.032
NH ₄ OH - H ₂ O – H ₂ O	0.027

3.6 Particle induced x-ray emission (PIXE) analysis

The results obtained from the PIXE analysis of the as-received coal sample and the water-alkaline-water leached coal sample

Table 3: Concentration of relevant elements in the as-received Chikila coal sample

Elements	As-Received (mg/g)	(%)	H ₂ O-NH ₄ OH-H ₂ O (mg/g)	(%)	% Change
Sulphur (S)	16.80	1.68	11.14	1.11	33.93
Sodium (Na)	3.71	0.37	2.62	0.26	29.73
Magnesium(Mg)	6.78	0.67	3.56	0.36	46.27
Silicon (Si)	77.08	7.70	74.31	7.43	38.57
Potassium (K)	2.89	0.29	2.21	0.22	24.14
Calcium (Ca)	8.62	0.86	3.87	0.39	54.65
Iron (Fe)	9.07	0.91	8.13	0.81	10.99
Titanium (Ti)	1.81	0.18	0.67	0.07	61.11

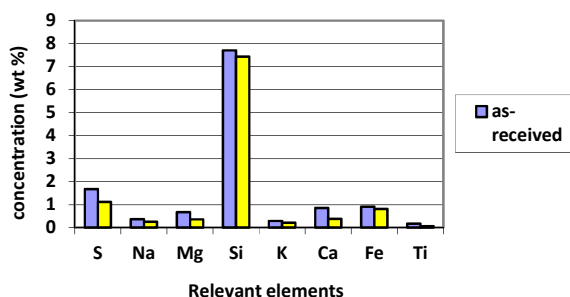


Fig.4: Graphical view of the concentration of relevant elements in the as-received and as-leached coal sample.

4.0 CONCLUSIONS

The sulphur contents of the fractions of Chikila coal -425+300 µm were successfully reduced by multistage alkaline leaching that involved the use of NH₄OH of 1 molar concentration and water. Reduction obtained for sulphur content from 1.68 % to 1.11 % is very significant and it indicates that Chikila coal, can be used as a blend with coal of prime grade coals with low ash and sulphur content for cost effective metallurgical cokemaking.

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(Table 3) when compared indicate that the sulphur content of the coal has been reduced from 1.68 % to 1.12 %, this shows that using multistage leaching method, ammonium hydroxide is an effective reagent that is capable of leaching sulphur out of Chikila coal. Furthermore, the concentration of selected metals whose oxides are the major ash constituents present in the coal samples has been reduced. The extent of their reduction is show in figure 4. These metals constituent in the coal were reduced because some of their oxides were able to dissolve in water and in the NH₄OH used for the leaching.

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*AWODI, ENE AND GIWA, ABDULRAHEEM

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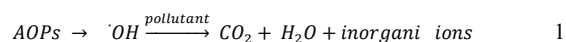
Colour elimination from textile wastewater has turn out to be a major scientific interest as indicated by the massive amount of related research reports. This article look at a range of Advanced Oxidation Processes (AOP) that are capable of decolorizing textile wastewater. It also discusses the mechanism, efficiency and the economics involved in both the pilot plant and the bench scale system. This is intended to assist textile industries and wastewater engineers in evaluating the applicability of AOP and also in selecting one or more process (es) for implementation.

Keywords: Advanced Oxidation Processes, wastewater, textile industries,

1. Introduction

The removal or destruction of toxic and refractory pollutants should be handled by non-biological technologies because the use of conventional textile wastewater treatment processes has become a big challenge with increasing restrictions on effluent quality by water authorities, so conventional treatment such as biological treatment discharges will no longer be tolerated as 53% of 87 colours are identified as non-biodegradable. Advanced oxidation processes hold great promise to provide alternative for better treatment and protection of environment. A large amount of sludge is produced which is very difficult to manage and there will be need for further treatment before ultimate disposal. These AOP technologies entails majorly of conventional phase separation systems such as adsorption

processes, microfiltration etc, or systems that destroy the contaminants (chemical oxidation or reduction). Chemical oxidation is aimed at the mineralization of the contaminants into carbon dioxide, water and inorganics. An example is shown below:



These advanced oxidation processes can be classified either as homogeneous or heterogeneous. Homogeneous processes can be further subdivided into processes that use energy and processes that do not use energy (Fig. 1).

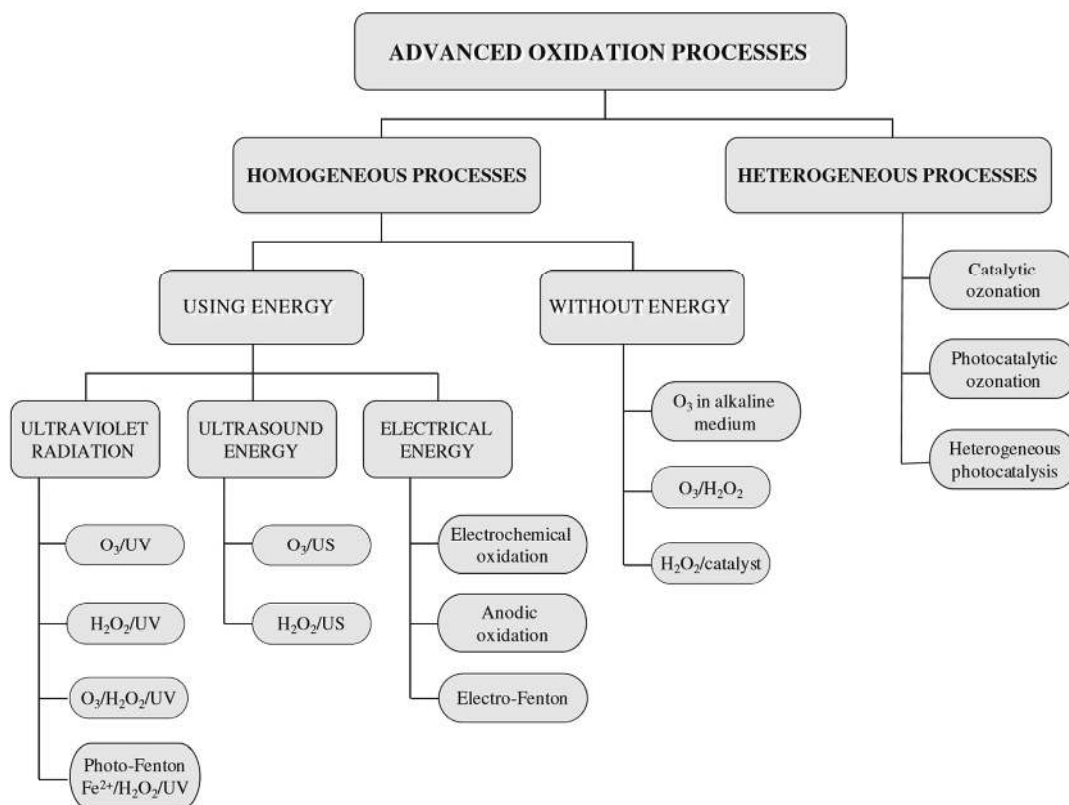


Figure 1: Broad Advance Oxidation Processes Classification

Methods based on chemical destruction, when properly developed, provide complete pollutant abatement, whereas those that only perform phase separation leave a consequent problem of final disposal. Much research has addressed this aim over the past decade highlighting the prominent role of a special class of oxidation techniques defined as advanced

oxidation processes (AOP), which usually operate at or near ambient temperature and pressure.

AOP, while making use of different reaction systems, are all characterized by the same chemical feature: production of OH• radicals (OH•). Production of hydroxyl radicals can be

achieved through homogeneous photochemical reactions (UV-irradiated H_2O_2), or alternatively by the well-known photocatalytic mechanism that occurs on the surface of semiconductors like TiO_2 (Silver et al., 2004; Stepnowski and Zaleska 2004).

The TiO_2 /UV-vis system has been widely studied, being noteworthy its application in the treatment of tannery wastewater (Schrack et al., 2004). Photochemical oxidation by the H_2O_2 /UV-vis process has also been successfully used (Legrini et al., 1993; Betran et al., 1997), but in this case formation of $HO\bullet$ species is due to dissociation of the H_2O_2 molecule. On the other hand, the combined H_2O_2 / TiO_2 /UV-vis process has given good results in the photo degradation of several non- biodegradable organic compounds Mazzarino et al., 1999; Chen and Ray, 1998).

In photo catalytic oxidation, oxygen is the most common electron acceptor and it is relatively efficient, but aiming at further inhibiting the electron-hole recombination effect, several studies have investigated the role of hydrogen peroxide as an alternative electron acceptor, because the potential for H_2O_2 reduction (0.72 V) is higher than that for oxygen (-0.13 V) reduction.

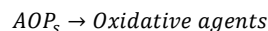
Hydrogen peroxide can present beneficial or detrimental effects on the photo catalytic degradation of organic contaminants. However, most photo catalytic studies on the effect of hydrogen peroxide have reported an optimal concentration that is dependent on the characteristics of the wastewater (type and concentration of organic compounds, pH, presence and type of inorganic ions), the concentration of oxygen in the solution, the intensity and wavelength of the UV light, the desirable extent of treatment and the cost of hydrogen peroxide. Thus, the hydrogen peroxide concentration should be optimized for each kind of wastewater.

In this article we looked at a range of Advanced Oxidation Processes (AOP) that are in use and capable of decolorizing textile wastewater. We also discussed the mechanism, efficiency and the economics involved so that it can assist textile industries and wastewater engineers in evaluating the applicability of one or more AOPs for implementation.

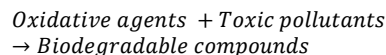
AOP Mechanism

Advanced *oxidation* involves several *steps* schematized in the figure below and explained as follows:

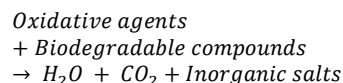
1. The formation of strong oxidants e.g. hydroxyl radicals.



2. Reaction of these oxidants with organic compounds in the water producing *biodegradable* intermediates.



3. Reaction of *biodegradable* intermediates with oxidants referred to as mineralisation (i.e. production of water, carbon dioxide and inorganic salts).



AOP TECHNOLOGIES

The following sections describe a wide range of advanced oxidation systems that are currently being studied for their possible use in wastewater treatment.

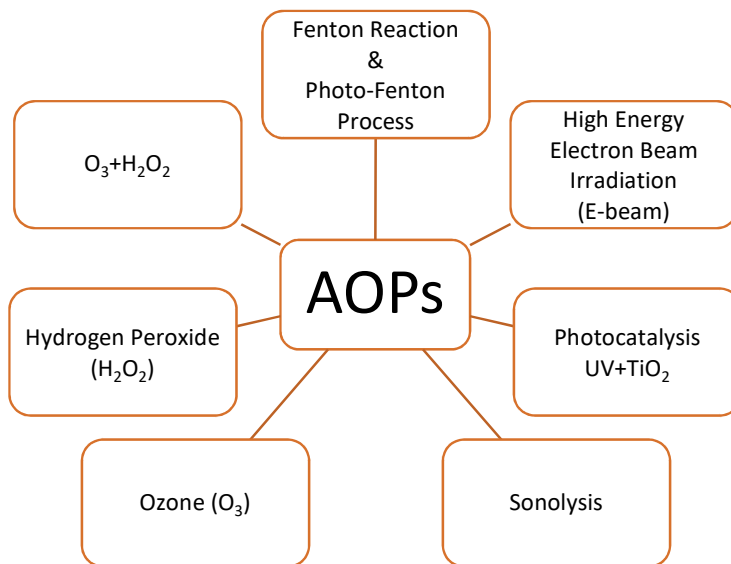


Figure 2: Basic Advanced Oxidation Processes

HYDROGEN PEROXIDE/OZONE

When H_2O_2/O_3 are simultaneously introduced to water, they react to form hydroxyl radicals which in turn oxidize most dissolved organic matter to form by-products. Oxidization of the textile wastewater with hydrogen peroxide alone has been found ineffective at both acid and alkali values. It was documented that H_2O_2 /UV process was more effective in an

acid medium (pH≈3-4) in term of discolouration. Non-efficient colour removal at alkaline pH is attributed to the fact that hydrogen peroxide undergoes decomposition leading to dioxygen and water, rather than producing hydroxyl radicals under UV radiation. Therefore the instantaneous concentration in $HO\bullet$ is lower than expected. Furthermore, the H_2O_2 /UV process is more sensitive to the scavenging effect of carbonate

at higher pH values, note also that temperature have no significant effect on decolourization. High concentration of the H_2O_2 acts as a radical scavenger, while; low concentration of H_2O_2 generates not enough of hydroxyl radicals ($OH\bullet$) that consumed by dye and this leads slow rate of oxidation. Thus a trade-off between them will result in an optimum H_2O_2 dose, which still needs to be verified experimentally. Ozone application can be generalized into two; a powerful disinfection and a strong oxidant to remove colour and odors, eliminating trace toxic synthetic organic compounds and assisting in coagulation (Langlais et al., 1991). According to previous studies, ozonation alone increased the biodegradability index of textile wastewater by about 1.6 times but in conjunction with hydrogen peroxide, it gets better. The type and concentration of the dyes also matter. A few researchers revealed that ozone decolorize all dyes, except non-soluble disperse and vat dyes which react slowly and take longer time (Namboodri et al., 1994). Higher initial dye concentration of textile wastewater causes more ozone consumption. Increasing ozone concentration enhances mass transfer that causes an increase in ozone concentration in liquid phase, which increase colour removal. (Adedl et al, 2005). Once dissolved in water, ozone reacts with a great number of organic compounds in two different ways: by direct oxidation as molecular ozone or by indirect reaction through formation of secondary oxidants like hydroxyl radical. The relationship between UV light intensity and dye decomposition in UV/ H_2O_2 process has been investigated by Shen and Wang (2002). The decomposition rate of dye was found to increase with increasing UV light intensity. This process has an advantage of been able to disinfect the water to be treated because of the ozone present and it is an established technology which have been used on industrial scale. Some of its disadvantages includes the fact that the treatment of excess hydrogen peroxide has to be treated due to potential for microbial growth also an ozone off-gas treatment and or permission would be needed due to its toxicity and the pH needs to be carefully monitored.

OZONE/UV

Hydroxyl radicals are generated when low pressure UV light is applied to ozonated water. Destruction of organic compounds occur by hydroxyl radical reaction, coupled with direct photolysis and oxidation by molecular ozone. According to Adel (2005), conventional ozonation of organic compounds alone does not completely oxidize organics to CO_2 and H_2O in many cases. Remaining intermediate products in some solution after oxidation may be as toxic as or even more toxic than initial compound and UV radiation could complete the oxidation reaction by supplement the reaction with it since the O_3 /UV process makes use of UV photons to activate ozone molecules, thereby facilitating the formation of hydroxyl radicals. The lamp must have a maximum radiation output of 254nm for an efficient ozone photolysis.

The O_3 /UV process is more effective when the compounds of interest can be degraded through the absorption of the UV irradiation as well as through the reaction with hydroxyl radicals. Again, one of the advantages here is the supplemental disinfectant, it is more effective compared to using ultraviolet or ozone alone, it is more efficient in generating hydroxyl radicals than H_2O_2 /UV for equal oxidant concentration.

Its disadvantages are that of energy and cost intensive, turbidity can interfere with UV penetration, ozone diffusion can result in mass transfer limitation, ozone off-gas treating and or permitting will be required, interfering compounds such as nitrates can absorb the UV light and UV lamp failure can cause contamination of the water with mercury.

HYDROGEN PEROXIDE/ULTRAVIOLET

Here, the hydroxyl radical route is the predominant removal mechanism. For hydrogen peroxide, a greater amount of hydroxyl radicals are produced when mercury lamps are used compared to other UV light sources.

The advantages of this process are when mercury lamp is used with pulsed UV irradiation can serve as a disinfectant, a full scale drinking water treatment system exists (e.g. in Salt Lake City UT), no off-gas treatment is required and it's not limited by mass transfer relative to O_3 process.

Some disadvantages include that turbidity can interfere with UV light penetration, less stoichiometrically efficient at generating hydroxyl radical than O_3 /UV process and interfering compound e.g. nitrates can absorb UV light.

HIGH ENERGY ELECTRON BEAM

Here electrons interact with water molecules and produce intermediates such as hydroxyl radical, hydrated electrons and hydrogen atoms which in turn react with the organic compounds.

Few of the advantages are minimal organic by-product formation, it can supplement the disinfection process, turbidity has minimal effect on the process and no off-gas treatment is required.

Disadvantages are no full scale implementation exists yet, it is energy intensive and its cost is not fully evaluated yet and this process required fully trained operators and this would definitely increase cost.

SONICATION/HYDRODYNAMIC CAVITATION

Includes the formation of cavitation micro bubbles which implode after reaching critical resonance size and generate high temperature and highly reactive radicals. Removal of organic pollutants occurs by thermal decomposition at bubble water interface and by reaction with radicals. Oxidation by cavitation is enhanced by O_3 or H_2O_2 .

Advantages are that the design and set up is simple so it has minimal set up and maintenance cost, it has less heat transfer compared to UV process and no off-gas treatment is needed.

The disadvantage is that there has been no full scale application and some O_3 or H_2O_2 may be required to reach target removal efficiency.

TiO_2 CATALYZED UV OXIDATION

When TiO_2 is illuminated by UV light, valence electrons are excited to the conduction band resulting in formation of holes, these holes react with water molecules to produce hydroxyl and other radicals which now break down the pollutants. It can perform at a higher wavelength than other processes (300-380nm).

It has no full scale application yet, pre-treatment is required to avoid fouling of TiO_2 catalyst, if the catalyst was added as a slurry, the filtration process is needed, rapid loss of catalyst, the reaction is highly pH dependent and so must be properly monitored and controlled.

PHOTO FENTON AND FENTON'S REACTION

Here, when Fe^{2+} react with H_2O_2 to produce hydroxyl radical (with UV light source for photo-Fenton process). Iron acts as a catalyst. Oxidation by Fenton's reagent is most effective under acidic pH (2-4), and it becomes ineffective under moderately to strongly alkaline conditions. In addition to the oxidation, the ferric ions generated during the oxidation stage, promote the

removal of other pollutants by coagulation and sedimentation. It's not energy intensive as compared with other AOP process, but the increasing quality of sludge, and the additional water pollution caused by the homogeneous catalyst that are added as an iron salt are its major disadvantage. So, many attempts have been made to enhance the efficiency based on Fenton process. Photo-Fenton process was used and the result showed that the production of hydroxyl radical increased and percentage mineralization was also increased. It is fast and no off-gas treatment is required, but it requires an iron extraction system, very low pH is required to keep the iron in the solution and this will increase operation and maintenance cost.

General Advantages of Advanced Oxidation Technology

- Rapid reaction rates
- Small foot print
- Potential to reduce toxicity of organic compounds
- Mineralization of organics, i.e. conversion to salt and CO₂
- Does not concentrate waste for further treatment, such as membranes
- Does not produce "spent carbon" such as activated carbon absorption
- Easily Automated and Controlled
- Reduced Labor Input
- Does not create sludge as with physical chemical process or biological processes (wasted biological sludge)

General Disadvantages of Advanced Oxidation Technology

- Capital Intensive
- Complex chemistry must be tailored to specific application
- For some applications quenching of excess peroxide is required

The selection of a specific advanced oxidation process is application dependent. It is expected to evaluate each application critically to see which AOP fits best based on the type of compounds to be removed, treatment objectives, concentrations, site considerations, budget, etc.

Strategies to Implement AOPs

Comninellis et al. 2008 estimated that the costs of AOPs are relatively high and directly related to the efficiency and operational time of the processes. It is therefore worth optimising implementation of AOPs at the right place to limit costs. Several strategies were found to achieve this:

- Simultaneous application of different AOPs promotes the rates of *organics oxidation*. Typical examples include *UV/H₂O₂*, *UV/H₂O₂/TiO₂*, *UV/Fenton* and *Ultrasound/UV/TiO₂*, among others. These types of combinations may lead to synergetic effects when treatment efficiencies are greater than the sum of efficiencies that could be achieved by the individual treatments alone.
- Sequential application of various AOPs can treat *effluents* containing a mixture of *organics*. This approach is useful when the compounds in the mixture present different levels of reactivity towards different AOPs.
- Application of separation treatment prior to AOP treatment to transfer pollutants to another phase so that they can be treated more easily. Such separation treatment includes *stripping*, *coagulation-flocculation*, *sedimentation*, *filtration*, *adsorption* etc.
- AOPs can be applied in *pre-treatment* stage to enhance biodegradability and to reduce toxicity followed by

biological *post-treatment*. This approach is based on the fact that *biological treatment* is perhaps less costly and more environmentally friendly than other destructive treatments and that complete mineralisation by AOPs incurs excessive treatment costs.

AOPs can be installed at different stages of waste (and also drinking) water treatment plants depending on *influent* composition and desired *effluent* quality. AOPs can be installed either as *tertiary treatment* after the biological (secondary) treatment of *wastewater*, or as *pre-treatment* stage in order to enhance the biodegradability of trace *organic* contaminants (Petrovic et al. 2011).

CONCLUSION

AOPs are promising methods to degrade and mineralize dyes. However, most experiments were carried out in the laboratory. The reason why AOPs are not being applied on industrial scales is mainly attributed to the utilization cost. Therefore, the most important issue for the application of AOPs is to reduce the cost. As the analysis above, the solution to lower the cost is to combine the AOPs with other technologies, the research about the catalysts combined with AOPs should be further studied. In these ways, the cost may be reduced, and the large scale application for industry dye wastewater treatment would be realized in the near future.

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OPTICAL AND ELECTRICAL CHARACTERIZATION OF CHEMICALLY VAPOUR DEPOSITED ALUMINIUM DOPED ZINC OXIDE THIN FILMS

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Abstract

Aluminium-doped ZnO (AZO) thin films were deposited by chemical vapor deposition technique to study its properties toward application in photovoltaics. A starting solution was prepared from zinc acetate dehydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$) dissolved in methanol and acetic acid. Aluminium acetylacetonate ($\text{C}_{15}\text{H}_{21}\text{AlO}_6$) was also dissolved in deionized water and acetic acid. The aluminium solution was then added to the zinc solution in order to dope the later solution with a concentration of 3%wt, and aluminium zinc-acetylacetonate solution was formed. The dried precursor of aluminium zinc-acetylacetonate obtained from the synthesis was used to deposit aluminium doped zinc oxide onto sodalime glass substrate at different substrate temperatures ranging from 390°C to 450°C with a flow rate of $2.5\text{ dm}^3/\text{min}$ for 2 hours deposition period. We report the optical transmittance of AZO films deposited at different temperatures varying from 75 to 95% in the visible range of wavelength 400–700 nm and an optical band gap energy value between 3.27 eV and 3.30 eV. Scanning Electron Microscopy (SEM) analysis showed that films are polycrystalline with grain size ranging from 19.2 to 23.7 nm for different substrate temperatures using origin software. The electrical analysis of AZO films deposited at different substrate temperatures revealed resistivity value between 0.074 and $0.011\ \Omega\text{ cm}$, an average mobility of $2.55\text{ cm}^2/\text{Vs}$, and an average carrier concentration of $1.39 \times 10^{20}\text{ cm}^{-3}$. Film deposited at 420°C with thickness 133 nm revealed to be the best as it possessed very good optical and electrical properties. The deposited thin film is found to be a promising candidate as a window layer for cost effective photovoltaics.

1. Introduction

Zinc oxide (ZnO) films have been investigated in recent years as transparent conducting oxide layers, because of their good electrical and optical properties in combination with large band gap, abundance in nature, and absence of toxicity (Zhou et al., 2007). ZnO is a II–VI group semiconductor material with wide direct band gap and wurtzite structure. In addition, the ZnO films could be deposited at relatively low deposition temperature (Bai et al., 2000), and good stability (in H_2 plasma). The electrical conductivity of ZnO is controlled by intrinsic defect, i.e. oxygen vacancies and/or zinc interstitials (Jimenez-Gonzalez et al., 1998), which act as n-type donors. The resistivity is lowered further by extrinsic doping with group III elements such as B, Al, Ga or In. Amongst them, Al-doped ZnO thin films are considered as candidate materials for electron transport layer (ETL) for inverted polymer solar cells (Zhu et al., 2016). Aluminium Zinc Oxide thin films are also being considered for manufacturing transparent electrodes in flat panel displays, solar cells and organic light emitting diodes (Chopra et al., 1983) due to their high electro optical quality, high material availability and low material cost for large area applications.

Among these methods employed so far to deposit AZO films, spray pyrolysis is a high temperature process and choice of suitable precursor solution is often not convenient. Sol-gel requires costly chemicals and electroless deposition is characterized with poor coverage. Successive ionic layer adsorption and reaction (SILAR) is a less used and less studied chemical techniques. Metal-organic chemical vapour deposition is a technique that is attractive because it makes use of a single solid precursor prepared cheaply from the appropriate reagents. Metal organic reactions occur at lower temperature than reduction reactions and do not attack the substrates chemically. MOCVD with thermal energy source is used for growing epitaxial films for many optoelectronic devices of compounds semiconductors for solar cells, Lasers, LEDs, Photocathodes, and quantum wells.

Single solid source precursors have been used to overcome the problem of vapour phase control and homogeneity of the unstable precursors. This enables the use of precursors with lower volatilities than the classical multi source precursors that allow synthesis of multi-component films with

a better control of composition and stoichiometry at higher reproducibility (Ajayi et al., 1994). It also controls the process parameters of MOCVD process for synthesizing a compound containing certain number of elements in the conventional multi-source MOCVD (Bosak et al., 2002). Akinwunmi *et al.*, 1999 used this procedure involving single solid source precursor reported by Ajayi *et al.*, 1981 to deposit Indium Tin Oxide (ITO) thin film. Since very few systematic reports are available on MOCVD deposition of AZO thin films, this study reports the doping effect of Al on ZnO in the synthesization and substrate temperature on the optical and electrical properties of these thin films which are explored for its application as window layer in photovoltaic devices.

2. Experimental details

Al-doped ZnO thin films were deposited by MOCVD technique. 0.2M starting solution was prepared from zinc acetate dehydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$) dissolved in methanol and acetic acid. Aluminium acetylacetonate ($\text{C}_{15}\text{H}_{21}\text{AlO}_6$) was also dissolved in deionized water and acetic acid at 0.2M concentration. The Aluminium solution was then added to the zinc solution in order to dope the later solution with a concentration of 3%wt, and aluminium zinc-acetylacetonate solution was formed with a precipitate. This was dried in a desiccator and the aluminium zinc-acetylacetonate precursor was filtered off. The dried precursor was grounded to fine powder which was easily transported by the carrier gas (Nitrogen gas) from an unheated receptacle to the reaction chamber where the film deposition takes place. This precursor was used to deposit Al:ZnO thin film on a soda lime glass substrate. The pyrolysis was carried out at a deposition temperature between 390°C and 450°C with a flow rate of $2.5\text{ dm}^3/\text{minutes}$ for 2 hours.

Transmittance and absorbance spectra were obtained using PYE UNICAM UV Visible spectrophotometer in the wavelength range 200–1100 nm. Structural analysis of films was performed by PANalytical X-ray diffractometer with $\text{CuK}\alpha$ ($\lambda = 1.5406\text{ \AA}$) radiation. SEM micrographs of the film were taken using Jeol 6700F Ultra High Resolution Scanning Electron Microscope. The elemental composition of the films was determined using Energy Dispersive Spectrometry (EDS). The film thickness was measured by a single stage 2 MeV

linear Van de Graaff particle accelerator. Hall measurements were carried out by the Van der Pauw method using a Walker scientific HV-4H equipment.

3. Results and Discussion

3.1 Optical Properties

The effect of substrate temperature on the optical transmittance of AZO thin films is presented in Fig. 1. The transmittance of films varied with temperature, and the maximum transmittance was observed for films deposited at 420 °C. The optical transmittance of all films with 3%wt. doping concentration and substrate temperatures was found to vary from 75 to 95% in the visible range of wavelength 400–700 nm. Transmittance of the doped film at 420 °C is near 95% and is higher than that of the film deposited at 390 °C and 450 °C. This may be due to the fact that the film deposited at 420 °C presents more voids than the films deposited at 390 °C and 450 °C, which may be attributed to the increased scattering of photons by crystal defects. This is a better result compared with (Babu et al., 2010) 2%wt. dopant concentration of Aluminium in AZO with 90% transmittance.

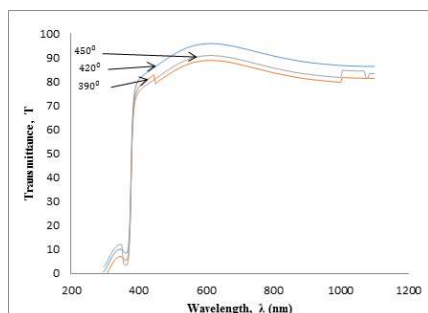


Fig. 1. Transmittance of film deposited at 390 °C, 420 °C, and 450 °C against wavelength

Bandgap energy of materials is another important parameter in optical analysis. The bandgap values are obtained by extrapolating the linear segments in the plot of the square of absorption coefficient $(\alpha h\nu)^2$ against Energy (eV) to $(\alpha h\nu)^2 = 0$ on the x-axis as shown in Fig. 2. Fig. 2a-c showed that there is a sharp change near the optical absorption edge due to the interband direct transition and this property is suitable for photovoltaic applications. The shift of absorption edge could be as a result of change of free-electron concentration in as-deposited Al doped Zinc Oxide films. This is in conformity with the report by Geng *et al.*, 2008.

The optical direct bandgap value of the films deposited at substrate temperature of 390 °C, 420 °C, and 450 °C are 3.30 eV, 3.27 eV, and 3.28 eV respectively. Although there is close proximity in their bandgap energies, but it was observed that the film deposited at 420 °C and 390 °C present the minimum and maximum optical direct bandgap energy respectively, and this shows that the higher the substrate temperature the less the bandgap energy. There is slight increase in bandgap energy with increasing temperature between the substrate temperature of 420 °C and 450 °C. This may be attributed to Burstein-Moss effect that an increase of the Fermi level in the conduction band of a degenerate semiconductor leads to an energy band-widening effect a “blue shift”.

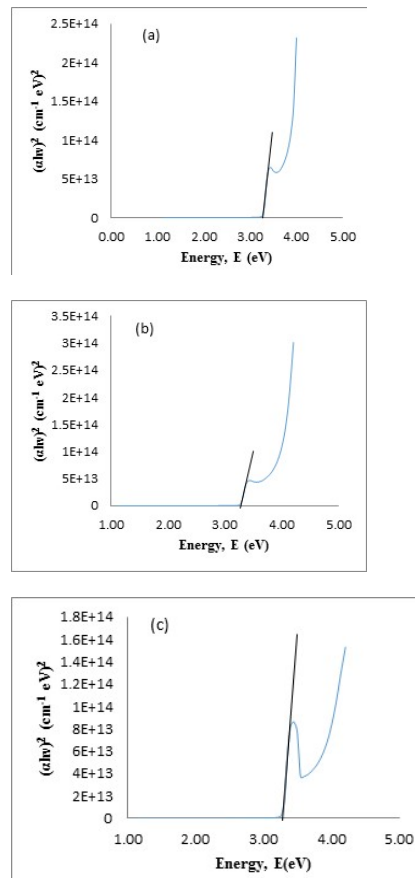


Fig. 2. Variation of $\alpha h\nu^2$ of AZO thin film with energy: substrate temperature at (a) 390 °C, (b) 420 °C, and (c) 450 °C

3.2 Surface Morphology

The SEM of AZO thin films deposited at 420 °C substrate temperature are shown in Fig. 3. at different magnifications. The SEM micrograph of the film revealed that the film is less porous in nature and is uniformly distributed at different geometry with slightly different grain sizes at lower magnification. As no cracks were detected in the film, a portion from lower magnification was enlarged to give a very fine pattern. The cross-sectional view of the film as observed in Fig. 3c. showed polycrystalline structure with very fine and uniform structure pattern. This result is in conformity with the report by Cheong *et al.*, 2003. The grain size of the AZO film at substrate temperature 390 °C, 420 °C, and 450 °C were determined to be 19.2, 20.5, and 23.7nm respectively.

1.1 Electrical Properties

The electrical properties of AZO film were carried out using Keithley four point probe instrument (model 2400). The electron mobility μ_n , conductivity σ_n , thickness t , carrier concentration n , and charge on electron $e(1.6 \times 10^{-19})$ are all related as shown in equation (1)

$$\mu_n = \frac{\sigma_n V t}{I B} = \frac{1}{n e \rho} \dots \dots \dots (1)$$

The effects of substrate temperature on the electrical resistivity, mobility and carrier concentration of the Aluminium (3%wt.) doped ZnO thin films are presented in Fig. 4. It was observed that resistivity of the films decrease with increase in deposition temperature from 390 °C to 450 °C.

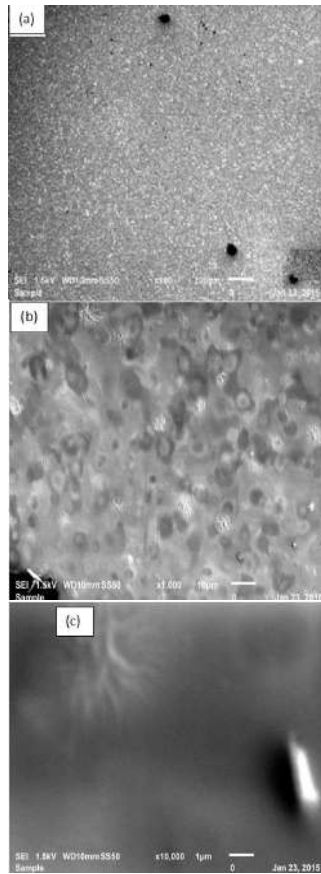


Fig. 3. SEM micrographs of AZO film

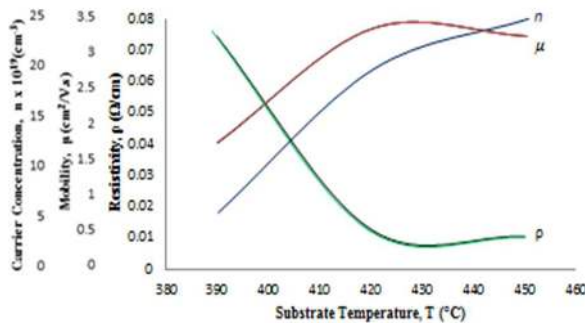


Fig. 4. Substrate temperature effects on electrical resistivity ρ , mobility μ_n , and carrier concentration n .

The electron mobility and the carrier concentration increases with increase in substrate temperature until 420 °C when electron mobility starts to decrease with increase in temperature. Aluminium doped zinc oxide (AZO) film deposited at different substrate temperatures has resistivity ranging from 0.074 to 0.011 $\Omega \text{ cm}$. The average mobility, μ and average carrier concentration, n are $2.55 \text{ cm}^2/\text{V.s}$ and $1.39 \times 10^{20} \text{ cm}^{-3}$ respectively.

4. Conclusions

AZO films were prepared by a chemically vapour deposited technique at different substrate temperatures. The deposition temperature effects on the optical and electrical properties of AZO thin films were examined. The optical transmittance was found to vary from 75 to 95% in the visible range of wavelength 400–700 nm. The direct bandgap of the films vary between 3.27 eV and 3.30 eV. SEM analysis revealed film's polycrystalline morphology with grain size ranging from 19.2 to 23.7 nm. The lowest resistivity 0.011 $\Omega \text{ cm}$ was recorded for the film deposited at 450 °C. These are very good optical and electrical properties and could be used as a window layer for solar cells.

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SELECTION OF PROPER MATERIALS FOR PLASTIC INJECTION MOULDS; THE NEED FOR STANDARDIZED AND OPERATIONAL STEEL MAKING INDUSTRIES IN NATIONAL DEVELOPMENT

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Abstract:

Mould making has become an inevitable process in engineering parts production all over the world. In this paper, the contributions of standardized and operational steel making industry in galvanizing the process of selecting proper materials are enumerated. Also, efforts were made to scrutinize the standard global best practices as it concerns selecting the proper materials for plastic injection mould making. Finally, the Iron and Steel industries' contributions to nation building are dissected in view of proffering solution to the challenges of steel production in Nigeria.

Key Words: Standard, SON, Iron and Steel.

1. INTRODUCTION

Standardization is the implementation and development of technical standards based on the consensus of different parties that include firms, users, interest groups, standards organizations and governments [1]. Standardization can help to maximize compatibility, interoperability, safety, repeatability, or quality. It can also facilitate commoditization of formerly custom processes. In social sciences, including economics, the idea of standardization is close to the solution for a coordination problem, a situation in which all parties can realize mutual gains, but only by making mutually consistent decisions [2].

The implementation of standards in industry and commerce became highly important with the onset of the Industrial Revolution and the need for high-precision machine tools and interchangeable parts [15].

A major advance in workshop technology was made by Henry Maudslay when, in 1800, he developed the first industrially practical screw-cutting lathe [4]. This allowed for the standardization of screw thread sizes for the first time and paved the way for the practical application of interchangeability (an idea that was already taking hold) to nuts and bolts [3].

In 1841, Joseph Whitworth's screw thread measurements were adopted as the first (unofficial) national standard by companies around Britain which later came to be known as the British Standard Whitworth (BSW), and was widely adopted in other countries [5], [6].

American Unified Coarse was originally based on almost the same imperial fractions. The Unified thread angle is 60° and has flattened crests (Whitworth crests are rounded). Thread pitch is the same in both systems except that the thread pitch for the ½ in bolt is 12 threads per inch (tpi) in BSW versus 13 tpi in the UNC.

By the end of the 19th century in London, differences in standards between companies, was making trade increasingly difficult and strained especially in the **Iron and Steel Industries** [15]. Then, the "Engineering Standards Committee" was established in 1901 as the world's first national standards body which subsequently extended its standardization work and became the "British Engineering Standards Association" in 1918, adopting the name British Standards Institution (BSI) in 1931 after receiving its Royal Charter in 1929 [7], [8].

After the First World War, similar national bodies were established in other countries. The "Deutsches Institut für Normung" was set up in Germany in 1917, followed by its counterparts both in 1918 are the "American National Standard Institute" and the "French Commission Permanente de

Standardisation" [3]. In mid to late 19th century, efforts were made to standardize electrical measurement of which Lord Kelvin was an important figure [7], [8].

The International Federation of the National Standardizing Associations (ISA) was founded in 1926 with a broader remit to enhance international cooperation for all technical standards and specifications. The body was suspended in 1942 during World War II [10].

After the war, ISA was approached by the recently formed United Nations Standards Coordinating Committee (UNSCC) with a proposal to form a new global standards body. In October 1946, ISA and UNSCC delegates from 25 countries met in London and agreed to join forces to create the new International Organization for Standardization (ISO); the new organization officially began operations in February 1947 [11].

In general, each country or economy has a single recognized National Standards Body (NSB) in the case of Nigeria, is the Standard Organization of Nigeria (SON).

2 Aim and Objectives

2.1 Aim

The aim of this paper is to look into the problems with Selection of Proper Materials for Plastic Injection Moulds; and then establish the Need for Standardized and Operational Steel Making Industries in National Development in the case of Nigeria with the following objectives:

2.2 Objectives

To achieve this aim, the following are the specific objectives.

- To evaluate the contribution of existing Iron and steel companies' and SON's contribution to the standardization of steel in Nigeria.
- To ascertain the reason the Nigerian steel industry is at the level they are at the moment and possible turn around.

3. Methodology

Material selection procedure was enumerated and various approaches were looked into as it concerns making a good mould for a plastic injection mould.

Contribution of steel industries, both government and private owed, are scrutinized in view of finding out the situation as it regards making standard steel for injection mould production.

Furthermore, the involvement of SON in ensuring that set standards are strictly adhered to is highlighted and dissected. Then, the various industries were highlighted and evaluated based on their contribution to steel making in Nigeria and their level of compliance to standard as adopted by SON.

Finally, rooms for improvement to the current situation were explored.

4. Analysis and Remedies

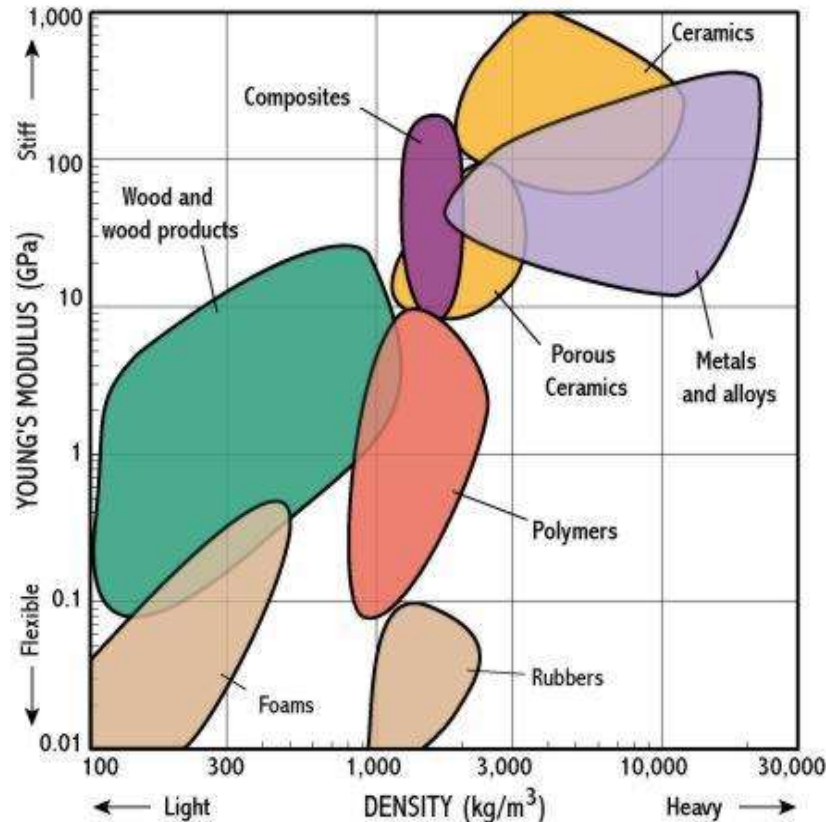
4.1 Material Selection for Plastic Injection Mould

The choice of material for plastic injection moulds is primarily one of economics provided it satisfies some or all the design criteria which are:

a) Machinability

- b) Smallest change in size upon heat treatment
- c) Good polishability
- d) Great compressive strength
- e) High wear resistance
- f) Sufficient corrosion-resisting quality
- g) Cost

In engineering material selection, the Ashby chart is a good guide to proper material selection.



Source: M. F. Ashby, (1999)

Figure 2.1: A schematic $E - \rho$ chart showing a lower limit for E and an upper limit for ρ

More so, the Digit Logic Method can be used to select the appropriate material based on the seven conditions enumerated above.

$$\alpha_i = \frac{N_i}{\sum_{i=1}^n N} \quad (1)$$

The possible material for the mould parts is the material with the highest value of α .

Having chosen the appropriate materials for the design, it is now time to move into the market to search for and purchase the chosen materials. If the materials are not in the market, the designer will be required to book for a customized material but most times designers design within a set standard to reduce cost.

4.2 The Steel Industries Contribution

The Ajaokuta Steel Plant is the biggest steel company in Nigeria located in Ajaokuta, Kogi State. The design of the steel making complex was based on the blast furnace route to iron production with initial capacity of 1.3 million tons of liquid steel per annum with built-in capacity for possible future expansion to 2.5 million tons per annum in the first phase and up to 5.2 million tons per annum in the second phase [16]. The

Ajaokuta Steel Company is supposed to be the engine of industrial emancipation of Nigeria [16] but reverse is the case.

Ajaokuta Steel Company was designed and specified in Russian System (GOSH) but in 2003 an American based Company was invited to run the steel complex at Ajaokuta with disastrous consequences [16].

The expected product of Ajaokuta steel complex consist of Rounds, ribbed bars, Angles, plates, strips, channels, Beams and Tees, Billets while the by-products which can still find usefulness in other industries are Slag from the Blast Furnace was to be used in road surfacing, aggregate for concrete, fertilizer for farmers, rock wool raw materials, cement and others [16]. But because of neglect, all these benefits are, for now, a fairy tale.

Delta Steel Company is located at Ovwian-Aladja, Warri, Delta State, Nigeria. It was established based on the German DIN standard [16]. Projected product mix are Direct Reduced Iron (DRI), Billets, rounds, ribbed bars, angles, strips and channels. It was desired by ambitious and patriotic Engineers in the middle eighties to modify the Continuous Casting Station to blooms production for the final production of plates but enemies of progress frustrated their efforts [16].

From the forgoing, it is obvious that the government owned steel industries are not doing enough to satisfy the steel needs of the country therefore, we look at the Private Steel Companies. It was observed that most of these private companies are based in Lagos and they produce majorly liquid steel and billets, pipes and rods. Quantity of steel products from private steel companies is a minuscule compared to the Steel products from operating Government Steel Companies [16].

4.3 Nigerian Standard as it Concerns SON and Steel Making

The Vanguard newspaper on January 8, 2011, reported that SON has adopted a new standard for Steel Industries. According to the newspaper, the decision to adopt this new standard was due to poor capacity utilization in the steel industry and **incessant cases of buildings collapse in the country**. Therefore, Federal Government, through Standards Organization of Nigeria (SON), took a decision to adopt the British standard of steel manufacturing (BSI) for local manufacturers to expand their capacity and boost income flow in the economy through steel export.

At the Vanguard interview with the director general, Standards Organization of Nigeria (SON), Dr. John Akanya, he stated that enforcement experts have been positioned to monitor compliance of this new adopted standard. The mechanism to monitor compliance is already in place because we would frequently embark on unscheduled visits to the manufacturers to have first hand information on the production processes.

The question now is after all these why is Nigeria not self sufficient in steel making especially in the area of materials for plastic injection moulds.

4.4 Remedies

To ensure that steel industries in Nigeria will grow to become one of the sectors to sustain the country's economy, these are the expected remedies.

Though, government effort is commendable over some policies and edits enacted over the years to place Nigeria in the world steel map. However, government should ensure that corruption is eradicated in the Nigerian Steel Industry so as to foster development in the Steel Industry and Nigeria. Also, the quota system, ethnicity, should not be part of the Steel Industry.

Steel industries shall ensure compliance with the set standard by SON. Also, they shall not only concentrate on the manufacture of weldable reinforcement steel bars because of it high demand. Instead, they should also include flat plate materials for plastic injection moulds.

Having adopted the BSI in steel, SON has deploy its monitoring team to ensure compliance to prevent production of low quality of material buy embarking on frequent unscheduled visits to the manufacturers to have first hand information on the production processes as they promised.

5. Conclusion

A stitch in time saves nine they say. We can start today and make a turnaround in the direction we all heading to. This could be achieved by making sure that government continue to make policies that will support steel industries in Nigeria as it concerns mould making materials. All hands shall be on deck to ensure that government policies, policy implementation and the agent of policy implementation are not politicized in the Steel Industry.

The government shall encourage the public and private owned Steel industries not to concentrate mostly on weldable reinforcement steel bars but on other areas of steel types especially for mould making. Also, steel industries are encouraged to comply with the set standards of SON.

Finally, SON on the other hand is encouraged not to do the "frequent unscheduled visits to the manufacturers" from their various offices but to the field where the actual steel making is going on. Also, while on this mission of monitoring, the team shall not allow themselves to be influenced by any factor.

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MODIFICATION OF ASHAKA AND TANGO BENTONITES WITH TETRAPHENYL PHOSPHONIUM AND HEXADECYL PYRIDINIUM BROMIDES FOR POSSIBLE USE IN POLYMER- CLAY NANOCOMPOSITE PREPARATION

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ABSTRACT

Bentonites from Ashaka (GA) and Tango (GT) of Gombe State, Nigeria were surface modified with Tetraphenyl phosphonium and Hexadecyl pyridinium bromides by cation exchange method for their possible use in Clay/polymer nanocomposite preparation. The surfaces of the modified products were characterized by means of Fourier-transformed infrared spectroscopy (FTIR), X-ray diffraction (XRD) and scanning electron microscopy (SEM). The FTIR spectra of the TPP and HDP modified bentonites showed bands at 1588 cm⁻¹ which were due to C=C stretching vibration in the phenyl ring, 1443cm⁻¹, 1486cm⁻¹ and 1436cm⁻¹, 1439cm⁻¹ were due to attachment of the phenyl rings to phosphonium ion; 2918; 2851 and 1469cm⁻¹ were due to C-H asymmetric ($\nu_{as}CH_2$), symmetric (ν_sCH_2) stretching and bending (δ) vibrations in methylene groups of surfactant alkyl chains respectively. The basal spacing of the unmodified bentonite samples, determined by means of X-ray diffraction (XRD) was 1.52nm and 1.29nm and after modification with TPP and HDP it increased to 1.86nm, 1.74nm and 2.15nm, 2.11nm respectively. Results of the SEM images revealed rougher surfaces with uniformly dispersed small particles of grain-like structures characteristic of the organomodified bentonites.

Keywords: Bentonite, Surface modification, Nanoclay, Nanocomposite, Quaternary phosphonium surfactants,

1. INTRODUCTION

Surface modification is necessary for making natural bentonite clays suitable in wide spectrum of applications, such as adsorption, catalysis development of polymer/clay nanocomposites etc (Tabak *et al.*, 2007; Abdallah and Yilmazer, 2011; Ezquerro *et al.*, 2015). Although the term nanocomposite represent a new and exciting field in material science and technology. Using natural materials and polymers such as carbohydrates, lipids and proteins, nature makes strong, nanocomposites such as bones, shells and wood (Hussain *et al.*, 2006). Consequently the nanocomposite technology has emerged as an efficient and powerful strategy to upgrade the structural and functional properties of synthetic polymers. The polymer/clay nanocomposite is the new science, so referred recently in nanotechnology, and was started by the Toyota report (Okada *et al.*, 1990) on the superior improvement in the properties of nylon-6 by the preparation of exfoliated nylon-6/clay nanocomposites and has been continued by more recent studies with carbon nanotubes, carbon nanofillers, exfoliated graphite, nanocrystalline metals and fibers modified with inorganic fillers used in polymeric composites (Olad, 2011).

Polymer nanocomposites have attracted great attention worldwide academically and industrially due to their potential for enhanced physical, chemical, and mechanical properties compared to conventionally filled/pure polymer through addition of small amount of organoclay (2-5% by weight). They have the potential of being a low-cost alternative to high-performance composites for commercial applications in both the automotive and packaging industries (Olad, 2011; Tijen, 2010). A nanocomposite is defined as a composite material in which at least one dimensions of at least one component is in the nanometer size scale (< 100 nm) (Olad, 2011), while Polymer nanocomposites are formed by dispersing a refined form of nanoclay (organoclay) into polymer resins, or they can be defined as two-phase materials in which the polymers are reinforced by nanoscale fillers (Tijen, 2010; Olad, 2011). An exfoliated structure results when the individual silicate layers are completely separated and dispersed randomly in a polymer matrix. Usually exfoliated nanocomposites are preferred because they provide the best property improvements (Olad, 2011; Donald and Nguyen, 2006). For the preparation of polymer/clay nanocomposites, modification of layered silicate

is very important, because natural or unmodified clays are difficult to disperse in polymers due to their hydrophilic nature, therefore in order to have a successful development of clay-based nanocomposites, it is necessary to organically modify a natural clay so that it can be compatible/ dispersible with a chosen polymer-resin matrices which are hydrophobic (Donald and Nguyen, 2006; Zykova *et al.*, 2009; Pathavuth *et al.*, 2011)

Organo-montmorillonite (OMMT) has a better effect on improving the physical and mechanical properties of composites because of its large interlayer distance and compatibility with non-polar polymers (Liu *et al.*, 2015; Liu *et al.*, 2010). Hydrophilic montmorillonite clay is made organophilic through the process of compatibilization (intercalation). Organic-cation substitution can be used in producing organophilic montmorillonite nanoclay through several routes, although the most convenient and straight forward method to prepare organoclays was cation exchange reactions that replace interlayer cations with quaternary alkylammonium or alkylphosphonium cations. (Liu *et al.*, 2010; Ezquerro *et al.*, 2015). Quaternary ammonium surfactants used in commercially available organoclays usually incorporate short aliphatic chains, benzyl rings and sometimes hydroxyl groups. They may also contain at least one long aliphatic chain (C₁₂–C₁₈) to cause expansion of the distance between the layers. Other ammonium surfactants are more complex molecules (Abdallah and Yilmazer, 2011; Calderon *et al.*, 2008). Although the choice of modifiers for the surface modification of the clay depends on its application for instance, alkyl ammonium modified clays are thermally not very stable above 250 °C and start to degrade at nanocomposites processing temperature (200–300°C). Therefore, organoclays prepared using quaternary alkyl ammonium salts are less suitable for most engineering plastics with high processing temperature, hence in the synthesis of polymer-clay nanocomposite other cations, such as phosphonium, Pyridinium, stibonium and imidazolium have been used due to their higher thermal stability (Patel *et al.*, 2007; Calderon *et al.*, 2008; Abdallah and Yilmazer, 2011; Mittal, 2012; Ezquerro *et al.*, 2015).

Another important factor in nanocomposite preparation is the initial d₀₀₁ spacing (a measure of the distance between planes of atoms) of the organically modified clay. The organic modification not only improved the compatibility of

the clay with the polymer but also increased the distance between the silicate layers, which may facilitate the insertion of the polymer chains and thus producing an exfoliated or intercalated nanocomposite (Tijen, 2010; Wang *et al.*, 2011; Ezquerro *et al.*, 2015).

Several methods have been reported to synthesize clay/polymer nanocomposites; however, three methods (in situ polymerization, intercalation in solutions and melt processing) developed during the early stages of this field are widely applied (Ezquerro *et al.*, 2015). The melt processing technique is mostly used because this process played an important role in speeding up the progress of the commercial production of clay/polymer nanocomposites (Patel *et al.*, 2007).

The present study describes the preparation and characterization of Organoclays from bentonites of different origin with tetraphenyl phosphonium and hexadecyl pyridinium bromides for its possible use in polymer/clay nanocomposite preparation.

2. MATERIALS AND METHODS

2.1 Materials

The bentonites used in this study were from Gombe State in Nigeria (Ashaka and Tango) deposits and are labeled as GA and GT respectively. The clay fraction was obtained by sedimentation process (Stokes' Law), where 100 g of bentonite was dispersed in 1L of 10% H₂O₂ solution, then re-suspended in 1 L 0.5 M NaOH solution for a period of 2 hr with moderate agitation. Afterwards the resulting suspension was diluted with de-ionized water and collecting the supernatant dispersion of particles <2 µm. The slurry was then dried at 90 °C (Patel *et al.*, 2007; James *et al.*, 2008). The cation exchange capacities (CEC) of purified bentonites, measured by the standard ammonium acetate method, were 0.72 Meq/g and 0.63 Meq/g respectively on dry basis (dried at 110 °C). The chemical compositions of the purified bentonites given in Table 1 as determined by XRF, showed that the purified bentonites were rich in montmorillonite with Na⁺ and Ca²⁺ as exchangeable cations

The mineralogical compositions of the samples as determined by XRD showed that the purified samples contained some minor impurities of opal, quartz, feldspar and calcite. The surfactants were of ≥ 97% purity (Sigma, Aldrich) and used as received. Deionized water was used for the preparation of all solutions.

2.2 Modification of the bentonites

5 g of the sample was dispersed in 100mL of deionized water and subsequently heated to around 80°C under continuous stirring. When the clay was completely dispersed, 2.26g, 1.98g of TPPB and 2.77g, 2.42g of HDPB equivalent to 1.5x and 2.0x the CEC of GA and GT bentonite clays respectively were slowly added, and stirring was maintained for 4h at 80°C. The resultant product was recovered by vacuum filtration and washed several times with deionized water until no halide anions were detected using the silver nitrate test. The product was then dried at 80 °C overnight and finally ground manually in an agate mortar and sieved into a plastic container (Prau *et al.*, 2006; Patel *et al.*, 2007; Abdallah and Yalmizer, 2011; Rodriguez *et al.*, 2012; Banik *et al.*, 2015; Ezquerro *et al.*, 2015).

2.3 Characterization of unmodified and modified bentonites

The Fourier transform infrared spectra (FTIR) of the clays were measured with FTIR Cary 630 Agilent Technology USA, Spectrometer in the range of 4000–400 cm⁻¹ at a resolution of 4 cm⁻¹. XRD patterns were obtained on a GBC EMMA (Enhanced mini material) Analyzer, which generates a voltage of 40 kV and current 40 mA from monochromatic Cu K α radiation source (λ = 1.54Å) Cu K α radiation. The diffraction

angle 2 θ was scanned from 2° to 65° at scanning rate of 2°/min and step size of 0.05°. In order to calculate the distance between the silicate layers, Bragg's law was used. The surface morphology of the bentonite samples was obtained using Scanning electron microscope (Phenom Proxy, PW 100-002, magnification-255x, Accelerating Voltage- 10KV).

3. RESULTS AND DISCUSSION

Table 1: Chemical analysis of metal oxide composition of the bentonite samples

Chemical oxide (wt %)	GA	GT
Na ₂ O	1.66	1.43
MgO	2.08	2.08
Al ₂ O ₃	14.86	14.98
SiO ₂	48.16	49.87
P ₂ O ₅	1.06	1.01
K ₂ O	1.60	1.76
CaO	1.16	1.81
TiO ₂	0.94	0.87
Fe ₂ O ₃	4.80	5.12

Table 2: IR-bands (cm⁻¹) in the spectra of purified bentonites

Purified bentonites		Assignment
GA	GT	
3693	3693	ν (Si-OH)
3622	3622	ν (Al-OH)
3400	3406	Asymmetric C-H in (CH ₂) _n
1639	1639	δ (H-O-H)
1115	1113	ν (Si-O) out-of-plane
996	994	ν (Si-O) in-plane
912	912	δ (Al-Al-OH)
801	801	δ (Al-Mg-OH)
782	782	ν (Si-O) of silica and quartz
694	693	ν (Si-O) of silica and quartz
596	596	δ (Si-O-Al)
459	482	δ (Si-O-Si)

The FTIR spectra of the purified and modified bentonites are shown in Fig. 1 and the assignments of the bands are summarized in Tables 2-4. In the FTIR spectra of the purified bentonites different characteristic bands are seen in several regions of the spectra. In the high-frequency region, bands between 3400 cm⁻¹ and 3700 cm⁻¹ of the bentonite clays (GA and GT) are indication of montmorillonite (Patel *et al.*, 2007; Abdallah and Yalmizer, 2011). The bands at 3622 and 3693 cm⁻¹ refer to OH stretching region, which is assigned to hydroxyl groups coordinated to octahedral and tetrahedral cations; OH stretching mode of Al-OH and Si-OH of montmorillonite structure respectively (Patel *et al.*, 2007). The bands at 3400 cm⁻¹, 3406 cm⁻¹ and 1639 cm⁻¹ of GA and GT

are respectively the stretching and bending vibrations for the hydroxyl groups due to adsorbed water. The most intense bands of the spectrum were found in the low-frequency region. The characteristic peaks at 1115 cm^{-1} and 1113 cm^{-1} are due to Si–O stretching mode, (out-of plane) for montmorillonite. The band at 996 and 994 cm^{-1} is attributed to Si–O stretching (in-plane) vibration for layered silicates. At lower frequencies, there were several bands associated to the bending vibration modes of metal-to-metal hydroxyl groups and contained information about the presence of minority metals, such as Mg and Fe; 912 cm^{-1} (AlAlOH) and 801 cm^{-1} (AlFeOH).

Moreover, the bands at 782 cm^{-1} and 699 cm^{-1} might be due to the presence of quartz in the sample (Patel *et al.*, 2007; Avalos *et al.*, 2009; Abdallah and Yalmaz, 2011; Ezquerro *et al.*, 2015). In the FTIR spectra of phosphonium and Pyridinium organo-bentonites (Fig. 2 and Tables 3 and 4), certain changes were observed; such as slight changes on the wave bands of the purified bentonites and appearance of some bands that were absent in the original spectra of the purified bentonites. There were increase in the wave numbers associated to the –OH stretching mode of hydroxyl groups coordinated to tetrahedral cations (Si–OH) of montmorillonite structure from 3693 cm^{-1} to 3696 cm^{-1} /3695 cm^{-1} and 3695 cm^{-1} (TPP-GA and TPP-GT and HDP-GA respectively). There was no change in wave band associated to the –OH stretching mode of hydroxyl groups coordinated to octahedral cations (Al–OH) at 3622 cm^{-1} . The bands at 3400 cm^{-1} /3406 cm^{-1} and 1639 cm^{-1} associated to the stretching and bending vibrations for hydroxyl groups due to adsorbed water disappeared in both phosphonium and Pyridinium organo-bentonites. Peaks at 2918 cm^{-1} and 2851 cm^{-1} are ascribed to the asymmetric and symmetric vibration of methyl groups (CH_2)_n of the aliphatic chain of the HDP modified samples. Praus *et al.*, (2006); Patel *et al.*, (2007); Avalos *et al.*, (2009); Abdallah and Yalmaz, (2011); Rodriguez *et al.*, (2012); Banik *et al.*, (2015) reported similar values. Bands at 1639 cm^{-1} and 1490 cm^{-1} are associated to stretching vibration of Pyridinium ring (Zhang *et al.*, 2012). A strong methylene/methyl band (around 1470 cm^{-1}) due to stretching of aliphatic C–C bonds and a weak methyl band (around 1380 cm^{-1}) characteristic of methyl groups, plus a band at 724 cm^{-1} (methylene rocking vibration) is indicative of a long-chain linear aliphatic structure (Avalos *et al.*, 2009; Abdallah and Yalmaz, 2011). To this effect bands at 1469 cm^{-1} , 1378 cm^{-1} and 724 cm^{-1} respectively were observed in the HDP modified samples. For the TPP modified bentonites (GA and GT) sharp bands of low intensity at 1485 cm^{-1} , 1486 cm^{-1} and 1443 cm^{-1} , 1439 cm^{-1} are associated to the vibration modes of the phenyl rings attached to the phosphorus atoms respectively. Patel *et al.*, 2007; Avalos *et al.*, 2009; Abdallah and Yalmaz, Ezquerro *et al.*, 2015 obtained similar values (1430, 1465; 1486, 1439; 1436; 1485 cm^{-1} and 1439 cm^{-1}). At lower frequencies, bands appeared at 728 cm^{-1} and 724 cm^{-1} which were attributed to P–C stretching modes.

Increasing the interlayer distance is important in order to be successful at nanocomposite processing, because the intercalation of the chains of the polymer between the aluminosilicate layers would be more probable with a higher interlayer distance, and this is important in order to get exfoliated and/or intercalated nanocomposites with higher improvement in properties (Ezquerro *et al.*, 2015). XRD analysis was carried out in order to determine the basal space or interlayer distance (d_{001}) of the organo-modified bentonites.

The XRD diffraction patterns of the purified bentonites (GA and GT) and modified bentonites (TPP-GA, GT and HDP-GA, GT) are as shown in **Figure 2** and the values summarized in

Table 5. From the diffraction patterns, the basal spacing of the purified GA and GT samples increased from 1.52nm and 1.29nm to 1.86nm, 1.74nm and 2.15nm, 2.11nm (TPP and HDP) respectively. This increase resulted in the shift of the diffraction peak toward lower angles (from 5.8° and 6.8° to 4.75° and 5.08°; 4.10° and 4.19°) respectively. This implies that the interlayer distances were increased due to the intercalation of the surfactants between the silicate layers. Patel *et al.* (2007) reported basal spaces of about 1.5–1.8nm for several single aryl phosphonium compounds at surfactant concentrations equivalents to the CEC of the clay. Avalos *et al.*, (2009) obtained 1.85nm for aryl phosphonium modified montmorillonite at surfactant concentration equivalent to 1.2 times the CEC of the clay. Abdallah and Yilmazer, (2011), reported 1.78nm for phosphonium surfactants with phenyl and benzyl groups at 1.1 times the CEC of the clay. Ezquerro *et al.*, 2015 obtained for double aryl phosphonium salt (Dim-Mt) at different concentrations ranging from 0.5CEC to 4.0CEC of the clay, basal spaces of 1.14nm–2.18nm. Praus *et al.*, (2006); Banik *et al.*, (2015); Bertagnolli and Silva (2012); Rodriguez *et al.*, (2015); reported values for HDP modified MMT 1.66nm; 2.16nm; 1.62nm; 1.76nm at surfactant concentration equivalent to the CEC and twice the CEC of the clay respectively.

It has been reported that the basal spacing of organoclays depends on the CEC of the clay mineral, the amount of organic cations, the chemical structure and molecular weight of the surfactant, the arrangement and packing density of the organic cations within the clay interlayer (Abdallah and Yilmazer, 2011; Calderon *et al.*, 2008; Paiva *et al.*, 2008; Changchaivong and Khaodhiar, 2009; Xi *et al.*, 2007; He *et al.*, 2006). The higher basal spacing in the Pyridinium and the moderate in the phosphonium modified bentonites from this study will facilitate the intercalation or even the exfoliation of the modified bentonites in a polymer nanocomposite.

The surface morphology of purified and modified bentonite samples are shown in figure 4. In the SEM images of purified bentonites, massive plates with some phase separations are observed as a heterogeneous surface morphology. It showed a soft surface where large lamellas tend to form big agglomerates with a layer disposition. After the modification with organic surfactant significant changes were seen in the morphology. The surface of the bentonite turned rougher than in the purified samples with more fractionated lamellas and uniformly dispersed small particles with the form of flakes or grain-like structures (Banik *et al.*, 2015; Ezquerro *et al.*, 2015).

Conclusion

Ashaka and Tango bentonite samples were successfully modified with tetra phenyl phosphonium and hexadecyl pyridinium bromides by means of the cation exchange method. This achievement was confirmed by means of FTIR spectroscopy. In addition, the modification turned the surfaces of the aluminosilicate layers more hydrophobic and reduced the water content of the organoclays. XRD analysis showed that the basal spaces of organoclays were higher especially in the HDP-modified bentonites when compared with the purified bentonites. These larger basal spacing could promote the exfoliation of the organo bentonites particles by compounding with the polymer. The morphology of these materials was assessed by SEM microscopy and showed that the surface of Organoclays turned rougher than in purified bentonites with more fractionated lamellas and particles with the form of flakes. Therefore these hybrids developed in this study could be applied for the development of polymer/layered silicate nanocomposite

Table 3: IR-bands (cm⁻¹) in the spectra of TPP modified bentonites,

TPP Modified bentonites		Assignment
GA	GT	
3696	3695	ν (Si-OH)
3655	3655	
3622	3622	ν (Al-OH)
1600	1600	δ (H-O-H)
1588	1588	ν (C=C) in phenyl group
1485	1486	
1443	1439	δ (C-C) in aromatic
1112	1110	ν (Si-O) out-of-plane
1004	998	ν (Si-O) in-plane
918	914	δ (Al-Al-OH)
803	801	δ (Al-Mg-OH)
756	758	ν (Si-O) of silica and quartz
695	693	ν (Si-O) of silica and quartz
		δ (Si-O-Al)
		δ (Si-O-Si)

Table 4: IR-bands (cm⁻¹) in the spectra of HDP-modified bentonites

HDP Modified bentonites		Assignment
GA	GT	
3695	3693	ν (Si-OH)
3652	3652	
3622	3622	ν (Al-OH)
2918	2918	Asymmetric C-H in (CH ₂) _n
2851	2851	Symmetric C-H in (CH ₂) _n
1639	1639	vibration due to pyridinium ring
1490	1490	CH ₂ scissoring Vibration due to Pyridinium adsorption.
1469	1469	δ (C-H) /strong C-C stretching
1378	1378	Weak C-C stretching
1168	1168	
1104	1104	ν (Si-O) out-of-plane
998	994	ν (Si-O) in-plane
912	912	δ (Al-Al-OH)
799	799	δ (Al-Mg-OH)
776	778	ν (Si-O) of silica and quartz
724	724	δ (CH ₂ rocking, asymmetric)
683	687	ν (Si-O) of silica and quartz
		δ (Si-O-Al)
		δ (Si-O-Si)

Table 5: diffraction angles and basal spacing of purified and modified samples

Sample	Unmodified		TPP Modified		HDP Modified	
	2 Θ (°)	Basal spacing (Å)	2 Θ (°)	Basal spacing (Å)	2 Θ (°)	Basal spacing (Å)
GA	5.80	15.23	4.75	18.59	4.10	21.53
GT	6.80	12.99	5.08	17.38	4.19	21.05

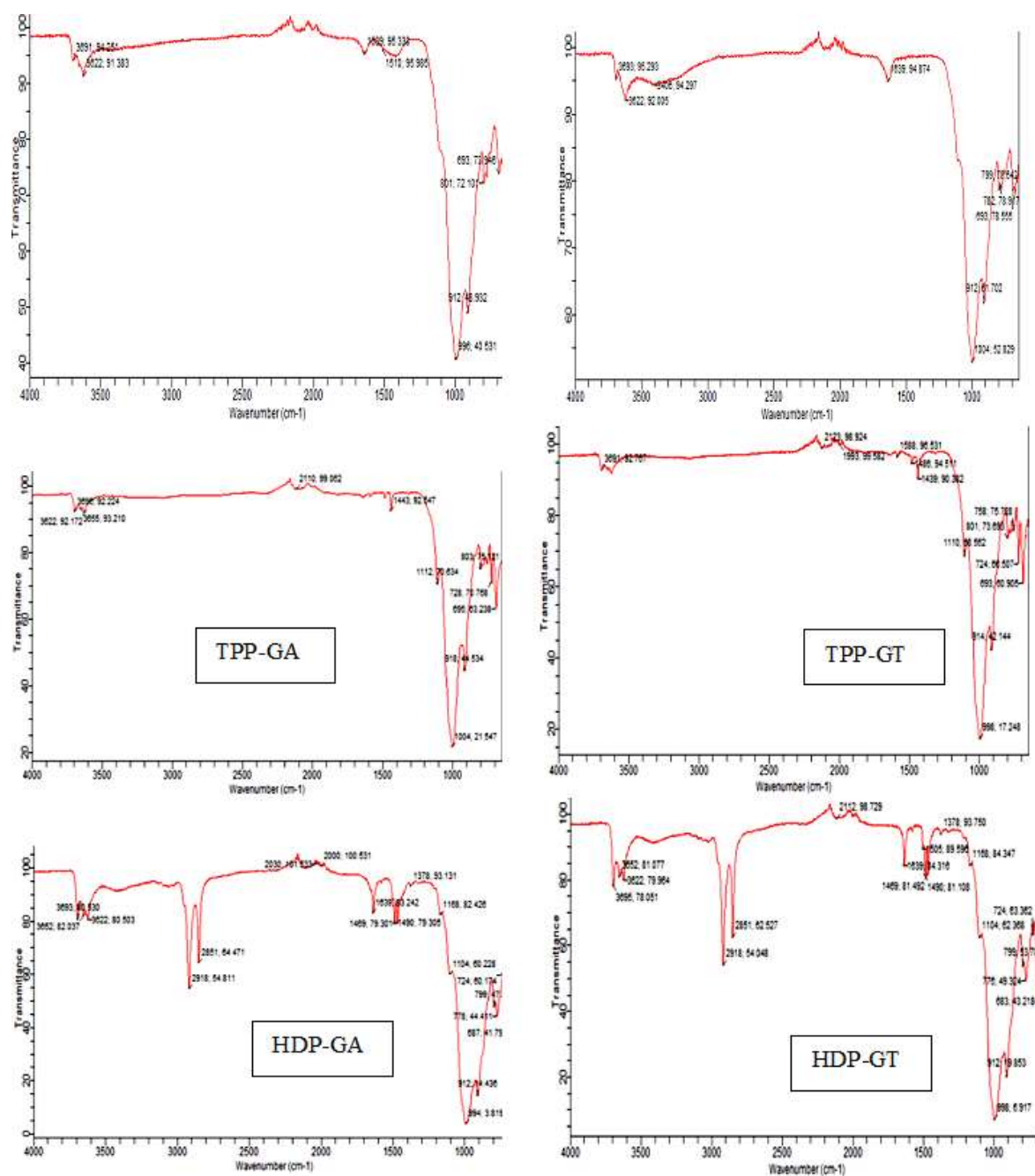


Fig. 2: FTIR spectra of purified (GA, GT) and modified (TPP-GA, TPP-GT), (HDP-GA, HDP-GT) bentonites

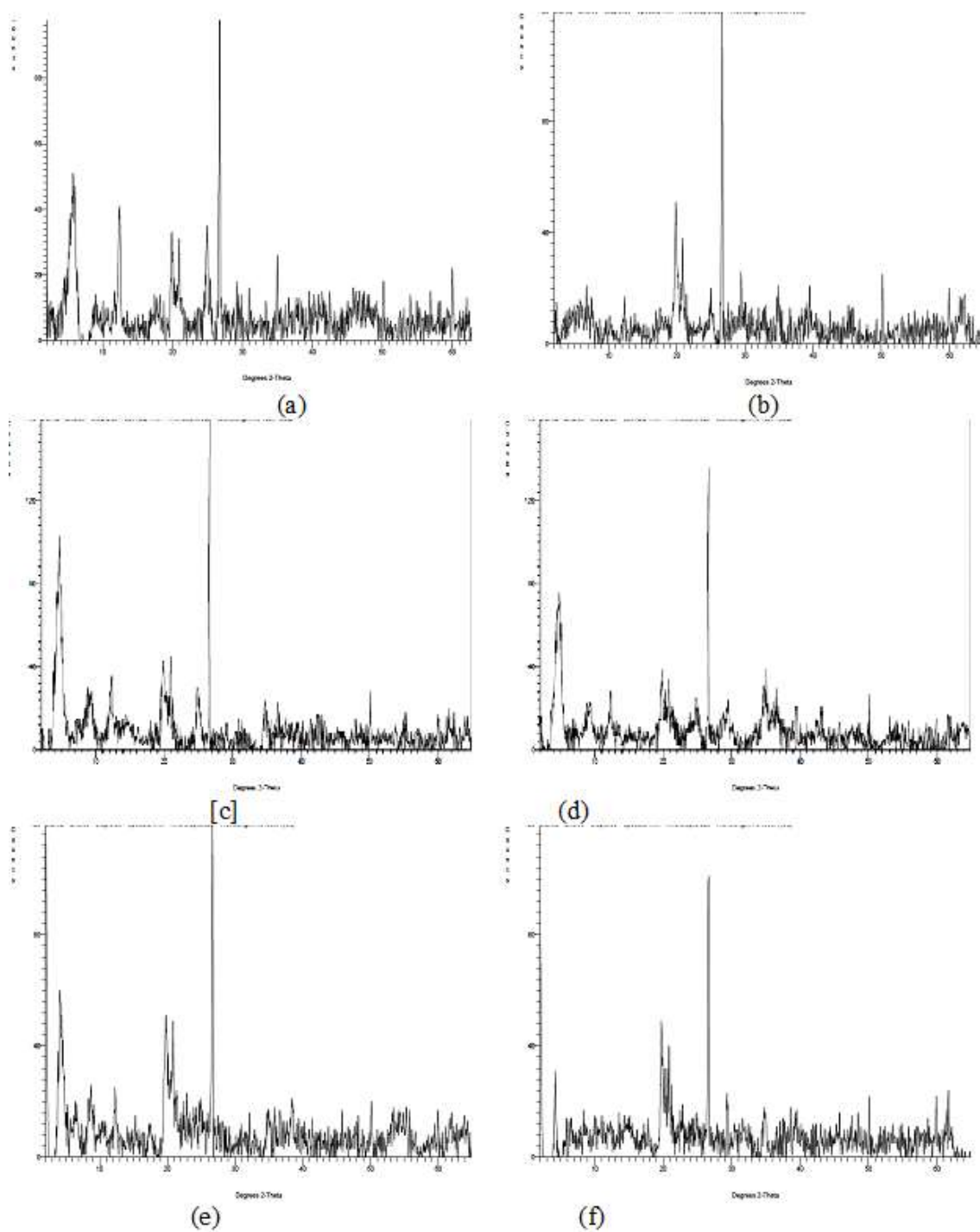


Fig. 2a-f: X-Ray diffractograms of the purified (a, b) TPP modified (c, d) and HDP modified (e, f) GA and GT bentonites

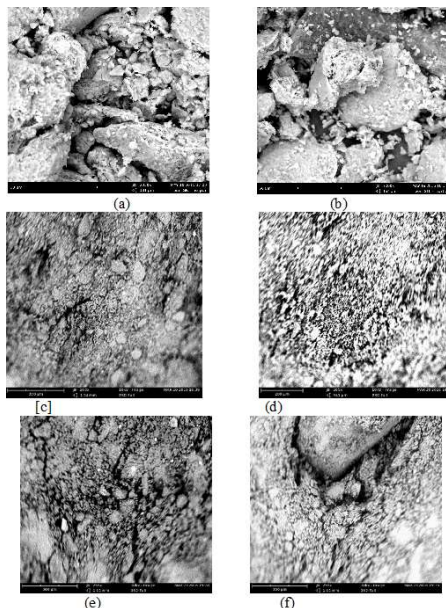


Fig. 3a-f: SEM images of purified (a, b), TPP modified (c, d), HDP modified GA and GT bentonites

Recommendation

The authors recommend that thermogravimetric analysis (TGA) and TEM analyses of the modified samples should be carried out in order to assess the thermal stability and the clay layer thickness so as to know if the organobentonites could really be used in polymer/clay nanocomposite preparation.

Acknowledgements

The authors wish thank Mr Muhammad Musa from Bayero University Kano, Dr Wagini from Umaru Musa Yar adua University, Katsina and Mr Paul for their technical assistance in the provision the of FTIR, SEM micrographs and XRD spectra measurements respectively. The financial support to ASL by the Tertiary Educational Trust Fund of Nigeria (TETFUND) is highly appreciated.

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NANOINDENTATION PROBE OF ALUMINA-DOPED LOW DENSITY POLYETHYLENE (LDPE/ALUMINA) NANOCOMPOSITES

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ABSTRACT

Nano-sized kaolin also known as alumina was synthesised from local kaolin subsequently suspended in low density polyethylene (LDPE) to produce nano-polymer for application in electrical insulation. The alumina was prepared by acid leaching via digestion, precipitation, peptization and drying. It was subsequently used to dope the LDPE at varying compositions. The mechanical properties of the samples produced in this work, was investigated by Nanoindenta and it showed that the presence of alumina in the LDPE improved the Young's modulus and hardness of the samples.

1.0 INTRODUCTION

Polymer nanocomposites have sparked a lot of academic interest and generated waves of industrial revolution in recent years because as matrix or parent materials, they offer superior mechanical performance and some enhanced physical properties like thermal and flammability resistance and decreasing in gas permeability (Ali *et al.*, 2008). Generally, natural clays can easily be reduced to nanoscale and are usually used for the preparation of polymer nanocomposites due to their structure and availability as a cheap raw material. These polymeric materials must perform under strenuous mechanical, chemical, thermal and electrical conditions imposed by the requirements of a specific application (Sihama, 2013).

Low density polyethylene (LDPE) has a key role to play in the industry of polyolefins due to its wide range of applications. This is because they have good properties, such as: high flexibility, good processability; excellent resistance to dilute and concentrated acids, alcohols, bases and esters; impact resistance; and dimensional stability (Gustavo *et al.*, 2013).

Nanoindentation testing is a method of measuring the mechanical properties of a material such as hardness and Young's modulus on the microscopic scale (Ah-Young *et al.*, 2010 and Zhi-Qiang *et al.*, 2010).

2.0 MATERIALS AND METHODS

2.1 MATERIALS

Low density Polyethylene (LDPE) (commercial grade), Hydrochloric Acid (HCl) of M. W., 36.48 and purity 35.38% was supplied by BDH Chemical Ltd, Poole England. Ethanol (Absolute) of purity 99.7% was gotten from Johnson Solomom (Export) Ltd, London, England. NaOH of M. W. 40.0g/mol was also supplied by BDH. Polyvinyl Alcohol (PVA) of 98% purity was supplied by BDH. Raw kaolintic clay sample. Toluene Analar-M.W. 92.14 and 0.86g/mol.

2.2 METHODS

Nanoindentation was performed on all the samples to determine the localized mechanical properties of polymer nanocomposites. Thin film samples were prepared and tested for all systems. The parameters used for each test series were the same except for the different contact depth and contact area. Nanoindentation software performed all calculations of young's modulus and hardness based on the input parameters, and generated 3D topography plotting between maximum force exerted on the sample to the indentation depth for each sample.

When a polyethylene sample is subjected to external stress there is an initial deformation prior to yield that is homogeneous and is largely recoverable when the stress is removed. This initial region of elasticity can vary from 1% to 2% for highly crystalline samples up to 50% or more in high co-unit copolymers and ionomers (Andrew, 2000).

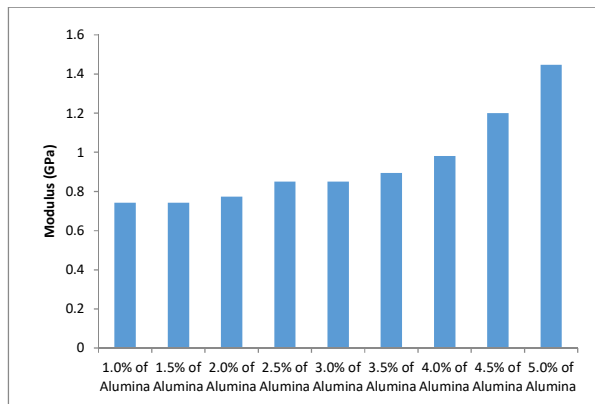


Fig 2.1: Nanoindentation elastic modulus summary results showing the variation of modulus with concentration of alumina

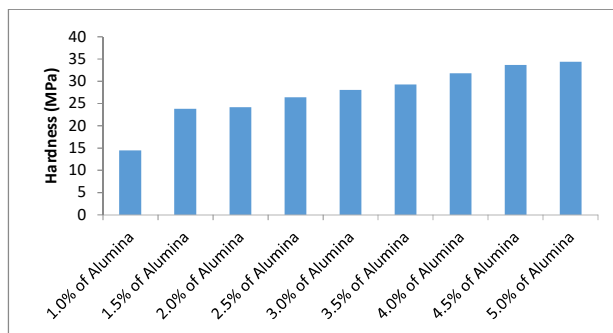


Fig 2.2: Nanoindentation hardness summary results showing the variation of hardness with concentration of alumina.

From Fig 2.1, and Fig 2.2, there was increase in hardness and elastic modulus across all the doping points. The hardness of ordinary LDPE is 13.5MPa Andrews (2000). After doping with alumina, it was found to have increased within the range of (14 – 34MPa) in this work. As for elastic modulus, (Maziyar and Hassan., 2014) got a maximum of 0.48GPa by using carbon nanotubes on LDPE while this work produced (0.74 – 1.44GPa). This may be associated with the fact that the alumina used in this work is denser than the carbon nanotubes used by Maziyar and Hassan, (2014).

3.0 DISCUSSION

Microhardness increases when a sample is dried or fired, rising with increased crystallinity and lamellar thickness. The increase in the samples hardness and modulus from fig 2.1 and fig 2.2 shows that these two properties have been enhanced. When the microhardness of various polymers is compared,

their ranking is similar to that of the elastic modulus (Andrews, 2000).

The Modulus of elasticity for LDPE doped with alumina increased in all compositions compare to the pure LDPE whose value is 0.3 GPa. The result is due to the presence of more alumina filler and good interaction between the filler and the matrix. The behaviour of alumina in the LDPE as it affects modulus of elasticity according to Supri *et al* (2008), is that the nanoparticles reduces the molecular mobility of the polymer chains resulting in a less flexible material with a higher Young's modulus. This improvement in hardness and elastic modulus is encouraging because insulating materials should have certain mechanical strength to withstand vibrations depending on the area of application to which they are subjected

4.0 CONCLUSION

The nanoindentation result showed that the elastic modulus and hardness are largely enhanced across all the concentrations of alumina. The samples (LDPE/alumina) possessed comparatively good elastic modulus and hardness within the range with which it was fabricated for use.

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THE EFFECT OF COBALT ON THE MECHANICAL PROPERTIES AND CORROSION RESISTANCE OF Al-Si-Fe ALLOY IN 0.5M H₂SO₄ SOLUTION

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ABSTRACT

The effect of cobalt on the mechanical properties and corrosion resistance of AlSi-Fe alloy was investigated. Alloys of varying percentages of cobalt from 0.1 to 0.5% at 0.1% interval with the percentages of iron and silicon kept constant were sand casted into cylindrical test bars of dimension 15×400mm. The casts were machined into test specimen sizes, heat treated and the mechanical properties (Tensile strength, Hardness and impact energy) of the alloy samples were determined and also the corrosion characteristics of the alloys in 0.5M H₂SO₄ solution at room temperature (280C) were investigated by electrochemical methods.. The results showed that there was a decrease in tensile strength with increase in wt% cobalt addition, the percentage decrease in strength been from a maximum value of 71.6 N/mm² at 0 wt% to a minimum of 52.1N/mm² at 0.4 wt% of cobalt addition. The impact energy increases to a maximum value of 15.2 Joule at 0.1 wt% cobalt addition and then decreases with further cobalt addition. The maximum hardness value of 70266.6 Mpa was obtained at 0.1 wt% cobalt addition, and a minimum corrosion rate of 0.000713 mm/year and maximum linear polarization resistance of 30228Ω at 0.2 wt% cobalt addition.

KEY WORD: Polarization resistance, Cobalt addition, Mechanical properties,

1.0 INTRODUCTION

Foundry aluminium alloys based on the Al-Si system are widely used in the automobile field since they provide excellent fluidity and castability, good resistance to corrosion and mechanical properties (Leo and Cerri, 2003; El Sebaie et. al., 2008; Haghshenas et. al., 2008; Hassan and Aigbodon, 2009). The presence of Si, Mn, Cr and Fe in aluminium causes various precipitates to form during solidification of the alloys (Allen, 1979). The development of dendritic network, precipitation of AlFe phases, eutectic reaction involving the precipitation of Si and Fe phases and formation of complex eutectic phases of MnAl₂, CrAl₂, (FeCr)₃ SiAl₁₂, (FeMn)₃ SiAl₁₂ all took place during the solidification (Rajan et al, 1988). However the formation of these phases depends solely on the composition of the alloys and the cooling rates (Avner, 1974). Manganese and Chromium complexes are easily visible under the optical microscope because of their distinct grayish-white colour tinged with reddish shadings and steel-gray like colour respectively (Brumbough, 1979). While the iron phase is present in both needles (β) and Chinese script form α (Ghosh et al, 2004 and Avner, 1974). The mechanical properties of these alloys are solely dependent and guarded by the composition and the types of phases that are formed and precipitated during the solidification of the alloys immediately after casting (Metal Hand Book, 1979A). Aluminium – Silicon – Iron alloys is also a casting alloy with major alloying element Si followed by iron. The iron content in this alloy in small amount increases the strength and hardness of the alloy and reduces hot - cracking tendencies in casting (Kenneth, 1999). However, it has been known since 1920's that plates and needles of Al-S-Fe constituent reduce the strength of aluminium-silicon-casting alloys (Smith, 1981). Because of the combined excellent mechanical properties and corrosion resistance, aluminium alloys have found wide applications in aviation, automotive, marine Industries, etc. (Avner, 1974).

The research is aimed at investigating the effect of cobalt on the mechanical properties and corrosion resistance of Al-Si-Fe alloy in 0.5M H₂SO₄ solution in age hardened condition at room temperature.

2.0 METHODOLOGY

2.1 MATERIAL

The materials used for this research for the production of Al-Si-Fe (control) and Al-Si-Fe-Co alloy systems includes high purity aluminum obtained from Northern Cable Company NOCACO Kaduna, Cobalt metal powder gotten from Steve Moore chemicals in Zaria and solid Ferro-Silicon alloy (FeSi) obtained in required proportion from Metallurgical and Material Engineering Workshop, Ahmadu Bello University, Zaria. etchants, baker, 0.5M H₂SO₄ acid solution, thread (for suspending the coupons in media), measuring cylinder, Charcoal, Graphite crucible, 2kg Silica sand and Bentonite, moulding boxes from National Metallurgical Development Center (NMDC), Jos.

2.2 EQUIPMENTS

The following equipment were used; Newman Sand mixing machine, FD1051, 1425rpm, serial no-H04194, Sx-5-12 box electric resistance furnace, max temp 1200°C, 10kg/15m³ capacity, Ramming flask, ramming stick, Graphite crucible, Pattern (15mm dia by 400mm). Denison impact tester, MicroVickers Hardness tester machine, Hounsfield extensometer type 'W', Polishing machine, Camry weighing scale, max weight FD 216, 1-20kg, 0.95p, AUTOLAB potentiostat (model type-PGSTAT204), Harrison Lathe machine, M300, Bench vice, Hack saw.

2.3 EXPERIMENTAL PROCEDURE

Six different compositions of alloys were produced in which the amount of cobalt in the alloy was varied from 0.1 to 0.5% in steps of 0.1% while the percentage of silicon and iron were kept constant as shown in Table 2.1. Each composition was melted separately in graphite crucible. The melting was done using an electric resistance furnace that was allowed to heat to 750°C with the required mass of Aluminum before the crucible was removed and other alloying elements allowed to melt then the ferro-silicon was added, After about 10 minutes cobalt powder was added into the crucible and the alloy was stirred for one minute and the crucible was removed from the furnace and the molten alloy was poured into the already prepared pattern in the sand mould (Abdulwahab, 2007).

Table 2.1: Chemical Composition of the produced Alloy

S/N	% Al	% Si	% Fe	% Co
1	97.2	2.1	0.7	-
2	97.1	2.1	0.7	0.1
3	97.0	2.1	0.7	0.2
4	96.9	2.1	0.7	0.3
5	96.8	2.1	0.7	0.4
6	96.7	2.1	0.7	0.5

2.3.1 Sample Preparation

The charcoal furnace which uses charcoal as fuel was turned on, charcoal was then added and pressured air was supplied to the furnace system. A graphite crucible was set on the furnace and heated. The required mass of Aluminum was the first element to be put into the crucible, it was allowed to melt then the ferro-silicon was added. After about 10 minutes cobalt powder was added into the crucible and the alloy was stirred for one minute and the crucible was removed from the furnace and the molten alloy is poured into the already prepared pattern in the sand mould (Abdulwahab, 2007). The cast samples produced were machined on a lathe to standard tensile, hardness, impact, and corrosion test specimens.

2.3.2 Heat treatment process

Heat treatment improves the strength of aluminum alloys through a process known as precipitation-hardening which occurs during the controlled heating and cooling of an aluminum alloy leading to the formation of precipitates in the aluminum matrix. The improvement in the mechanical properties of Al alloys as a result of heat treatment depends upon the change in solubility of the alloying constituents with temperature (Mohamed and Samuel, 2012). The samples after machining were then artificially age hardened with the aid of an electric resistance furnace, the samples were solution heat treated at temperature of 490°C, soaked at this temperature for 6 hours, and then rapidly quenched in warm water. The quenched specimens were cooled at controlled rate through the critical range of 450°C to 200°C for six hours before cooling in air (Abdulwahab, 2007).

2.4 Potentiodynamic Polarization method

Each of the samples were prepared for the test by passing an electric wire through the drilled sample and insulating every other part of the sample except the contact area as shown in plate 2. Potentiodynamic polarization tests were carried out using three electrode glass cells with an AUTOLAB potentiostat (model type-PGSTAT204) which was connected to a personal computer to control the experiments (shown in plate 3). A graphite rod, saturated Ag/AgCl, and aluminum alloy specimen were used as counter, reference and working electrode respectively. The working electrode samples were positioned at the glass corrosion cell, leaving an area of 0.76 cm² in contact with the solution. Polarization tests were carried out in a solution of 0.5M H₂SO₄ solution with each aged hardened Al alloy with varying concentrations of cobalt metal powder at room temperature using the potentiostat. The polarization experiments data were analyzed by NOVA software version 1.10.1.9. The polarization curves were carried out with -1.5V cathodic potential and +1.5V anodic potential at a scan rate of 0.0120V/Sec. in accordance with ASTM G59-97



Plate 2: Corrosion test sample



Plate 3: Corrosion test set up

2.5 MECHANICAL PROPERTIES

2.5.1 Determination of Tensile Strength

The tensile test was performed using the Hounsfield extensometer. Dumbbell shapes were cut from each sample with total length of 40mm, gauge length of 30mm and 6mm diameter and the larger diameter as 10mm. The sample were mounted on the machine and the tensile forces together with the corresponding extensions were recorded. Test procedure was in accordance with ASTM1391-1947 and tensile strength was calculated using equation 1.

$$\sigma = \frac{P}{A} \quad 1$$

This test was carried out using the Izod Impact testing machine. The samples were machined to 45mm length and 10mm diameter with a V notch made at a distance of 31.75 mm from the top at a depth of 2.0 mm and a notch tip radius of 0.02 mm at an angle of 45°. Impact strength was calculated by equation 2. The experimental procedure was replicated three times and the averages of required parameters were recorded in accordance with ASTM D3763

$$\text{Impact strength} = \frac{I}{A} \quad 2$$

2.5.3 Determination of Hardness Value

The hardness test was done using the Micro Vickers hardness tester which is a visual hardness testing machine with 500g capacity. The Vickers hardness number was recorded from the results obtained from the machine.

3.0 RESULTS AND DISCUSSION

3.1 RESULTS

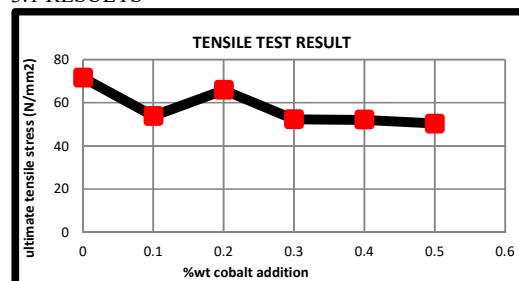


Fig 3.1: Variation of Ultimate tensile strength with %wt Cobalt addition

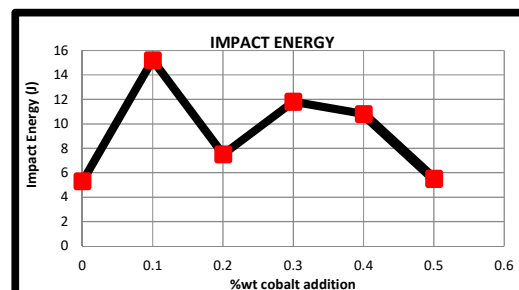


Fig 3.2: Variation of Impact Energy with %wt Cobalt addition

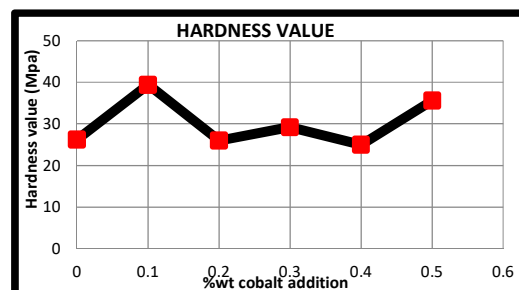


Fig 3.3: Variation of Hardness Value with %wt Cobalt addition

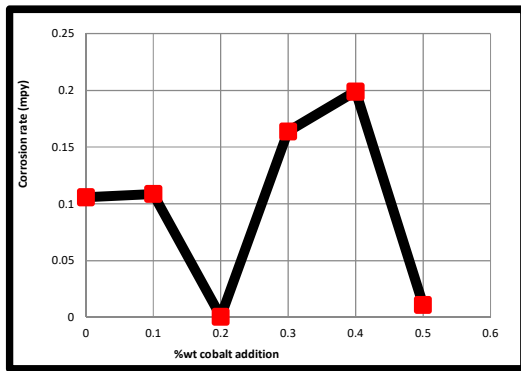


Fig 3.4: Variation of Corrosion rate with %wt Cobalt addition
Tafel plots

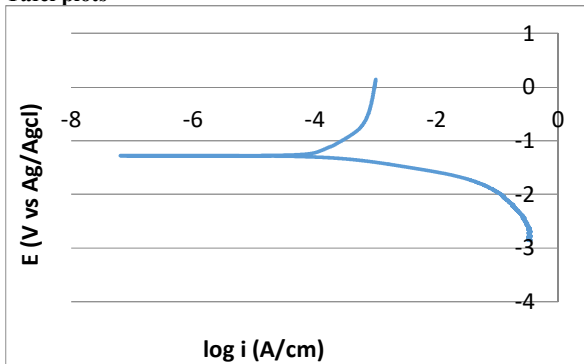


Fig 3.5: Alloy with 0.0 %wt Cobalt

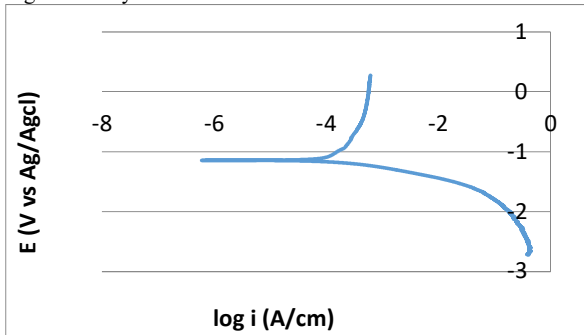


Fig 3.6: Alloy with 0.1 %wt Cobalt

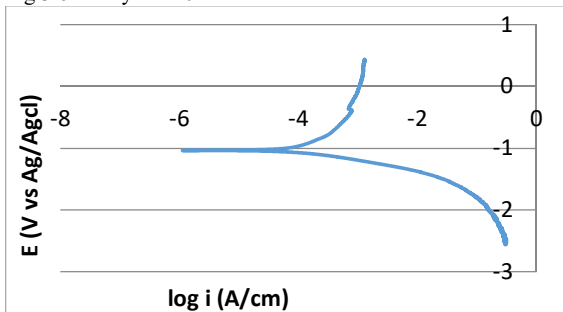


Fig 3.7: Alloy with 0.2 %wt Cobalt

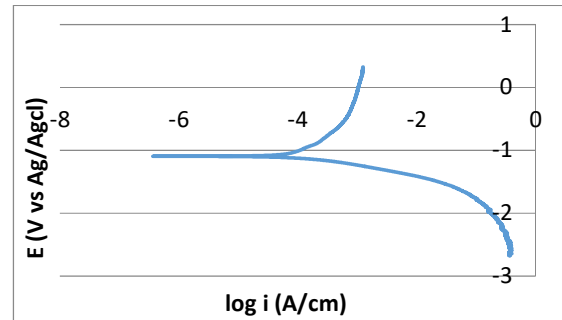


Fig 3.8: Alloy with 0.3 %wt Cobalt

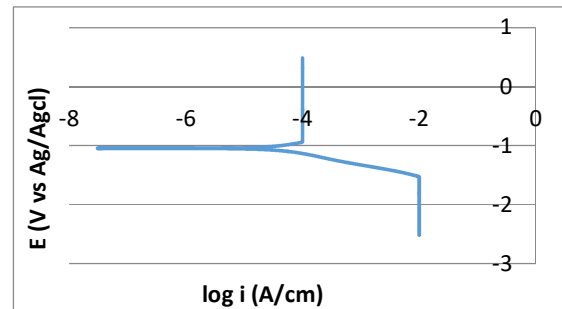


Fig 3.9: Alloy with 0.4 %wt Cobalt

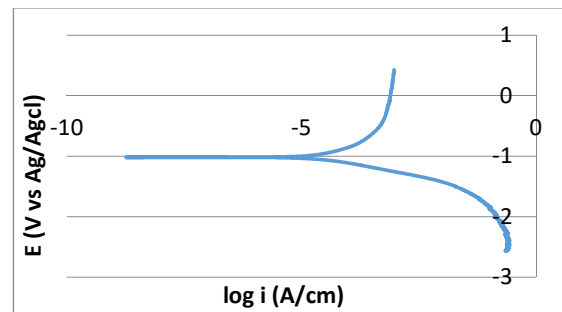


Fig 3.10: Alloy with 0.5 %wt Cobalt

3.2 DISCUSSION

The mechanical properties of the experimental alloys are shown in (Figure 3.1 - 3.3), the results obtained from the tensile test shows that there was a gradual decrease in ultimate tensile stress with %wt cobalt addition. The highest value of the ultimate tensile strength is at 0.0% cobalt addition (control sample). Therefore for any high stress application, no cobalt addition is recommended. The impact test result shows that there was an increase in the toughness or impact energy of the modified alloys, with the maximum impact energy of 15.2 J resulting at 0.1 %wt cobalt addition but dropped sharply beyond 0.1 %wt Cobalt addition. Therefore for areas where toughness is an optimum requirement, cobalt addition of 0.1 % wt is recommended for the alloy. The results obtained for the hardness test shows an increase in the hardness value of the alloy with the addition of cobalt, the maximum hardness value results at 0.1 %wt cobalt addition. The result obtained from the electrochemical corrosion test showed minimum corrosion rate at 0.2 %wt cobalt addition. The Tafel plots of the test specimens are shown on the figures 3.5 to 3.10, the tafel plots was performed by polarizing the specimen anodically (positive going potential) and cathodically (negative going potential) from the corrosion potential. The electrochemical kinetic parameters obtained relating to the curves are given on table 3.1. It can be seen that the current density i_{corr} decreases with increase in cobalt concentration, with the least current density obtained at 0.5% cobalt addition.

TABLE 3.1: Corrosion test result

% cobalt	Current density (A/cm ²)	Anodic constant (v/dvc)	tafel Cathodic constant (v/dvc)	Linear polarization (?)	Corrosion potential (v)	Corrosion rate (mm/yr)
0.0						
0.1	9.71E-06	0.4959	0.082351	402.25	-1.2898	0.1059
0.2	9.97E-06	0.55097	0.052427	265.54	-1.1632	0.10874
0.3	6.54E-08	0.076478	0.067141	30228	-1.1067	0.000713
0.4	1.50E-05	0.16111	0.68601	479.97	-1.04	0.16395
0.5	1.83E-05	0.47118	1.1462	1012.2	-1.0534	0.19896
	1.00E-06	0.13952	0.031769	1424.9	-1.0322	0.010953

CONCLUSION

The results obtained from the investigation of the effect of cobalt on the mechanical properties and corrosion resistance of Al-Si-Fe alloy in 0.5M H₂SO₄ solution was used to draw the following conclusions.

- The results of corrosion and mechanical test carried out showed that there was a decrease in the tensile strength of the modified alloy from 71.6 to 50.4 N/mm².
- There was also an increase in the hardness value of the modified alloy with a maximum hardness value of 70266.6 Mpa resulting at 0.1% cobalt addition.
- There was increase in the toughness value of the modified alloy, with the highest toughness value of 20.6 Joule resulting at 0.1% cobalt addition.
- The electrochemical corrosion test showed that the minimum corrosion rate of 0.000713 mpy results at 0.2 %wt cobalt addition.

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EFFECT OF BAGASSE ASH RE-INFORCEMENT ON THE MECHANICAL AND PHYSICAL PROPERTIES OF POLYMER BLEND COMPOSITE

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ABSTRACT

The research presents the “Effect of bagasse ash re-inforcement on the mechanical and physical properties of polymer blend composite”. The polymer blend matrix was re-inforced with bagasse ash particles (BAP) from 0-25 wt%. addition at an interval of 5 wt%. The mechanical properties test showed that there was an average decrease in the impact energy value with increase in the BAP addition. 0 wt%. of the BAP addition gave the maximum impact energy value of 1.6 J. the hardness value increases from a minimum hardness value of 5.87 HV0.2 at 0 wt% BAP addition to a maximum of 11.26 HV0.2 at 25 wt% BAP addition, 20 wt% of the BAP addition gave the highest tensile strength of 21.65 N/ [mm] ^{^2}. While the physical properties test results showed that the percentage Water absorption increases with increase in BAP addition, 25 wt%. Bagasse particle addition gave the highest percentage water absorption of 1.92 %. This shows that the polymer blend matrix is hydrophobic but with increasing BAP addition, it gains hydrophilic tendencies. The percentage thickness swelling also increases with increase in BAP to a maximum at 25 wt%. with highest percentage thickness swelling of 13.726 % and for the Density test, 0 wt%. of the BAP addition gave the lowest density value of 0.93 g/cm³.

Keyword: Polymer blend, Bagasse ash, Mechanical properties, Impact energy

1. INTRODUCTION

A polymer blend is a mixture of two or more polymers that have been blended together to create a new material with different physical properties. Generally, there are five main types of polymer blend: thermoplastic–thermoplastic blends; thermoplastic–rubber blends; thermoplastic–thermosetting blends; rubber– thermosetting blends; and polymer–filler blends. (Jyotishkumar et al, 2015). Blending of two or more polymers offers a good possibility to modify thermoplastic material so as to improve their properties (Tresa et al., 2013). Polymer blending has attracted much attention as an easy and cost-effective method of developing polymeric materials that have versatility for commercial applications. In other words, the properties of the blends can be manipulated according to their end use by correct selection of the component polymers. (Jyotishkumar et al, 2015). Today, the market pressure is so high that producers of plastics need to provide better and more economic materials with superior combinations of properties as a replacement for the traditional metals and polymers (Jyotishkumar et al, 2015).

Like numerous other petroleum-based polymers, many properties of polypropylene (PP) can also be improved through blending and composite formation. (Yu et. al, 2006). In recent years there is pressure from environmentalists to reduce forest use and regulatory legislation pending on the disposal of agro-fibres and polymer wastes (Pothana et. al., 2003; Sausa et. al., 2004). The use of lignocellulosic natural fibres/particles as fillers or reinforcements has been gaining acceptance in polymer applications in the past few years (Bibo et. al., 1997; Godwin and Matthews, 1980) . The natural fillers can be obtained from several sources, both from forestry and agricultural resources. Waste from agriculture delivers renewable, abundant, natural materials that serve as fillers for polymers, with the benefit of lower cost and improved mechanical properties (Atuanya et. al., 2014). Many researches have been reported on natural filler reinforced thermoplastic composites, which have successfully proved their applicability in various fields (Pothana et. al., 2003). Thermoplastics such as polyethylene (PE), polypropylene (PP) and polyvinylchloride (PVC) have been compounded with natural fillers such as wood, hemp, cotton, coir pineapple leaf, oil palm and banana to prepare composites (Casaurang et al., 1999; Joseph and Thomas, 1993; Aigbodion et al., 2010). The recycled low

density polyethylene (RLDPE) is a polymeric waste found littering the streets and is popularly known as “*Pure water Sachet*” used in packaging of drinking water.

Polypropylene (PP), a semicrystalline polyolefin polymer with very interesting mechanical properties (ductility and stiffness), good thermal properties, and excellent chemical and moisture resistance is also easy to process. Limitation of PP is its poor adhesion to the surface of other phases such as rubber or polar materials. This is primarily a result of the nonpolar nature of PP (Pothana et. al., 2003; Sausa et. al., 2004). Traditional fillers for PP are calcium carbonate, talc, glass fiber, wollastonite, mica, glass beads and wood flour (Emi, 2014)

Bagasse is the residue fiber remaining when sugar cane is pressed to extract the sugar. Bagasse is composed of fiber and pith, the fiber is thick walled and relatively long (1.4 mm) (Aigbodion, 2010). Bagasse is a plentiful lignocellulosic waste typically found in tropical countries that process sugar cane, such as Brazil, Indian, Cuba, China and Nigeria (Aigbodion et al, 2010). The bagasse fiber (BF) bundles are usually coarse and stiff. It is used either as a fuel for boilers by the sugar factory or as a raw material for the manufacture of pulp and paper products (Maldas and Kokta, 1990).

The incorporation of proper filler increase interfacial adhesion between matrix and disperse phase, refines blends morphology and therefore leads to an improvement of processing and application properties of the final material (Emi, 2014).

2.0 EXPERIMENTAL PROCEDURE

2.1 MATERIALS AND EQUIPMENT

The polypropylene (PP) used was purchased from NILEST, Samaru Zaria-Kaduna. It was supplied in solid pellets form (see plate 1) and was used as one of the materials for the formulation of the polymer blend composite, the RLDPE used were collected literally from the streets of Samaru, Zaria and around refuse dumps, the RLDPE were washed, dried and shredded using a Changda single shaft shredding machine, as shown in plate 2. The bagasse used in this work was obtained from ‘Makarfi’ area of Zaria in Kaduna state Nigeria.



Plate 1: Sample of polypropylene pellet



Plate 2: Changda single shaft shredding machine

The equipment used in the research were: Steel mould (100mm×100mm×3mm), Set of sieves, digital weighing balance, hack saw, grinding machine, Vernier caliper, Two roll mill compounding machine, molding machine Wenzhou Zhiguang heavy duty pressing machine, Foil pape, bending and Hounsfield Tensometer (TYPE W), Micro Vickers hardness tester (Model MV1-PC) , Charpy Impact testing machine (cat.Nr.412), Electronic compact weighing scale (Kerro BL3002), Changda single shaft shredder, Charcoal furnace

2.2 Preparation and processing of bagasse ash particles (BA_p)

The Sugarcane/bagasse fibre as collected were thoroughly washed with distilled water to get rid of dirt and excess sugar, it was then dried to remove moisture and treated using 1% NaOH solution (see plate 3). To obtain bagasse ash, the fibres were packed air tight in a graphite crucible, placed on a charcoal furnace and heated to a temperature of about 1000°C for about 6hr.

After carbonization the bagasse ash was ball milled at 200 rpm for 3 h to form carbonized bagasse particles (CBp). The particle size analysis of the bagasse particles was carried out in accordance with ASTM-60. 100 g of the bagasse particles was placed onto a set of sieves arranged in descending order of fineness and shaken for 15 min which is the recommended time to achieve complete classification. The weight retained on 75µm (plate 4) was used in this research (Pothana et al., 2003).



Plate 3: Treated Bagasse fibre



Plate 4: Bagasse ash particles (75µm)

2.3 Composite preparation and Fabrication

2.3.1 Blending and Compounding

The composite was prepared by mixing the polypropylene (PP), Recycled Low Density polyethene (RLDPE) in a blend ratio of (80 %PP and 20 % RLDPE) and bagasse ash particles BA_p varied from 0 to 30 wt% with a 5 wt% interval in a rapid two roll mill compounding machine. This machine contains two heated cylinders (rotating at selected speeds) which recasts the components together as they are gradually applied into the rolls. The temperature of the rolls was set at 160 °C for 30 mins to allow for preheating. The PP was then applied to the compounding machine and allowed to melt properly before adding the shredded Recycled low density polyethene (RLDPE). This also melts and blends properly with the already melted polypropylene. The Bagasse ash particles (BA_p) reinforcement was then added and properly blended to a near homogenous mixture, which was collected in a pan below the heated roll using a scraping tool.

2.3.2 Pressing

After the compounding process, the polymer blend composite material was then wrapped in foil paper and lubricated with curing oil (to avoid the material from sticking to the foil or the machine surface), it was placed in a mould (100×100×4mm) and placed in a Wenzhou Zhiguang heavy duty pressing machine which further hot press and consolidate the various layers of the polymer blend at a condition of (pressing pressure, temperature and time of 130 psi, 150 °C and 5 mins respectively). Test specimen samples were cut from the composites for the physical and mechanical test according to the recommended standards. Prior to the test, all the samples were conditioned at a temperature of 23 ± 2 °C and relative humidity of 65% according to ATM D618-08 (Atuanya et al., 2011).

2.4 Physical and Mechanical Properties Determination

Test piece specimens were machined to require test dimensions according to standards from the polymer blend composite samples produced.

2.4.1 Determination of Density

A clean sample of the polymer blend composite specimen with dimension 30mm wide and 20mm long was weighed in air using a laboratory balance and the volume of the sample was determined by multiplying the length, width and thickness. It was noted that Archimedes principle could not be used because of the light weight of the composite which causes it not to be totally immersed in water, thereby causing partial water displacement. The density of the sample was estimated from equation 1 (BSI, 1993):

$$\text{Density} = \frac{\text{Mass}}{\text{Volume}} \quad 1$$

2.4.2 Determination of the Percentage Water Absorption (WA)

Specimens with dimensions of 50 mm × 50 mm were prepared for evaluation of the Water Absorption. The initial weight of the sample W₀, was obtained using a laboratory weight balance then the sample was immersed in water to be soaked for 24 hr before further measurement of the weight, after all moisture have been wiped off. The values of the WA in percentage was calculated using the expression (BSI, 1993)

$$\text{WA} = \frac{(W_{24} - W_0) \times 100}{W_0} \quad 2$$

Where WA is the Water Absorption rate (%), W₀ and W₂₄ are the initial weight before immersion in water and final weight of the specimen after immersion for 24 hrs.

2.4.3 Tensile Strength Determination

The tensile strength measurement experiments were performed on Hounsfield Tensometer testing machine. For tensile tests the composite samples were cut into dumb-bell shape with cross sectional dimension of 135×14×4 mm in accordance with ASTM D638. The tests were performed at a constant strain rate of 0.5 mm/min. Tensile strength was calculated by the formula:

$$S = P/A \quad 3$$

Where P is the maximum load (N); A is the area of the specimen (mm²).

2.4.4 Determination of Hardness Value

The hardness test was done using the Micro Vickers hardness tester which is a visual hardness testing machine with 100kg capacity. The Vickers hardness number was recorded from the results obtained from the machine.

2.4.5 Determination of Impact Energy (IE)

The impact test was performed according to ASTM D256 standard using the impact testing machine. The test method determines the charpy impact strength of the polymer blend

composites. Charpy type test in which the specimen is held as a cantilever beam (usually vertical) and is broken by a blow delivered at a fixed distance from the edge of the specimen clamp was adopted. Three specimens for each sample having a size of 63.5 mm by 10 mm and 4 mm thickness were prepared and tested. The V notch was made at a distance of 31.75 mm from the top at a depth of 2.0 mm and a notch tip radius of 0.02 mm at an angle of 45° was used. Impact strength was calculated by (Husein et al., 2011)

$$\text{Impact strength} = \frac{J}{A} \quad 4$$

Where J = Energy absorbed (J), A = Area of cross section of the specimen below the notch (mm²).

3.0 RESULTS AND DISCUSSION

Density is one of the most important physical properties of a material. The density of the reinforced polymer blend composites is presented in Fig. 1. The results revealed that the presence of bagasse ash particulates (BAp) slightly increased the density of the polymer blend composites. The increase in density can be related to the fact that the BAp is dense in weight (1.477 g/cm³) compared to the polymer blend (0.93 g/cm³) and occupies a substantial amount of space. Hence, it can be said that with an increase of percentage of BAp the material becomes dense in weight. For example, the density of the reinforced composites increased from 0.93 g/cm³ at 0 wt% BAp addition to 1.17 g/cm³ at 25 wt% BAp. Which is 26% increase in weight and within limits.

The percentage Thickness Swelling (TS) and Water Absorption (WA) are shown in Fig. 2. Increasing the BAp wt% increased the TS and WA for 24 hours immersion. 25 wt% increases in BAp addition had the highest percentage thickness swelling and water absorption of 1.9% and 13.7% respectively which is an increase of 285% and 276%. This is due to increased porosity and easy diffusion on the polymer blend density as a result of the exposure offered by the hydrophilic BAp on the hydrophobic polymer blend (80% PP and 20% RLDPE). The swelling that occurs is the sum of two components, namely, swelling by hygroscopic particles and the release of compression stresses imparted to the composite during the pressing of sample in the hot press.

The tensile strength of PP/RLDPE at various filler loadings of BAp and as well of pure blends are shown in Fig. 3. The tensile strength enhancement is found up to a filler loading level of 20 wt% (21.65 N/mm²) and thereafter a slight decrease was observed at 25 wt% (19.9 N/mm²). The tensile strength increased from 10.93 N/mm² for the pure blend matrix to a maximum of 21.65 N/mm² which is a remarkable 98% increase in strength and work may be due to the good distribution and dispersion of the BAp in the polymer blend resulting in strong particles/pure blend matrix interaction which consequently increases the ability of the BAp to restrain gross deformation of the polymer blend matrix. The decrease in tensile strength as the BAp increased beyond 20 wt% is due to the interference of particles in the mobility or deformability of the matrix through the physical interaction and immobilization of the polymer blend matrix by the presence of mechanical restraints, thereby reducing the strength (Amir et al., 2011; Punyapriya, 2012).

The results of hardness values are shown in Fig. 4, it is observed that with increase in wt% BAp in the polymer blend matrix the hardness values of the composites increases from 5.9 Hv_{0.2} for pure blend to maximum value of 11.2 Hv_{0.2} at 25 wt%. The increments are attributed to an increase in the percentage of the hard and brittle BAp as revealed by the composition of the bagasse particles in (Aigbodian, 2013). Also the differences in coefficient of thermal expansion (CTE) between the bagasse

particles and polymer matrix resulted in elastic and plastic incompatibility between the matrix and the bagasse particles (Shibata et al., 2005). A substantial improvement in hardness values was obtained in the reinforced polymer matrix. This is in line with earlier researches of (Maldas and Kokta, 1990; Amir et al., 2011; Punyapriya, 2012).

Fig. 5 illustrates the variation of impact strength with bagasse particle loading. It is clear from the Fig. that the impact strength decreases with BAp addition. An increase in the concentration of BAp reduces the ability of matrix to absorb energy and thereby reducing the toughness. The reduction in impact energy with increasing bagasse particle loading might also be due to the decreased deformability of a rigid interface between the BAp and polymer blend matrix. The pure blend and the composite with 5 wt% BAp have the highest impact energy, indicating the greater toughness values of all the investigated samples.

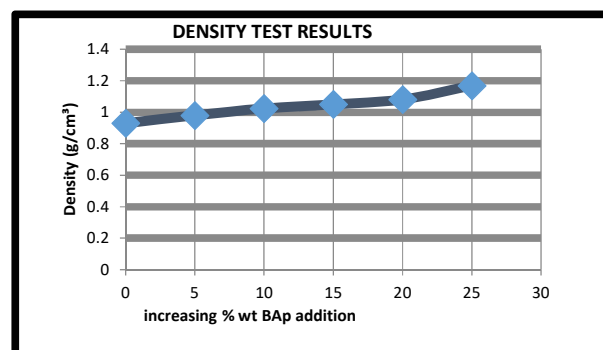


Fig. 1: Variation of density with wt% BAp.

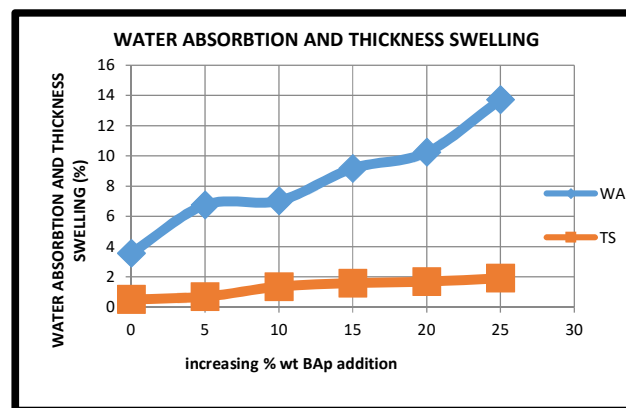


Fig. 2: Variation of % Water absorption and % Thickness swelling with wt% BAp addition.

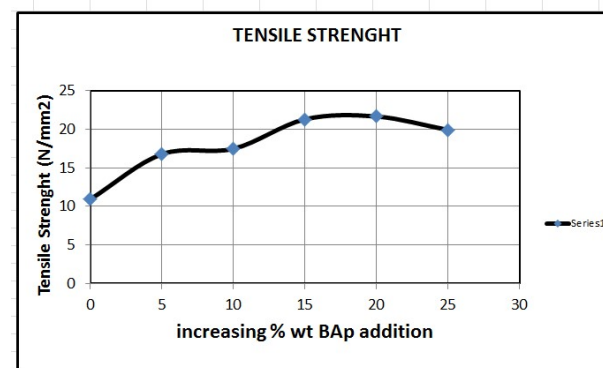


Fig. 3: Variation of Tensile Strength with wt% BAp.

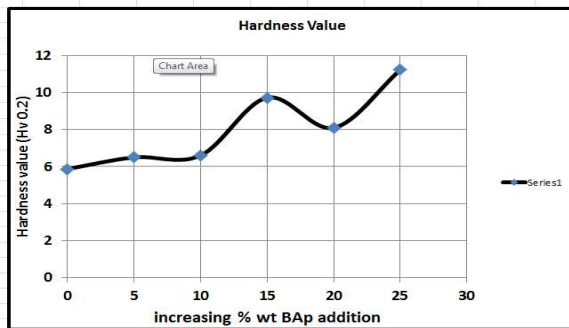


Fig. 4: Variation of Hardness Value with wt% BAp.

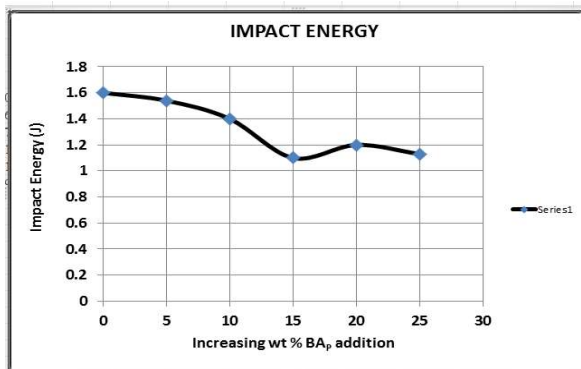


Fig. 5: Variation of Impact energy with wt% BAp.

4.0 Conclusions

In this present work, some physical and mechanical properties of polymer blend composites reinforced with BAp has been investigated. From the results and discussion presented above, the following conclusions can be made;

- This work shows the successful fabrication of polymer blend and the BAp composite by compounding and compressive molding.
- The bagasse particles added to the pure polymer blend improved its rigidity and hardness values of the composites.
- The tensile strength of the composite increased with increasing percentage of the BAp to maximum of 21.65 N/mm² at 20 wt% BAp.
- The impact energy decreases with increase wt% BAp
- The developed composites have better properties at the ranges of 20 wt% BAp additions, and for optimum service condition, carbonized bagasse particles addition should not exceed 20 wt%.
- Based on the results obtained in this study, it is recommended that these grades of polymer blend composites can be used in the production of low strength car bumpers and other structural applications.

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CHITIN AND CHITOSAN A RAW MATERIAL FOR ENGINEERING IN NIGERIA: PANACEA FOR NATIONAL ECONOMIC DEVELOPMENT - CHALLENGES AND PROSPECTS.

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ABSTRACT

There was an increasing interest in application of chitosan and chitin in a wide range of the technologies taking advantage of their special properties such as low density, biocompatibility, biodegradability, reactivity, non-toxicity, adsorption properties, etc. Production, cost of chitin and its derivatives continue to be the prime factor limiting more widespread application of these substances. Despite its huge availability, the utilization of chitin in Nigeria has been restricted by lack of knowledge of what is chitosan by a layman. The challenge that the quality of our environment over the years has declined as a result of various human activities. The waste of these natural polymer (chitin) is a major source of surface pollutant in the coastal area. Today Chitosan is no longer considered as just a waste product from sea food industries. The production of Chitosan from crustacean shells as a food industry and composite industry, waste is economically feasible. The proper utilization of those water resources (aquaculture) in terms of research in chitin and chitosan can bring the economic and academic prosperity of the nation. The paper highlighted Science and technology play a vital role in a nation's development. The paper also enlighten the public and attempt has been made to understand the importance and characteristics, properties of chitosan by describing the various aspects, including the physical and chemical properties, processing, and applications. In view of this, the paper will attract the attention of entrepreneurs, industrialists, academicians, and environmentalists. It also discusses the various attempts reported on solving this problem from the point of view of science and technology has to a reasonable extend demonstrated the use of chitosan as a sources of material for composites production. Especially polymer industries cannot absolutely rely on synthetic fibres for finishing: But can complement the available synthetic fibres with natural fibre such as chitosan.

Keywords: Chitosan, Science, Technology, Production, Environment, Application Challenges.

Introduction

The eastern part of Nigeria is a sedimentary basin that is virtually riverine and estuarine. The major occupation of the people is fishing. Both shell and fin fishes are caught, processed, sold or eaten by the fishermen. Types of fishes consumed in coastal area are periwinkle, *Tympanotonus fuscatus*, clam (*Chione subrugosa*, *Geloina erosa*) and the mangrove oyster, *Crassostrea gasar*. These shell fishes are typically processed for consumption by removing the inedible shells. This waste shells which are the main source of chitin/chitosan are thrown away, which causes environmental pollution. Even in Korea, marine pollution by waste oyster shell has become one of the most serious problems of the aquaculture industry causing nasty odours (Yoon et al, 2004). Fish and other aquatic products account for a large proportion of the people's diet and intensification of fishing activities have led to the production of large quantities of these waste shells of chitin.

Several dumps of sea shell of chitin are common in many cities in the Niger delta including Port Harcourt, Warri, Yenogoa, Calabar, Oron, Uyo etc. Ansa and Bashir (2007) reported that the mean weight of the mangrove oyster in Port Harcourt was to be 24.67g (n=100) with only 8.63% as edible meat, while the rest consists of mostly shell wastes of chitin. The distribution of livestock and industry including fish and other sea food is increasing substantially in GDP of the country which accounts for over 30 % total agricultural sector and 21 % of GDP. This contribution would have been much greater had the waste been efficiently utilized. Efficient utilization of by-products has direct impact on the economy and environmental pollution of the country. Non-utilization or under utilization of waste shell chitin not only lead to the added and increasing cost of disposal of these products. Non-utilization and hazard aspects, in many cases, fish and other aquatic animals and their processing wastes have a potential for recycling raw materials or for conversion into useful products of higher values.

Waste in the sea food industry is characterized by high ratio of product specific waste not only does this mean that the generation of this waste product is unavoidable, but also that the amount and kind of waste product which consists primarily

of organic residue of processed raw materials, can scarcely be altered if the quality of the finished product is to be consistent. The utilization and disposal of product specific waste is difficult, due to its inadequate biological stability, potentially pathogenic nature, high water content, potential for rapid auto oxidation and high level of enzyme activity. The diverse types of waste generated by various branches of the food industry can be quantified based on the respective level of production.

As a way of waste management, a number of useful materials have been produced from sea shell wastes Agocha (2007) produced useful biomaterials such as chitin and chitosan from wastes periwinkle shells. Elsewhere, an arc based plasma torch operated at 25kW was used to convert fresh oyster shells into a useful product such as calcium oxide, CaO (Chae et al, 2006). Malu and Bassey (2003) evaluated the suitability of periwinkle shells as substitute for lime in glass manufacturing.

The entire coastline of Niger Delta is dotted by several communities, which rely closely on environmental resources particular fisheries for survival. However, the production of shell fish waste (chitin source) threatens the sustainability of the local fish industry and the environment in general. typically, the crustacean are caught and processed for food. While the fleshy portions are removed for consumption, the shells of chitin are thrown away freely causing environmental pollution. Examination of waste shell dumps show that the organisms are commonly found in the mangrove areas, where they are caught and their fleshy bodies used as source of protein and the waste shells discarded. Also because of the distance of these communities away from upland areas, construction aggregates, chipping, gravel, etc. are unavailable in these communities. Many communities in the Niger Delta are now converting waste crustacean shells which is rich in chitin for use in civil construction, erosion control materials and other related activities.

This paper has aimed to enlighten the communities in coastal region what is chitin/chitosan, applications of chitin, and how to make use of waste sea shell of chitin for other scientific and engineering materials. The results in the effective

management of waste shells (which is rich in chitin) is also given. The strategies taken to increase the applications of chitin in the Nigerian industries. The production of chitosan from waste shell obtained, a part of food industry and other scientific and technological applications is economically feasible, especially if it includes the recovery of the nutrients. The proper utilization of those water resources (aquaculture) in terms of applications of chitin/chitosan can bring the economic and academic prosperity of the nation.

What is Chitin/Chitosan?

Chitin is the second most abundant polysaccharide in nature after cellulose. It is widely distributed in animal and vegetable kingdom, constituting an important renewable resource. It is mainly derived from the exoskeletons of crustaceans, insects, mollusks and the cell wall of microorganisms (Muzzarelli, 1977). Chitin is generally represented as a linear polysaccharide composed of β -(1 $\rightarrow$ 4) linked units of N-acetyl-2-amino-2-deoxy-D-glucose. Chitosan is a modified natural carbohydrate polymer derived from chitin which has been found in a wide range of natural sources such as sea foods, shrimps, crustaceans, fungi, insects and some algae (Tolaimate *et al*, 2000). The shell of selected crustacean consists of 30-40% protein 30-50% calcium carbonate and calcium phosphate, and 20-30% chitin.

Chitosan is the deacetylated derivative of chitin, which is chemically defined as a homopolymer of β -(1 $\rightarrow$ 4) linked units of N-acetyl-D-glucosamine. While chitin is a linear chain of acetyl glucosamine groups and chitosan is obtained removing enough acetyl groups ($\text{CH}_3\text{-CO}$) and this is soluble in most diluted acids. It is white to light red solid powder, insoluble in water but soluble in organic acids. In essence, the actual difference between chitin and chitosan is the acetyl content of the polymer.

Chitosan is very reactive because of its free amino group. Chitosan is a non-toxic, biodegradable polymer of high molecular weight. Unlike plant fiber, chitosan possesses positive ionic charges (the amine group), which give it the ability to chemically bind with the negatively charged fats, lipids, cholesterol, metal ions, proteins, and macromolecules (Li *et al*, 1992). Chitosan has attained increasing commercial interest as suitable resource materials due to their excellent properties including biocompatibility, biodegradability, adsorption, and ability to form films, and to chelate metal ions (Rout, 2001).

Chemical Properties of Chitosan

This biopolymer has a number of chemical properties that make it suitable for several biomedical applications. Some of them are listed below (Dutta *et al*, 2004).

1. Chitosan is a linear polymer.
2. It has reactive amino groups ($-\text{NH}_2$).
3. There is availability of reactive hydroxyl groups ($-\text{OH}$).
4. It has chelating ability for many transitional metal ions.

Biological Properties of Chitosan

Besides the various chemical properties, chitosan shows diverse biological properties which are summarized (Younes and Rinaudo 2015) as follows:

1. Biocompatible : (Natural polymer, Safe and non-toxic, and Biodegradable to normal body constituents.
2. Binds to mammalian and microbial cells aggressively
3. Regenerative effect on connective gum tissue
4. Accelerates the formation of osteoblast responsible for bone formation

5. Haemostatic (causing stop bleeding)
6. Fungistatic (inhibiting the growth of fungi)
7. Spermicidal (birth control)
8. Antitumor or anticancer (inhibiting the growth of tumor cells)
9. Anticholesterol lowering agent
10. Central nervous system depressant (slow down the brain activity)
11. Immunoadjuvant (involved in the improvement of immune response)

Applications of Chitin and Chitosan in Industries

The poor solubility of chitin causes limitation in its applications. Besides these limitations, its various applications have been reported such as raw material for man-made fibers as absorbable sutures and wound dressing materials besides these chitin and chitosan fibres are also used in waste water treatment (Sridhari *et al*, 2000).

Chitin and chitosan have potential application in hair care. Chitin and acylated chitosan with an organic diacid anhydride are used for skin care, chitosan can be used in shampoos, hair colourants, styling lotions, hair sprays and hair tonics (Rinaudo, 2006). Chitin and chitosan are found to be used in creams as a moisturizer, nail enamel foundation, eye shadow and lipstick cleansing materials and bathing agents, chitin and chitosan are used in toothpaste, mouthwashes and chewing gum. Chitin is also used as dental filler (Dutta *et al*, 2004).

Chitosan act as chelating agent and heavy metals trapper (Khor and Lim, 2003). Chitosan N-benzyl sulphonate derivatives are used as sorbents for the removal of metal ions in acidic medium and chitosan can be used to remove the colour from dye house effluents as reported (Weltrowski *et al*, 1996). Chitin and chitosan are also found to be used effectively to remove arsenic from contaminated drinking water as well as to remove petroleum products from waste water (Saha and Sarkar 2013).

Chitosan is non-toxic therefore it is used in food industry. Microcrystalline chitin (MCC) is used as flavouring and colouring agent, shelf life as well as dietary fibre in baked food (Jianglian and Shaoying 2013). Chitin treated seeds (Wheat) have shown the growth accelerating and growth enhancing effects. The addition of chitin to the soil reduces the root knot worm infestation and suppression of fungal pathogens Dutta *et al*, (2004).

Tissue engineering is the development and manipulation of laboratory-grown cells, tissues or organs that would replace or support the function of defective or injured parts of the body (Khor and Lim 2003: Vankatesam and Kim 2010). The special attention on chitin has been paid for the repair of articular cartilage. Microporous chitosan/calcium phosphate composite scaffolds have been synthesized and characterized for tissue engineering. They reported that chitosan provides a scaffold form and calcium phosphate encourages osteoblast attachment and strengthens the scaffold (Zhang and Zhang 2001: Elzein *et al*, 2002).

Chitosan show good effect on wound dressing/wound healing process. Chitin can also be used as a coating on normal biomedical materials. Standard silk, and cargin sutures coated with regenerated chitin or chitosan show wound healing activities slightly lower than the chitin fibre (Murakami *et al*, 2010).

Chitin and chitosan are inexpensive and non-hazardous. They can be used for the preparation of dosage forms in commercial drugs (Andrady and Xu 1997) such as spread dry chitosan acetate and ethyl cellulose can be used as new compression

costs for 5-aminosalicylic acid (ASA) tablets was reported by Nunthanid *et al.* (2009). Chitin/ chitosan controlled delivery systems are in developing stage. It is being used for a wide variety of reagents in several environments Surini *et al.* (2003).

Gene therapy is a treatment of human disorders by introducing the genetic material into specific target cells of a patient where the production of the encoded protein occurs (Coesi *et al.* 2003).

The development of efficient and safe gene carrier systems that are capable of transferring DNA in the cells is a major goal of the gene therapy. Several literature survey show that chitosan is a suitable material for efficient non-viral gene therapy (Jayakumar *et al.* 2010).

Besides many good characteristics, chitosan has growth-inhibition effect on tumor cells (Carreno-Gomez and Duncan, 1997). The ligand-targeted approach is expected to deliver drugs to tumor tissues selectively with high efficiency. Although in vivo studies of targeted chitosan nanoparticles are currently limited, results from in vivo studies have demonstrated their promise for applications in cancer treatment and diagnosis (Hang, 2010).

As chitosan shows antimicrobial activity so its film have shown great promise for their application in food preservation. The antimicrobial activity limits or prevents microbial growth by extending the interval period and reducing the growth rate or decreasing live counts of microorganisms (Han, 2000) which support the chitosan film for its potentiality in packaging of food items and food preservation.

Gavhane and co-workers (2013) reported wide biomedical applications of chitin and chitosan, however, he also heighted some limitations such as allergy and constipation. Furthermore people with intestinal malabsorption syndroms should not use chitosan. Its adverse effects on the growth of children and on the outcome of pregnancy was also reported. However, application of chitin and chitosan have faced some limitation with high viscosity and low solubility at neutral pH (Kim and Dewapriya, 2014).

Properties of Chitosan in Engineering and Composite Applications

The elements for capacity that are necessary in the developing of advance engineering materials in Nigeria are availability of raw materials, human resource capital, infrastructure and appropriate technology. Development of advanced polymer composites materials having superior mechanical properties opened up new horizons in the engineering field. The so-called advanced composites have replaced metals because of their excellent properties and low density giving them high specific strength and stiffness. Such weight savings are highly desirable for applications in aerospace to transportation to reduce weight and associated fuel consumption. Another distinct advantage is ability to be engineered to obtain required properties in different directions by appropriate fibre placing in different layers of the laminated structure.

In this point of view, chitosan is an excellent candidate for all of these properties. Most of the synthetic polymer composites used today are non-biodegradable they are persistent in the environment. Chitosan is totally biodegradable. In this sense it is not a burden to the environment. The composite industry continues to look for eco-friendly processes that substitute for toxic chemicals and lightweight materials.

Chitin display interesting properties such as biocompatibility, biodegradability, low density, and its degradation product are

non-toxic, non-immunogens and non-carcinogenic. Therefore chitosan has perspective applications in the polymer and composites. Recently there has been a growing interest in the chemical modification of chitosan in order to its solubility and widen its applications in so many fields. The reaction of chitosan is more versatile than cellulose due the presence of amino groups (Dutta *et al.* 2004). An important advantage of chitosan is the possibility of agents that perform chemical modifications on its structure by binding to amino and hydroxyl groups.

Nutritive Values and the Chemical Consequents of Chitosan

Commercial chitin is extracted from crustacean waste of the fishing industry, the main chitin sources being the shells as shrimp, crab, lobster, prawn and krill. These crustacean wastes consist of chitin (20-30%), protein (30-40%), inorganic salts (mainly calcium carbonate and phosphate) (30-40%) and lipids (0-14%). These percentage vary considerably with the species and the season Synowlecki, (2003).

Consequently, the extraction techniques reported are very wide-ranging, since they depend significantly on the composition of the source. The majority of the techniques developed rely on chemical processes of hydrolysis of the protein and the removal of the inorganic material. A feasible sequence of isolation steps is a schematically represented in scheme 1. Some processes include a decolouration step of chitin by solvent extraction or oxidation of the remaining pigments. These isolation methods generally consume great amounts of water and energy a frequently give rise to corrosive wastes. At present, enzymatic treatments are being investigated as a promising alternative. To this end processes have been reported that use enzymatic extracts or isolated enzymes and biological fermentations, but they still lack the effectiveness of the chemical methods, mainly with respect to the removal of the inorganic materials (Goycoolea *et al.* 1997; Percot *et al.* 2003 Divya *et al.* 2014).

The procedure most frequently used to separate the proteins consists of treating the crustacean shells with diluted aqueous NaOH solutions (1-10%) at elevated temperatures (65-100°C). other reagents employed for removal of the proteins include: Na_2CO_3 , NaHCO_3 , KOH, K_2CO_3 , $\text{Ca}(\text{OH})_2$, NaHSO_3 , Na_3PO_4 , and Na_2S Roberts, (1992). The protein extracted can be recovered by lowering the pH of the solution to its isoelectric point for precipitation.

The recovered protein can be used as a high grade additive for livestock starter feeds. This decreases the manufacturing costs of chitin. The deproteinization processes using enzymatic extracts or isolated enzymes and biological fermentation have been tested with relative success, since they minimize the chemical degradation of chitin and lead to environmentally cleaner operations. However, enzymatic/microbiological treatments have the drawback of being time consuming and leaving the material with 1-7% of residual protein. These remnants cannot be diminished with the use of detergents Synowieki, (2000) or with the application of physicochemical techniques Goycoolea *et al.* (1997).

The main inorganic component of crustacean shell is calcium carbonate, which is usually eliminated with dilute HCl solutions (up to 10 wt %) at room temperature, although other acids (e.g. HNO_3 , HCOOH , HNO_3 , H_2SO_4 and CH_3COOH) have also been employed. It is evident that if the amount of acid employed is below the stoichiometric ratio, the demineralization reaction will not be completed. The acid concentration and the reaction time depend on the source, but these parameters must be carefully controlled in order to

minimize the hydrolytic depolymerization and deacetylation of chitin. High temperature treatments must also be avoided to prevent thermal degradation Percot *et al.*, (2003). An alternative treatment for demineralization makes use of the complexing agent EDTA (ethylenediamine tetra acetic acid) in basic media Austin *et al.*, (1981).

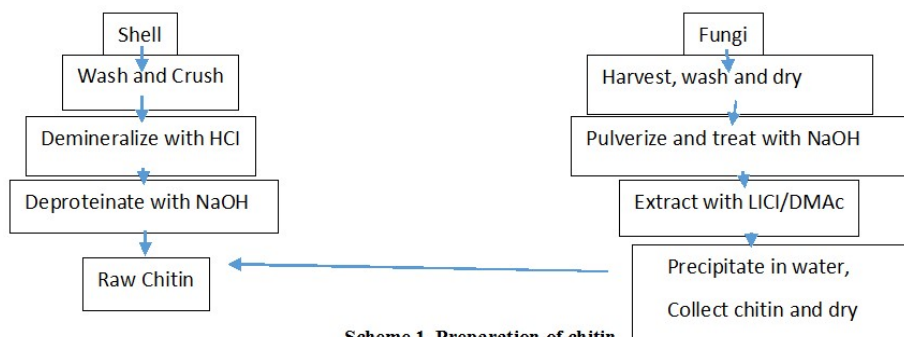
The presence of crustacean shells is mainly due to the presence of pigments such as astaxanthin, cantaxanthin, astacene, lutein and β -carotene. The above treatments are usually capable of eliminating these pigments which are frequently extracted at room temperature with acetone, chloroform, ether, ethanol, ethyl acetate or a mixture of solvents. Traditional oxidizing agents such as H_2O_2 (0.5-3%) and $NaClO$ (0.32%) have also been employed, but these reagents may attack the free amino groups and introduce modifications in the polymer. For strongly coloured shells, such as those of the common lobster carapaces, treatments with mixtures of acetone and $NaOCl$ at room temperature have been reported.

Extraction of Chitosan from Shrimp Shell Waste

Most of the methods for extraction of chitosan from shrimp shell are laborious and time consuming or low yielding. The most simple and effective method of extraction of high purity yield chitosan from shrimp shell waste is that which is

prepared using a combination of three procedures Puvvada *et al.*, (2012), Biswas and Gargi, (2013, and Annadurai (2012). A specified quantity of ground (250 microns) shrimp or oyster shell is treated with 4% $NaOH$ or KOH solutions at room temperatures above $100^\circ C$ for 24 hours. The alkali is drawn from the shell mixture and washed with distilled water repeatedly till pH dropped to neutral. This processed is called deproteinization of shells.

The deproteinization shells again are treated with 4% HCl at room temperature for 12 hours for demineralization to yield chitin. The acid is drawn off from chitin, washed with distilled water and finally dried at room temperature. This is repeated with 2% $NaOH$ and % HCl . The chitin obtained may still have a slight pink colour. Further decolorization is achieved by soaking chitin in 1% oxalic acid for 30 minutes to 2 hours. The decolorized chitin is deacetylated to form chitosan by treating with 65% $NaOH$ for 3 days at room temperature. Alkali is drawn off and washed repeatedly with distilled water till pH is lowered. Chitosan obtained is further dried at room temperature and stored in airtight container Divya *et al.*, (2014). Method is shown in scheme 1.



Scheme 1. Preparation of chitin

Environmental Issues of Chitin/Chitosan: The Challenges and Prospects in Nigeria

Waste disposal and by-product of sea food processing industry pose problems in the environmental protection and sustainability Russ and Pittroff, (2004). Typically, the crustacean are caught and processed for food. While fleshy portions are removed for consumption, the shells which contains the chitin are discarded. Previously, the shells are thrown away freely causing environmental pollution, now they are gathered for re-using. The waste which are the main source of chitin/chitosan instead of using these materials in science and technology aspects are now used in unscientific ways.

Waste shells are now commonly used as filling materials for other uses, such as civil construction works. In response to the ecological problems in the Niger Delta, some of the communities are using waste shells as filling and erosion control materials. In Odoma, waste shells are used as shoreline protection material to control shoreline erosion. Among the commonest use of waste shells in all the eastern communities is in the area of building construction.

Non-utilization of this waste of chitin in a proper may create major aesthetic and catastrophic health problems. Non-utilization or under utilization not only lead to loss of potential revenues but also lead to added and increasing cost of disposal of the products. Processing waste shell of chitin/chitosan have a potential for recycling raw materials or conversion into useful product of higher values.

Generally speaking, raw and auxiliary materials, as well as one of the following a desire product, a non-product-specific waste or a product-specific waste. Product specific waste unavoidably accumulates as a result of processing of raw materials. It is produced during the various steps of production, in which the desired components are extracted from the raw materials. After extraction, there are often other potentially useful components present in the remaining materials especially the chitin. This is because of the ecological challenges of erosion, flooding and subsidence affecting the communities (CEDA, 1997 UNDP, 2006).

The current methods for further utilization of waste have been developed along traditional lines and are closely bound to the agricultural origins of the raw materials themselves. The two general methods of traditional waste utilization have been to use the waste as either animal feed or fertilizer. Many of the existing agricultural solutions to waste disposal balance out between legal regulations and the best ecological and economical solutions. Another characteristic of product-specific waste is that the generated mass of waste relative to production levels can only be altered through technical means, which unavoidably leads to a change in product quality. The product waste from sea food is characterized by its high proportion of organic material.

The disposing of this waste can be difficult for the following reasons:

Biological stability and the potential growths of pathogens:

- A high water content increases transport cost of the waste. Mechanical removal of water through use of a press can lead to further problems with waste disposal due to the high levels of organic matter in the water.
- Rapid autoxidation: waste with high fat content is susceptible to oxidation, which leads to the release of foul smelling fatty acids.
- Changes due to enzymatic activity in many types of waste arising enzymes are still active which accelerates or intensify the reactions involved in spoilage (Russ *et al*, 1997).

The major challenge lies in translating substantial public investments for effective what's and access to the people. This requires more involvement by communities to identify local needs and better planning to deliver holistic and sustainable solution to our problems. Rural-urban migration will add to pressure on sanitation infrastructure throughout the country. There is an urgent need for manageable with these challenges to be established at state and the local government levels. Recent economic growth in the country has not generated enough jobs and its effect on poverty is not yet clear. The current policy suggest that the difficulty to meet the need and creating jobs will require the private sector to create an enabling environment providing sustainable access to enterprise finance, social protection and poverty eradication.

Strategies Areas to increase the Application of Chitosan in Nigerian Industries:

- I. **Partnerships:** In collaboration with government, local authorities and citizens' partnership will help immensely with people at lower level to produce simple items (e.g. Black soap, hair shampoo, cosmetics etc.).
- II. **Business Call to Action:** The business call to action aims to accelerate progress towards the challenging companies to develop inclusive business models that offer the potentials for both commercial success and development impact. The available chitin in our community can be utilized in industry is small business and can successfully fit in the programme by training people in this area.
- III. **Cooperation with Private Sector:** In cooperation with the private sector, make available the benefits of science and technologies. In this case science of chemistry and chemical engineering subjects will benefit much in this area to develop the people with small business as such.
- IV. **Cooperation with Medical and Pharmaceutical Companies:** Chitosan using science and technology in medicine and pharmacy will provide access to affordable and essential drugs wound healing/ wound dressing process, burn treatment, artificial skin e.t.c, in developing country like Nigeria.
- V. **Empowerment Women:** The application of chemistry of chitin/chitosan in these areas mention above will engage women with business and create jobs, and hence empower them.

The Role of Chitosan in Science and Technology for National Economic Development

- A. **Employment Opportunities:** Chitosan technology through small scale industries will give job opportunities for many youth who are unemployed. The establishment of cottage industries in all the states of the federation will encourage the youth to depend on themselves. Local production and

processing are given maximum support, so that they can employ other people to booster the production.

- B. **Self- Reliance:** With the help of the science and technology will be self-employ and self-independence to achieve success in their life. Those with experience in certain production (local) are employed to produce in large quantity.
- C. **Deducing Poverty:** Before chitosan technology, there is a high level of employment which resulted in the low income in the rural and urban areas. Basic necessities of life become almost impossible to the common man. But when small scale industries through chitosan technology are established many people would get what to do in which to some extent reduced the hardship of people staying within the areas.
- D. **Industrial Orientation:** the industries established in the area through chitosan technology will resulted in economic development. New methods and procedures of production and local production will be discovered.
- E. **Economy Creativity:** science and technology are the bedrock of any society; it brings about innovation within the society. Therefore chitosan technology through industries helps in realizing new technique in production and also encourages creativity. This will transform the society into a self-productive society, and the local raw materials should be process locally and of modern standard.
- F. **Social Integration:** the application of chemistry of chitin in industry will brings people together to form co-operative societies. The spirit of oneness and mutual understanding among the people of the society is fostered. It is of great achievement to bring people together and foster the local raw materials of the nation development.

Conclusion

This brief review highlighted in these paper, an attempt have been made to increase the understanding of the importance and characteristics of chitin/chitosan in terms of chemicals and biological properties, processing and applications. Waste shells of chitin found in the coastal areas of Nigeria, where they cause environmental pollution can now be used for scientific and technological activities in the country, thus effectively managing the waste. Chitin have a potential for recycling raw materials, or a conversion into useful products of higher value for industries. This study will also attract the attention of the entrepreneurs, industrialists, academicians, and the environmentalists. The production of chitosan from waste shell obtained as a food industry waste is economically feasible, especially if it includes the recovery of the nutrients. The proper utilization of those water resources (aquaculture) in terms of applications of chitin/chitosan can bring the economic and academic prosperity of the nation.

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PHOTOCATALYTIC DEGRADATION OF COMMERCIAL TEXTILE DYE IN AQUEOUS BUFFER SOLUTION USING ANATASE TITANIA

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ABSTRACT

Textile dyes present in waste water requires remover due to their hazardous and negative impacts on the environment. In this paper, the photocatalytic degradation of Vat Green 8 on anatase titania at a buffer pH of 7, 8 and 9 had been investigated. The effect of various operational parameters such as catalyst loading, pH, initial dye concentration and irradiation time of the photocatalytic degradation was studied on a laboratory scale photoreactor containing 100 W mercury bulb. Varying concentrations of the dye such as 5 mg/l, 12.5 mg/l and 20 mg/l was prepared and ran in the photoreactor and the dye removal was monitored using UV-Vis spectrophotometer. The results obtained revealed that much of the dyes were removed at an optimum pH of 9 and catalyst dose of 1 mg/l. The percentage efficiency of the colour remover reached a maximum of 99% at dye concentration of 12.5 mg/l and irradiation time of 90 minutes.

Keywords: Irradiation, Anatase, Photocatalytic degradation, Photoreactor and pH

1.0 INTRODUCTION

Textile industry is one of the top industries that consumes large volume of water and at the same time generate large amount of wastewater in the form of effluents. These effluents are heavily coloured and contains an amalgam of different dyes, surfactants and additives most of which are biorecalcitrant thus constituting threat to human life and that of the aquatics [1, 2]. It become very imperative to ensure the treatment of this effluents before discharge into water bodies as the influx of the untreated wastewater not only introduces aesthetic concerns, but far more importantly, it promotes eutrophication which adversely affects the environmental health of the region by reducing light penetration which affects aquatic life and limit utilization of the water media [3]. Industrial development and its association with discharge of organic matter into the aquatic systems demands the technological development to solve the environmental problems related to organic effluents [4]. Many practices have been widely applied in the treatment of organic effluent such as biological treatment, reverse osmosis, ozonation, filtration, adsorption on solid phases, incineration and coagulation [5]. However, the effluent treated by these techniques alone is not recyclable and require further treatment thus indicating the limitation of the process.

In recent era, advanced oxidation processes (AOPs) have been found as an effective and alternative way for the treatment of organic effluent in aqueous system [6, 7, 8]. The recent research demonstrates that AOPs based on photocatalyst are valuable and this method benefits complete mineralization of organic molecules into nontoxic CO₂ and H₂O at the atmospheric conditions [9, 10, 11, 12]. Further, AOPs result in the generation of hydroxyl radicals ($\cdot\text{OH}$) as main oxidizing agents which can remove even nonbiodegradable organic compounds from wastewater stream [13, 14]. Photocatalytic degradation of organic effluent emerged as one of the best methodologies for the treatment of toxic organic effluents which uses the semiconductor as catalyst such TiO₂, ZnO, ZnS, WO₃, CdS and Fe₂O₃, and SrTiO₃ [15, 16, 17, 18]. Among them TiO₂ and ZnO have been widely applied as photocatalyst due to their high activity, nontoxicity, chemical stability, lower costs, optical and electrical properties and environment friendly characteristics [19, 20, 21, 22, 23].

This paper represents the photocatalytic degradation of Vat Green 8 in the presence of Anatase titanium dioxide using aqueous buffer solution. The influence of various operational parameters such as the initial concentration of the dye, initial pH, catalyst loading and irradiation time was evaluated and the photocatalytic efficiency was examined.

2.0 Materials and methods

2.1 Materials

2.1.1 Reagents: Vat Green 8 was purchase from Zigma Aldrich. TiO₂-P25 Anatase with surface area $50 \pm 10 \text{ m}^2 \text{ g}^{-1}$ and average size = 21 nm was purchased from Degussa Company. All other chemicals used in the study were of analytical grade and were bought from Zigma Aldrich. Doubled distilled water was used in the preparation of the buffer solution corresponding to the various pH and in preparing the dye solution after dissolution of the dye in dimethyl formamide (DMF).

2.1.2 Apparatus: A laboratory scale Photoreactor equipped with 100 W mercury bulb was used for the photodegradation. UV-VIS spectrophotometer of model number Jenway-6305, was used for spectral monitoring and analyses of dye concentrations. A Whatman filter was used for separation of photocatalyst from solution while digital pH meter, Jenway-3505 model was applied for controlling of buffer solution pH.

2.2 Methods:

0.1 g of the dye was dissolved in 100 ml DMF to serve as stock solution of the dye. Varying concentration of the dye (5 mg/L, 12.5 mg/L and 20 mg/L) were then prepared from the stock solution using the aqueous buffer solution of varying pH. The photocatalyst was then added in different amount between 0 - 2 g/L after which it was kept in the dark for 15 minutes to establish equilibrium between adsorption and desorption. The dye solution containing the photocatalyst was then irradiated inside the photoreactor over a period of time specified by the experimental design after which an aliquot was taken and filtered in order to separate the dye solution from the photocatalyst. The absorbance value of the photolyte was determined using UV-Vis spectrophotometer. In each run, the percentage photodegradation was calculated using the expression;

$$(\%) \text{ Photocatalytic degradation} = \frac{C_0 - C_t}{C_0} \times 100 \quad 1$$

where C₀ and C_t represents the concentration before irradiation and concentration at any time of irradiation respectively.

A Box Beckhen design of experiment was used in generating the experimental runs as shown in Table 1.

Table 1: Design of experiment for Vat Green 8

Run Order	Concentration (mg/L)	Catalyst Loading (g/L)	pH	Time (min.)	Degradation %
1	5.0	2	9	45	74.42
2	12.5	1	8	0	0
3	12.5	0	9	0	0
4	20.0	1	8	45	58.58
5	12.5	2	9	90	76.73
6	5.0	1	8	45	84.92
7	12.5	1	9	45	97.38
8	20.0	1	9	0	0
9	12.5	2	9	0	0
10	12.5	2	8	45	86.84
11	12.5	1	9	45	97.38
12	5.0	1	9	0	0
13	12.5	0	8	45	11.23
14	5.0	0	9	45	04.36
15	12.5	2	10	45	66.72
16	5.0	0	8	45	03.13
17	5.0	1	9	90	92.04
18	12.5	1	9	90	99.58
19	12.5	0	9	90	41.22
20	12.5	1	9	45	97.38
21	12.5	0	10	45	05.48
22	20.0	1	10	45	59.06
23	20.0	2	9	45	68.16
24	12.5	1	8	90	87.45
25	12.5	1	10	0	0
26	20.0	1	9	90	79.12
27	5.0	1	10	45	74.63

4.0 RESULTS AND DISCUSSION

3.1 CALIBRATION CURVES FOR THE STANDARD SOLUTIONS

The standard solutions of the dye at pH of 7, 8 and 9 were prepared and the absorbance vs. concentration at $\lambda_{\max}$ was plotted. The curve is linear and in agreement with the Lambert–Beer law as shown in Figure 1.

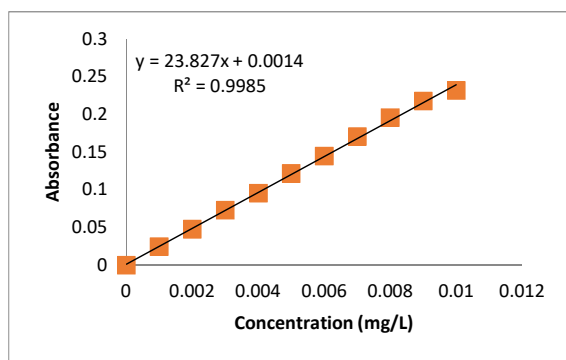


Figure 1: Calibration curve of Vat Green 8

The pigment sample was dissolved in DMF so as to improve intermolecular solute-solvent interaction force which enhances the dye solubility significantly. To ensure validity of Beer-Lambert's law, a set of 10 different calibration solutions were prepared. These pigment concentration were chosen since the solution for testing absorbance correlation are best kept in the absorbance range of 0.2 – 1.5. This procedure is similar to the one used by other researcher [42, 43].

3.2 Effect of pH

The influence pH on dye degradation cannot be over emphasized as it does not only determine chemical properties of the photocatalyst, but also influences adsorption behavior of the pollutants [35, 36]. It plays an important role in the photocatalytic reaction on the catalyst surfaces, where it affects the surface charge properties of the photocatalyst and the oxidation potential of the valence band [37]. The effect of pH on degradation of textile effluent containing Vat Green 8 was studied at varying pH of 7, 8 and 9. The results obtained as shown in Figure 2 indicates that increasing the pH of the dye solutions leads to increasing degradation and adsorption. The possible reason for this behavior is that alkaline pH range favours the formation of more $\text{OH}^\bullet$ due to the presence of large quantity of OH^- ions [38]. Further increase in pH beyond the optimum value of 9 for Vat Green 8 results in decrease in the rate of degradation and this could be as a result of columbic repulsion between the negatively charged surface of the photocatalyst and the hydroxide anions [39]. This could prevent the formation of the hydroxyl radicals which in turn reduces the rate of degradation.

Effect of initial dye concentration:

The effect of various dye concentrations on photocatalytic degradation has been investigated from 5 mg/L – 20 mg/L. The results shown in Table 1 and Figure 3 illustrated that an increase in the dye concentration will lower the removal rate. Similar results have been reported for the photocatalytic oxidation of other dyes [40]. The possible explanation for the decrease in removal rate is that as the initial concentration of the dye increases, the path length of the photons entering the solution decreases. Furthermore, when the dye concentration increases, the amount of dye adsorbed per molecule of the catalyst increases. This affects the active sites of the catalyst

and thereby decreases the efficiency of the catalyst. Moreover, at high dye concentration, a significant amount of radiation may be absorbed by the dye molecules rather than the catalyst and this may also reduce the efficiency of the catalyst.

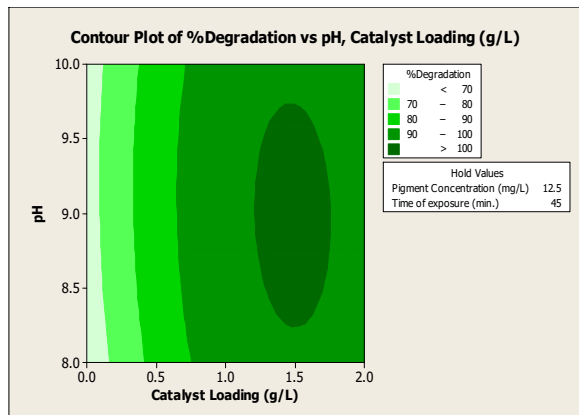


Figure 2: Contour Plot of %Degradation vs pH, Catalyst Loading (g/L)

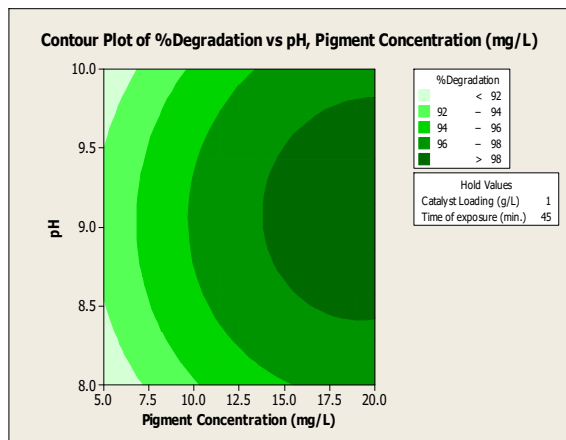


Figure 3: Contour Plot of %Degradation vs pH, Pigment Concentration (mg/L)

Effect of Irradiation time

The effect of irradiation time on photocatalytic degradation of textile wastewater containing Vat Green 8 is shown in Figure 4. The experiments were carried out at varying concentration and catalyst loading. The initial rate of the reaction was found to be very fast and thereafter was almost constant. At the beginning, generation of $\text{OH}^\cdot$ was very fast and a large number of vacant surface sites were available for adsorption. After a known period of time, the remaining sites were hardly occupied due to the repulsive forces between the molecules on the surface and in the bulk phase [41]. The formation of intermediates which compete with the parent molecules decreases the reaction rate on the long run.

3.2 Effects of catalyst loading:

The effect of catalyst loading on the degradation of the dye solution had been investigated using different concentrations of TiO_2 varying from 0 to 2 g/L and the results are presented in Figure 1. From the results obtained, it was observed that dye degradation increases as the catalyst loading increases up to certain level beyond which no degradation was noticed. This is in conformity with the findings of other researcher [24, 23, 25]. The increase in degradation as a result increase in photocatalyst amount can be attributed to increase in

hydroxyl radical generated from the irradiated photocatalyst [26, 27]. At lower catalyst loading, degradation of organic molecule is low, because more light is transmitted through the reactor and lesser transmitted radiation only will be utilized in the photocatalytic reaction [28, 29]. But beyond the optimum amount of photocatalyst, the degradation rate might be reduced due to increase in the opacity of the suspension, and thus increasing the light scattering and also the infiltration depth of the photons is diminished and less photocatalyst could be activated [30, 31, 32]. In addition to what is mentioned above, agglomeration of nanoparticles at high concentration could result to decline in the number of surface active sites available for the photocatalytic degradation [33, 34].

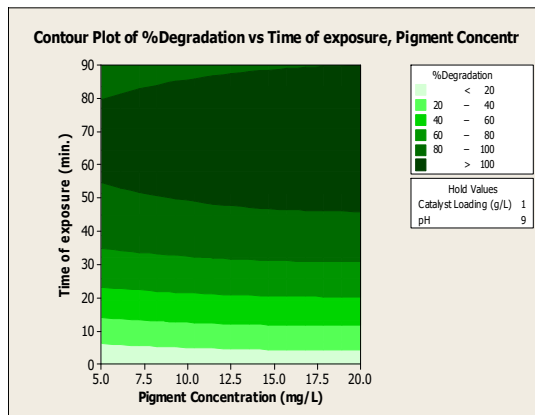


Figure 4: Contour Plot of %Degradation vs Time of exposure (min.), Catalyst Loading (g/L)

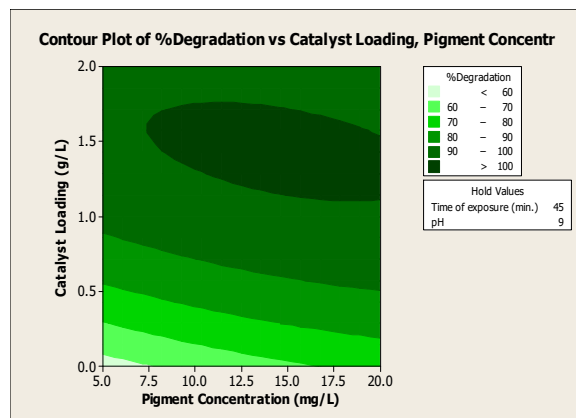


Figure 5: Contour Plot of %Degradation vs Catalyst Loading (g/L), Pigment Concentration (mg/L).

CONCLUSION

The photocatalytic degradation of Vat Green 8 was examined using Anatase TiO_2 catalyst under visible light. Some operational parameters such as irradiation time, pH of solution, catalyst loading and initial dye concentration were studied for their influence on the efficiency of the photocatalytic process. 1 g/l catalyst dosage, 25 mg/l concentration and pH of 9 were found to be the optimal conditions of the experiment. Hence, heterogeneous photocatalysis was proved to be an attractive method of removing pollutants from industrial wastewaters.

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DRAG REDUCTION IN PIPELINE BENDS AND CURVES FOR OIL-WATER FLOWS

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ABSTRACT

The often long distances between onshore and offshore petroleum installations and process facilities has necessitated the use of pipes and inevitably pipe fittings such as bends for the transport of multiphase fluids. The reduction of the frictional pressure drop in flow systems that results in energy savings by use of certain heavy molecular weight polymers as well as other means such as pipeline modifications has been a subject of research. Till date most of the drag reduction studies for liquid-liquid flows has been concentrated on flows through vertical, horizontal, inclined and undulated pipes. Little work has been done on the application of drag reduction agents (DRAs) for liquid-liquid flows in curves and bends. To this end experimental and model studies will be carried out for 12 mm and 20 mm pipes using middle distillate oil and water as test fluids. The hydrodynamic behaviour of oil-water flows through curves of various curvatures as well as 90° and 180° bends of various configurations before and after the addition of partially hydrolysed polyacrylamide (HPAM) will be studied. Reynolds numbers less than 100000 at polymer concentration of between 5ppm and 200ppm will be investigated. The pressure drop, flow patterns and in-situ volume fractions in and around curves and bends will be measured with the aid of pressure meter, impedance probes and high speed camera. Results from these studies will help provide some explanations of the effectiveness of DRAs on film inversion in bends, reattachment distances after elbow bends, flow configuration and curvature ratio. It is hoped that this study would provide better insight into the drag reduction phenomenon in curves and bends with the view of optimising both the design and operational processes of oil-water flows through pipes.

Keywords: curves, elbows, bends, polymer, pressure drop

Introduction

Petroleum installations are often located several kilometres from process facilities. This requires that the multiphase fluids be transported through pipes including pipe fittings such as bends to processing facilities and for separation (Abdulkadir et al. 2011; Ahmed 2014). A large percentage of the energy cost in petroleum production and transport is associated with pressure losses from drag. Hence, an economic design of multiphase transport would be such that incorporates means of reducing the effect of drag.

Additives such as polymers, surfactants and fibres called drag reducing agents (DRA) are often used for drag reduction. After the pioneering work credited to Tom (1948), a compendium of works have been undertaken to interrogate the effect of DRAs on liquid-liquid flows through straight pipes of various configurations (Abubakar, Al-Hashmi, et al. 2015; Abubakar, Al-Wahaibi, et al. 2015; Al-Wahaibi et al. 2007; Al-Yaari et al. 2009; Edomwonyi-Otu et al. 2015) and a few others through curves and bends (Fox et al. 2010; Gasljevic & Matthys 2009; Kamel 2011; Shah et al. 2006; Zhou et al. 2004). Other drag reduction techniques, involving pipe modification, are riblets, dimples, oscillating walls and compliant surfaces such as super-hydrophobic coating are also common (Chen et al. 2010; Abubakar et al. 2014; Abdulbari et al. 2014). Micro-bubbles injection at the boundary layers of fluid transport have also been used successfully for drag reduction (Merkle & Deutsch 1992; Sayyaadi & Nematollahi 2013). Drag reduction (DR) is associated with changes in turbulent heat transfer (Pak et al. 1991; Gasljevic & Matthys 2009; Zhang et al. 2013; Aguilar et al. 2006; Kazi et al. 1999). Besides the reduction in drag, addition of DRAs has also been found to affect phase distribution and flow regime transitions of multiphase flow in straight pipes (Abubakar, Al-Wahaibi, et al. 2015; Al-wahaibi et al. 2007; Al-Yaari et al. 2009; Deka et al. 2014; Edomwonyi-

Otu & Angeli 2014; Edomwonyi-Otu et al. 2015) and pipe bends (M Sharma et al. 2011; M. Sharma et al. 2011).

There appears to be a general consensus that the drag reduction by additives is higher in straight pipes than in curves (Fox et al. 2010; Gasljevic & Matthys 2009; Kamel 2011; Shah et al. 2006; Zhou et al. 2004) and the effectiveness of DR reduces with increase in curvature (Shah et al. 2006). However, the effect of DRAs on secondary flow, wakes, flow separation and reattachment distances (in elbow bends) remain unresolved. The aim of this research is to interrogate the effect of polymer and surfactant DRAs on pressure drop and secondary flow through curves/bends as well as their effect on flow separation and reattachment in elbow bends. The work also seeks to provide insight into the mechanism of drag reduction in curves and bends.

Materials and Method

The pressure drop, flow patterns and in-situ volume fractions in and around curves and bends are measured/observed with the aid of pressure meter, impedance probes/high speed camera and quick closing valves. Local heat transfer measurements are carried out to determine the Nusselt number. Velocity profiles of polymer and surfactants solutions through curves using Laser-Doppler Velocimetry (LDV). The experimental flow facility used in this work (see Fig. 1) is similar to that earlier reported by Edomwonyi-Otu (2015) and Al-Wahaibi et al., (2007).

Modification of the flow rig is carried out to suit the purpose of the current study. Key among these modifications is the addition of curves and bends alternately to the test section.

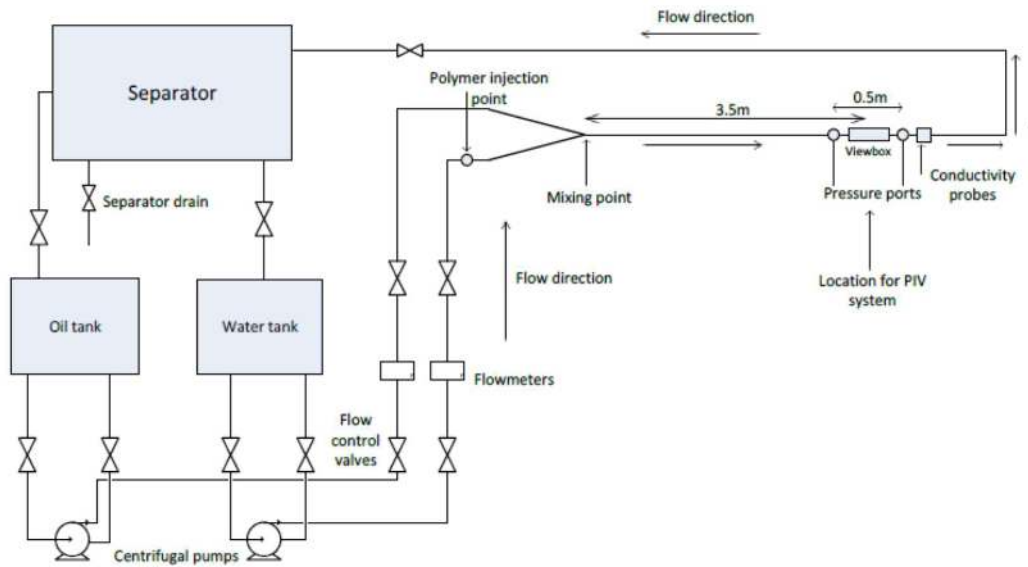


Figure 1. Schematics of experimental flow facility (Source: Edomwonyi-Otu 2015)..

Expected Outcome

We begin by examining the effect of addition of various concentration of DRA on pressure drop observed for single and two-phase flow through 12-mm diameter curves at various flow rates and curvature ratios (r/R) (where r is radius of the pipe and R is the radius of the curve). There appears to be a general consensus that the effectiveness of drag reducing agents is higher in straight pipes than in curves and bends (Fox et al. 2010; Gasljevic & Matthys 2009; Kamel 2011; Shah et al. 2006; Zhou et al. 2004).

The mathematical expression for DR is given by Eq. (1).

$$DR(\%) = \frac{f - f_{DRA}}{f} \times 100\% \quad (1)$$

where f is the fanning friction factor before the addition of DRA and f_{DRA} is the fanning friction factor after the addition of DRA. Drag reduction, expressed in terms of friction factor, is often represented on the Prandtl-Karman (P-K) coordinates i.e. $1/\sqrt{f}$ versus $Re\sqrt{f}$ (see Fig. 2). The relationship between these parameters for laminar and turbulent regimes in Newtonian fluids is given by Eqs. (2) and (3).

$$1/\sqrt{f} = \frac{Re\sqrt{f}}{16} \quad \text{Laminar flow} \quad (2)$$

$$1/\sqrt{f} = 4 \log_{10} Re\sqrt{f} - 0.4 \quad \text{Turbulent flow} \quad (3)$$

Such plots show that above a certain Reynolds number, the friction factor when DRP is added are lower than the case without DRPs. According to Abubakar et al. (2014), for flows through straight pipes with constant polymer concentration, DR increase with increase in Re until it reaches a maximum known as maximum drag reduction (see Fig. 2). The equation for maximum drag reduction asymptote (MDRA) is given by Eq. (4).

$$1/\sqrt{f} = 19 \log_{10} Re\sqrt{f} - 3.24 \quad \text{Turbulent flow} \quad (4)$$

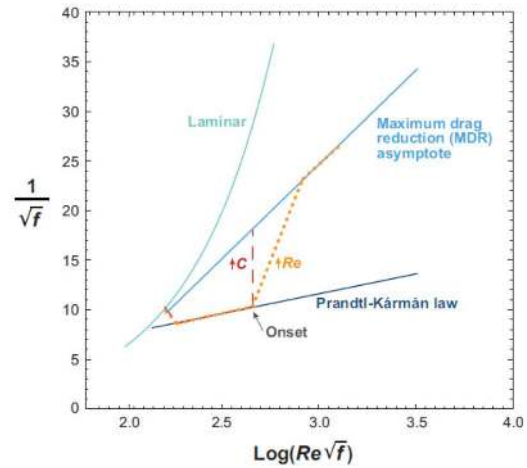


Figure 2. A schematic illustration of onset and different trajectories of polymer drag reduction. The dashed line represents the case in which Re is fixed (at the value when the onset of drag reduction is first observed) and polymer concentration, C , is increased. The dotted line represents the case in which C is fixed and Re is increased (Source: White & Mungal 2008).

It is understood that, for flow in straight pipes, drag reduction increases with concentration of polymer until an optimum concentration is reached. Further increase in concentration beyond the optimum produces no further increase in drag reduction and in some case a decrease in drag reduction is observed (Al-Wahaibi et al. 2007; Abubakar et al. 2014; Al-Yaari et al. 2009; Edomwonyi-Otu et al. 2015; Edomwonyi-Otu & Angeli 2014). Al-Yaari et al. (2009) linked this observed increase in DR with increase in concentration of DRA to the increase in the formation of aggregates. Edomwonyi-Otu et al. (2015) suggested that the optimum concentration reflects a saturation of the region of strong turbulence activity with the polymer beyond which no further changes in DR are noticeable. Contrary to the above findings, Shah et al. (2006) reported that there was no significant influence of concentration on DR and above a certain optimum concentration the DR effectiveness is reduced.

Gasljevic & Matthys (2009) defined a new relationship for computing DR in curves called turbulence reduction for drag (TRD). They claimed that the use of the simpler drag reduction parameter given by Eq. 1 is acceptable when considering flow in straight pipes, because of the large difference in turbulent and laminar friction coefficients for those pipes, and particularly at high Reynolds numbers. They argued that if DR is expressed in terms of (Eq. 1) there is a substantial difference between DR in straight pipes and curves whereas no significant difference exists if expressed in terms of TRD (Eq. 5). Similar to observations in straight pipes, Gasljevic & Matthys (2009) did not observe any significant drag reduction for laminar flow regime in coiled pipes.

$$TRD(\%) = \frac{f - f_{DRA}}{f - f_l} \times 100\% \quad (5)$$

Literature on the effect of DRAs on pressure drop is limited and one of the expected outcomes of this research is to gain further insight into the effect of DRAs on drag reduction in curves and bends.

Next we examine the effect of DRAs on secondary flow observed in curves and bends. Fig. 3 shows the flow lines in the cross-section, for flow through curves, from Dean's solution. The Figure shows that in the cross-section, the secondary flow streamlines form a pair of symmetrical vortices referred to as Dean vortices. Dean (1927) suggested that the secondary flows of the spiral form are superimposed on the axial primary flow.

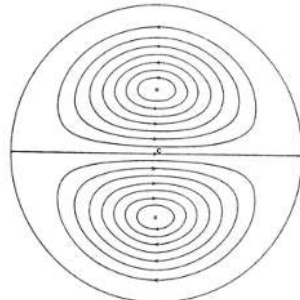


Figure 3. Secondary flow streamlines (Source: Dean 1927)

The contours of axial velocity of the cross section is shown in Fig. 4 for curvature ratio of $r/R = 1/100$, and Reynolds number $Re = 2050$. It is observed that the maximum axial velocity is shifted to the outer side of the curve.

Figs. 5 and 6 show the superimposition of axial velocity contours and secondary flow streamlines. Careful inspection reveals that as Dean number increases the secondary flow becomes more confined to a thin area near the pipe wall (Zhou 2006).

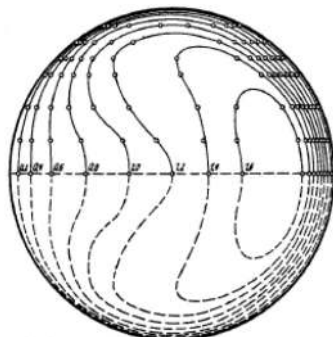


Figure 4. Contours of axial velocity, $r/R=0.01$ and $Re = 2050$ (Source: Zhou 2006).

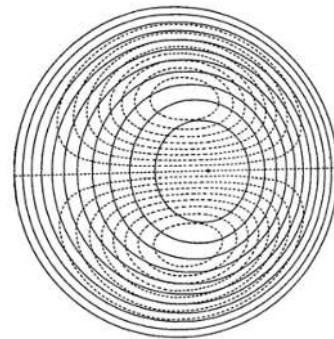


Figure 5. Axial velocity contours and secondary flow streamlines, $De = 96$ (Source: Zhou 2006).

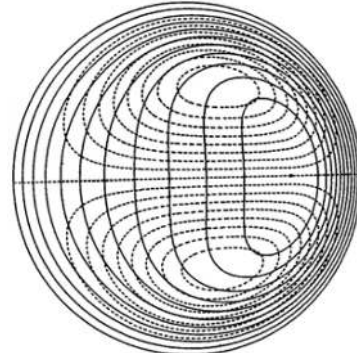


Figure 6. Axial velocity contours and secondary flow streamlines, $De = 481$ (Source: Zhou 2006).

The effect of DRAs on secondary flow is yet to be fully investigated. This research seeks to bridge this essential knowledge gap using experimental approach.

The effect of DRAs on flow pattern is another important area where further research is required. The effect of DRAs on pressure drop is expected to be strongly linked to the flow patterns before and after the DRAs are added as is the case for flow through straight pipes. In addition to the above, results from these studies will help provide some explanations of the effect of DRAs on film inversion in bends and reattachment distances after elbow bend.

We also investigate the effect of micro-bubble injection on drag reduction for flow through elbow bends. The ability of the micro-bubble to alter the structure of the boundary layer thereby resulting in drag reduction is thoroughly investigated. Comparison is made between the hydrodynamics of flow with DRAs and that for which micro-bubbles are injected.

Conclusion

The effect of addition of polymer and surfactant DRAs to flow in curves and bends is to be investigated. The various parameters that determine the effectiveness of DRAs in curves and bends are to be determined. The reattachment distance for single phase oil flow through elbow bends is computed. Some explanations of the mechanism of drag reduction in curves and bend will be suggested. The influence of injection of air micro-bubbles on single and two-phase flow through elbow bends is to be presented. It is hoped that this study would provide better insight into the drag reduction phenomenon in curves and bends with the view of optimising both the design and operational processes of oil-water flows through pipes.

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DEVELOPING NIGERIA'S COAL UTILIZATION POTENTIALS BY UNDERGROUND COAL GASIFICATION: A CLEAN ENERGY PERSPECTIVE

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ABSTRACT

Coal reserves are available in almost every country worldwide. According to published data from the World Coal Association and other sources, there is an estimated 892 billion tonnes of proven coal reserves worldwide. Nigeria is ranked sixth amongst African countries, behind South Africa, Zimbabwe, Mozambique, Swaziland and Tanzania, in proven reserves. Its coal has been found suitable for miscellaneous energy and chemicals manufacturing applications. Lamentably, in spite of the economic potential, the industry has remained shut down for over ten years, presumably because of over concentration on crude oil and natural gas resources. In addition, it is believed that the environmental and health hazards of traditional coal mining technology have also contributed to the reduced activities in this sector worldwide. This paper examines the potentials of Underground Coal Gasification (UCG), an emerging coal conversion technology, which has been embraced by the leading coal producers of the world, especially given the depletion of oil and gas resources, the threats of global climate change, and Nigeria's need for economic diversification.

Keywords: coal, technology, gasification, clean energy, and coal conversion

1. Introduction

Coal is the most abundant and widespread type of fossil fuels (BP Statistical Review, 2007). It is available from a wide variety of mines distributed globally. It has been an abundant source of energy and chemicals in many parts of the world.

The history of coal utilization in Nigeria dates as far back as 1909 when coal was discovered in Enugu. Six years on, the Ogbete drift mine was opened and its operations and others in the country were merged into the Nigerian Coal Corporation (NCC) in 1950. This new corporation was tasked with exploiting the country's coal resources, which it did until 1999. The discovery of oil in Oloibiri in 1956 caused attention to be shifted away from coal. This shift dealt a significant blow to the coal industry, as the main consumer of coal in the country, Nigerian Railway Corporation (NRC) began to replace its coal-fired trains with diesel-powered engines (Odesola et.al, 2013). The other major consumer, the Electricity Corporation of Nigeria (ECN) also began to convert its power generation equipment from coal to diesel and gas. In the aftermath of the Nigerian Civil War (1967-70), production, which had fallen during the war, never completely recovered.

In 1999, the NCC lost its monopoly over the coal industry as private investors were given licences to mine, in partnership with NCC. In 2002, NCC-operated mines closed. The knock-on effect of these closures was devastation to companies which depended on coal as their main raw material. Furthermore, thousands of personnel and workers lost their jobs and the economic strength of many cities which hosted the coal mining activities waned drastically. This led to a rapid urban migration. The closure of so many companies also resulted in a reduction of the country's GDP (Odesola et. al, 2013).

In spite of the negative state of affairs, in respect of Nigerian coal utilization, globally coal continues to be the most widely available fossil fuel resource. Among its many uses worldwide are electricity generation, steel and aluminium production as well as cement manufacture and as a liquid fuel. Indeed it forms the backbone of the world's electricity supply, providing about 30% of primary energy and 42% of global electricity needs. Coal use is forecast to rise over 50% by 2030, with developing countries responsible for 97% of this increase, primarily to meet improved electrification rates (World Coal Association [WCA] document, 2013). Ostensibly, energy remains critical to sustainable development – for building stronger

communities with hospitals and schools, and supporting business and industry. All these are precursors for the delivery of sustainable employment and economic growth. It is believed, and expected, that the depletion of proven oil reserves will lead to coal playing an increasingly important role, even while renewable energy sources are developed.

Coal is expected to be the bedrock on which energy access is built (WCA doc., 2013; International Energy Agency, IEA, World Energy Outlook, WEO, 2011). This is borne out by published data on world coal reserves. It has been estimated that there are over 860 billion tonnes of proven coal reserves worldwide. This means that there is enough coal to last at least 118 years at the current rates of consumption, as against 46 years for oil, and 57 years for gas, for proven reserves, at current consumption levels. Worldwide potential coal resources suggest that some deposits have as much as 400 years of production remaining and new technologies for utilizing coal resources, such as underground coal gasification, are likely to boost coal's future role in energy supply even further (IEA WEO, 2011). Coal reserves are available in almost every country worldwide, with recoverable reserves in around 70 countries. The largest reserves are in the USA, Russia, China and India.

Many African countries have coal reserves, with the most abundant reserves being found in South Africa, which has already developed a significant coal industry. A lot of the African states' reserves have not yet been properly assessed, leading to the belief that it could significantly increase the potential role for coal in the region. Tables 1 – 3 show surveys of coal resources.

From the tables South African reserves dwarf those of other sub-Saharan countries. Table 4 show Nigeria's coal production figures through the years.

From the table, it is seen that Nigeria has sizeable deposits that could supply secure and reliable energy from coal resources, to help grow its domestic economy. In Asia, coal mining plays a significant role in many of the national economies. In general, the major coal producing nations utilize much of their coal for domestic electricity generation (see Table 5 below), whilst maintaining large coal export markets.

Table 1: Proved Recoverable Reserves of Coal in Sub-Saharan Africa at end-2008

COUNTRY	TOTAL RESERVES (million tonnes)
South Africa	30,156
Zimbabwe	502
Mozambique	212
Tanzania	200
Nigeria	190
Swaziland	144
Democratic Republic of Congo (DRC)	88
Niger	70
Botswana	40
Zambia	10
Central African Republic	3
Malawi	2

Source: **World Energy Council, Survey of Energy Resources 2010**

Table 2: Proved Recoverable Reserves of Coal in Asia at end-2008

COUNTRY	TOTAL RESERVES (million tonnes)
China	114,500
India	60,600
Kazakhstan	33,600
Indonesia	5,529
Mongolia	2,520
Turkey	2,343
Pakistan	2,070
Thailand	1,239
Kyrgyzstan	812
Democratic Republic of Korea (South Korea)	600
Laos	503
Tajikistan	375
Japan	350
Philippines	316
Bangladesh	293
Georgia	201
Armenia	163
Vietnam	150
Republic of Korea (North Korea)	126
Afghanistan	66
Malaysia	4
Myanmar	2
Nepal	1
Taiwan	1

Source: **World Energy Council, Survey of Energy Resources 2010**

Nigerian coal reserves are estimated at about 3 billion metric tonnes in 17 identified coalfields and over 600 million tonnes of proven reserves (MSMD PDF document, 2008). The coal deposits of the Anambra Basin, located in south eastern Nigeria, are believed to contain the largest and most economically viable coal resources (Odesola et.al., 2013), covering an area of about 1.5 million hectares. These deposits are located in designated Coal Districts, namely, Kogi (covering 225,000 hectares with an estimated 228 million metric tonnes), Benue (covering 175,000 hectares with an estimated 188 million metric tonnes), and Enugu (covering 270,000 hectares with an estimated 150 million metric tonnes). Other potentially significant resources have been identified in Inyi (Oji River), Afikpo, Lafia Obi, Gombe and Asaba.

Table 3: Top Ten Hard Coal Producers as at end-2010

COUNTRY	TOTAL RESERVES (million tonnes)
People's Republic of China	3,162
United States of America (USA)	932
India	538
Australia	353
South Africa	255
Russia	248
Indonesia	173
Kazakhstan	105
Poland	77
Colombia	74

Source: **International Energy Agency (IEA) 2011**

Table 4: TOTAL COAL PRODUCTION FIGURES					
YEAR	TONS	YEAR	TONS	YEAR	TONS
1916	25,511	1951	562,270	1987	117,159
1917	83,405	1952	613,374	1992	27,686
1918	145,400	1953	679,437	1996	17,797
1919	137,844	1954	675,919	2002	41,771
1920	180,122	1955	750,058		
1921	187,027	1956	790,030		
1922	194,073	1957	846,526		
1923	112,818	1958	905,397		
1924	175,137	1959	684,800		
1925	220,161	1960	565,681		
1926	242,583	1961	596,502		
1927	353,274	1962	615,681		
1928	345,303	1963	600,229		
1929	363,743	1964	698,562		
1930	347,115	1965	730,183		
1931	327,681	1966	630,126		
1932	263,548	1967	94,563		
1933	259,860	1968	Nil		
1934	234,296	1969	19,840		
1935	258,892	1970	24,404		
1936	257,289	1971	176,927		
1937	310,308	1972	323,007		
1938	323,266	1973	314,457		
1939	300,091	1974	297,753		
1940	318,594	1975	271,397		
1941	402,640	1976	282,729		
1942	463,978	1978	201,601		
1943	528,421	1979	163,000		
1944	668,158	1980	118,317		
1945	314,576	1981	114,812		
1946	607,652	1982	56,017		
1947	572,354	1983	52,730		
1948	607,759	1984	83,461		
1949	550,517	1985	129,744		
1950	583,425	1986	117,499		

SOURCES: Nigerian Coal Corporation 32nd Annual Report of 1985 and various CBN Economic and Financial Review Issues

Table 5: Coal in Electricity Generation

COUNTRY	PERCENTAGE (%)
South Africa	93
Poland	92
People's Republic of China	79
Australia	77
Kazakhstan	70
India	69
Israel	63
Czech Republic	60
Morocco	55
Greece	52
USA	49
Germany	46

Source: **International Energy Agency (IEA) 2011**

With the foregoing data, it begs the question as to why there is such a low level of coal utilization in countries like Nigeria. Could it be because of reported health hazards associated with traditional coal mining, and increasing global environmental

concerns? Clean coal technologies have assumed increasing importance to address these challenges. In this context, gasification is considered to be a promising option for the future of coal (Shafirovich & Varma, 2009).

This paper provides an overview to one of these clean energy technologies, known as Underground Coal Gasification, and considers it apt to be part of the current energy mix as the country continues to search for stable energy to boost its economic development and diversification. The potentials are certainly great for Nigeria.

2. Clean Coal Technologies

2.1 Preamble

Traditional coal mining has been under scrutiny over many years. The technology of coal mining and the use of coal have been affected by the pollution caused by its transport, storage and combustion (Tsui and Eu, 2003). Coal contains a number of inorganic impurities, and its combustion results in the emission of the “criteria pollutants”, namely, sulphur oxide (SO₂), nitrogen oxides and particulates, as well as mercury (World Coal Institute (WCI) document, 2005). Thus, any viable coal combustion technology must be able to address the menace of these impurities. A complete removal of all pollutants is desirable.

In addition, coal-fired power plants have higher greenhouse gas (GHG) emission per generated energy due to lower efficiency of the process and a higher carbon-to-hydrogen ratio of coal. The resultant health hazards, and recorded fatalities (China Labour Bulletin, 2006), have led to the search for “cleaner” technologies for coal utilization. A recent report about the deleterious effects to water supply, of a traditional coal mine in Okobo community in Kogi State, Nigeria, (Ventures Africa, 2016), highlights the need for clean coal technologies.

Since the mid-1980s, a worldwide drive to minimize the environmental impact of coal’s conversion to energy has resulted in the advancement of a group of technologies known collectively as clean coal technologies (CCTs). Clean Coal Technologies are those which facilitate the use of coal in an environmentally satisfactory and economically viable way. Among other aspects, they meet various regulations covering emissions, effluents and residues (IEA Clean Coal Centre, 2016). A basic approach to the cleaner use of coal is to reduce emissions by reducing the formation of pollutants such as NO_x and/or cleaning the flue gases after combustion. A parallel approach is to develop more thermally efficient systems so that less coal is used to generate the same amount of power, together with improved techniques for flue gas cleaning, for effluent treatment and for residues use or disposal. Thermal efficiency may be increased by using a higher grade of coal (IEA Clean Coal Centre, 2016). The trend to cleaner processes is in compliance with the Kyoto Protocol of 2002 (Kyoto Protocol, 2002). CCTs have the combined goals of minimizing emissions and maximizing energy efficiency for each ton of coal processed. This would involve permitting or ensuring i] advanced pollution controls for new and existing power plants, including carbon dioxide capture and sequestration; ii] the use of advanced combustion technologies; iii] employing gasification-based systems; iv] fuel flexibility – allowing for the use of a range of different types of coals or combinations of coal with other fuel sources (petroleum coke or biomass) without impacting plant performance.

2.2 Advanced Combustion Technologies

2.2.1 Pulverized Coal Combustion

In the pulverized coal combustion (PCC) process, finely divided coal particles are combusted in air, in a boiler, to create steam that is passed through a turbine to generate electricity. This method accounts for over 90% of coal-fired capacity

worldwide (WCI document, 2005). Modern PCC technology is well developed, and today’s sub-critical coal-fired power plants operate at a steam temperature of 540°C and a steam pressure of 16.5MPa, yielding thermal efficiency of approximately 35%. Attempts at improving thermal efficiency through steam temperature and pressure increases have met with materials selection challenges. Because of its poor emission control and low efficiency in terms of energy conversion, PCC is generally referred as a ‘dirty process’.

2.2.2 Fluidized Bed Combustion

Fluidized bed combustion (FBC) systems burn coal and other carbon-containing feedstock in a bed of heated particles suspended in flowing air. The fluidizing action promotes more complete coal combustion at lower flame temperatures, between 760°C and 925°C, which greatly reduces NO_x emissions (nitrogen oxides are typically formed at temperatures approaching 1370°C). Furthermore, the particle bed includes a sulphur-absorbing sorbent such as limestone or dolomite, which can reduce SO₂ emissions by more than 95%. FBC systems can meet most environmental standards for SO₂ and NO_x without the need for post-combustion pollution controls. Materials challenges inherent to FBC systems depend primarily on the type of feedstock utilized, and they sometimes experience excessive materials wastage through corrosion and wear.

2.3 Gasification Technologies

In response to the call for cleaner energies, newer technologies have emerged utilizing coal using a coal gasification system. Coal gasification dates back to the 19th century. Indeed, up till early 20th century numerous towns owned their own gas works, responsible for making coal gas (also called town gas) from mined coal. The gas was piped to homes and industry (Mallett, 2015). Most coal-derived energy is obtained when the contained carbon reacts with oxygen (O₂), yielding CO₂ and releasing energy in the form of heat. If excess O₂ is present, combustion occurs with nearly all the carbon converted to CO₂. When coal is gasified in an O₂-deficient environment, some coal is converted to heat and CO₂ and this heat drives the conversion of the remaining coal to syngas.

Thus, the gasification technology reacts coal with steam and controlled amounts of air or oxygen at high pressures and temperatures to form a synthesis gas, composed primarily of carbon monoxide and hydrogen. The synthesis gas, also known as “syngas”, is used to fire steam turbines for the generation of electricity, for the production of liquid hydrocarbon fuels, natural gas surrogates and valuable chemical products. The technology’s fuel and product flexibility, combined with its relatively lower emissions of pollutants, compared to advanced combustion technologies, have led to a revival of interests in coal gasification processes. Though a marked improvement on advanced combustion technologies, accessing the coal still involves some traditional coal mining. Also, coal gasification generally requires construction of special plants, including large coal storage facilities and gasifiers. An alternative gasification method, underground coal gasification (UCG), emerged in 1910 and its development was stalled by the world war and the discovery of huge natural gas and oil reserves in Russia, in the same way that coal utilization was pegged back by the discovery of crude oil. More recently, the UCG momentum has picked up yet again as many countries including China, USA, Canada, Argentina, Chile, Australia and South Africa, have been running UCG projects.

2.4 Underground Coal Gasification

The total amount of coal potential including the economically non-recoverable part is about 18 terratons (Couch, 2009), and most of it is too deep or too costly to be mined by traditional methods. It is also believed that with the current trends of

energy consumption, and the rise of developing countries, the total fossil fuel reserve is expected to be the same while the total energy consumption is increasing around the world. Thus, finding an appropriate technology to extract the non-recoverable part of the reserves, economically, is important (Khan et.al, 2015).

Underground coal gasification is a method of *in-situ* conversion of deep un-minable coal into gaseous products with a higher heating value. The process involves the drilling of a matrix of wells into the coal bed. The coal is ignited and air/oxygen and water are pumped into the injection wells. Syngas, which is mainly a mixture of CO, H₂, CH₄ and CO₂ with trace amounts of ethane and other components, is produced. It can be used directly as a fuel for power generation.

It can also be used for industrial heating or the manufacture of hydrogen, synthetic natural gas or diesel fuel, and many useful applications.

The development of the underground (*in-situ*) coal gasification (UCG) technique is paving the way to access deep coal seams (Couch, 2009). UCG technology allows countries that are endowed with coal to fully utilize their resource from otherwise unrecoverable coal deposits in an economically viable and environmentally safe way. Nearly 85% of known coal reserves are unmineable with surface mining techniques. UCG turns this resource into high value products – clean power, liquid fuels, syngas and fertilizers and other chemical feedstocks (Couch, 2009).

Since the conception of the UCG idea in 1868 (Klimenko, 2009; Kumar et. al., 2014; Su et. al., 2013), much progress has been made through the years in the development of the technology. Different techniques have been developed for the operation. Earlier field tests were limited to shallow depths. The underground preparation of the seam and gasification are performed using drilled holes. The most common drilling configurations included the linked vertical wells (LVW) and steeply dipping seams (SDS) in earlier trials. Recent techniques include the controlled retraction injection point (CRIP), for its greater control and improved overall efficiency (Couch, 2009; Bhutto et. al., 2013), reverse combustion linking (RCL) (Blinderman et. al., 2008), and forward combustion linking (FCL). Establishing a highly permeable path between the injection and production holes is considered to be the single

most important task prior to gasification. The reason for this is that a highly permeable narrow channel can control gas leakage, water intrusion, liquid condensation, phenol contamination and oxidant bypass during UCG operation (Gregg and Edgar, 1978). Directional drilling, reverse combustion and hydrofracturing are the popular linking methods currently (Couch, 2009; Gregg and Edgar, 1978). Researchers have found that the preference for one technique over another may depend on the coal property. Nevertheless, the directional drilling has been found to be relatively independent of the coal properties (Couch, 2009).

UCG field tests have been carried out in different coal seams globally, using different techniques to enable the evaluation of the effects of various factors of overall UCG performance. Some significant field trials worldwide are summarized in Table 6 below. It is observed from the table that there is a significant increased heating value of the product gas for an injection gas of oxygen/steam mixture over air. It is also observed that the overall performance of the UCG process is largely affected by the properties of coal (ranks and chemical composition), coal seam geology (depth, thickness) and drilling configurations. This dependence indicates that the performance of UCG is site-specific. Site selection is thought to be the single most important decision that will determine the technical and economic feasibility of coal gasification (Perkins, 2005). However, for the same site, seam preparation and operating conditions – temperature, pressure, are the key factors for the successful performance of Underground Coal Gasification.

2.4.3 Chemical Reactions in UCG

The Underground Coal Gasification process occurs in three different zones: drying, pyrolysis, and combustion and gasification of solid char. In the drying zone, wet coal is heated and converted into dry coal by removing moisture attached to it. Upon further heating of the coal, the pyrolysis reactions begin at temperatures around 350–400 °C (Anthony and Howard, 1976) and coal loses its weight, generating volatile matters and the solid known as char. Finally, the char reacts with the injected/pyrolyzed gases to produce the syngas. The three essential types of char layer reactions which govern the UCG product gas composition are: oxidation, reduction, and pyrolysis. Table 7 shows the main reactions in the gasification process.

Table 6: Summary of Significant UCG Field Trials Worldwide

COUNTRY	SITE	START-UP YEAR	COAL RANK	WELL CONFIGURATION	INJECTED GAS	SEAM DEPTH (m)	SEAM THICKNESS (m)	GAS CALORIFIC VALUE (MJ/m ³)
Russia	Gorlovka (Ukraine)	1937	Bituminous	SDS	Air	40	1.9	3.95
					O ₂ /H ₂ O	40	1.9	5.82-10.34
	Podmoskova/Tula	1947	Lignite	LVW	Air	55	3	3.4
	Yuzhno-Abinsk	1955	Bituminous	LVW	Air	100	2	4.1
	Angren (Uzbekistan)	1961	Lignite	LVW	Air	110	4	3.5-3.9
	Hanna II	1975	Bituminous	LVW	Air	85	9	4.2
	Hoe Creek IA	1976	Bituminous	LVW	Air	40	8	3.6
	Hoe Creek IIB	1977	Bituminous	LVW	O ₂ /H ₂ O	40	8	9.0
	Price town	1979	Bituminous	LVW	Air	270	2	6.1
	Rawlins IA	1979	Sub-bitum.	SDS	Air	105	18	5.6
USA	Rawlins IIB	1979	Sub-bitum.	SDS	O ₂ /H ₂ O	105	18	8.1
	Centralia A	1984	Sub-bitum.	CRIP	O ₂ /H ₂ O	75	6	9.7
	Centralia B	1984	Sub-bitum.	LVW	O ₂ /H ₂ O	75	6	8.4
	Rocky Mountain IA	1987	Sub-bitum.	CRIP	O ₂ /H ₂ O	110	7	9.5
	Rocky Mountain IB	1987	Sub-bitum.	LVW	O ₂ /H ₂ O	110	7	8.8
	Alaska SHR	2012	Lignite/Sub-bitum.		Air	50-650	1-12	3.3-5
Belgium	Thulin	1986	Anthracite	LVW	Air	860	6	7.0
Spain	El Tremedal	1997	Sub-bitum.	CRIP	O ₂ /H ₂ O	580	2	6.6
Australia	Chinchilla	2000	Sub-bitum.	LVW	Air	140	10	6.6
	Bloodwood	2011	Sub-bitum.	CRIP	Air	200	8-10	6.4
China	Suncan	2002	Bituminous	Tunnel	Air	80	2	8.5
South Africa	Majuba	2007	Bituminous	LVW	Air	285	3.5-4.5	6.2

Source: *Energies* 2015, 8, pg. 12608

Table 7: Gasification Process Reactions

Reaction	Reaction No.	Equation
Drying	1	Coal $\rightarrow$ Dry Coal + H ₂ O
Pyrolysis	2	Dry Coal $\rightarrow$ Char (C) + Volatiles
Coal Combustion	3	C + O ₂ $\rightarrow$ CO ₂
CO ₂ gasification	4	C + CO ₂ $\rightarrow$ 2CO
Steam gasification	5	C + H ₂ O $\rightarrow$ CO ₂ + H ₂
Methanation	6	C + 2H ₂ $\rightarrow$ CH ₄
Water-gas shift	7	CO + H ₂ O $\rightleftharpoons$ CO ₂ + H ₂
	8	CO + $\frac{1}{2}$ O ₂ $\rightarrow$ CO ₂
Gas phase oxidations	9	H ₂ + $\frac{1}{2}$ O ₂ $\rightarrow$ H ₂ O
	10	CH ₄ + 2O ₂ $\rightarrow$ CO ₂ + 2H ₂ O

Source: www.mdpi.com/journal/energies 2015

The reactivity of the char to O₂, H₂O, CO₂, and H₂ determines the rates at which the desired products are formed (Kariznovi et. al., 2013). Reactions 3, 5, and 8 are the main chemical reactions considered for both shallow and deep coal gasification processes. The hydrogasification (reaction 6) is favourable at a high hydrogen pressure. In the UCG, at low pressure, this reaction is not significant. Reactions 3–6 take place on the wall of coal seams, while reactions 7 and 8 occur at the gaseous stage (Yang, 2005). Different reactions are favourable at different temperature ranges.

A study of equilibrium constants as a function of temperature for some of the important reactions in the gasification process (Table 6), revealed that the equilibrium constants for reactions 4, 5, 6, 7 and 10 are at unity at approximately 1000 K, and the temperature becomes the key factor in determining the shift of chemical equilibria towards the product or reactions. For example, at temperatures above 1000 K, the formations of H₂ and CO are favourable since reaction 4 and reaction 5 are endothermic (Perkins, 2005). Similarly, other reactions seem to be favoured at temperatures below 1000 K. Reactions involved in UCG are not fundamentally different from the reactions of coal and char in the surface gasifiers. In gasification reactions, the combustion of coal and volatiles provides the necessary heat for endothermic gasification reactions.

2.5 Current Global Status of UCG

The inherent environmental benefits of UCG are the simplicity of surface plant, the absence of coal storage and transportation, and the ability to remove minor polluting constituents such as SO_x, particulates and heavy metals from the production syngas. UCG also avoids completely the safety issues associated with equipment and of men working underground (Shafirovich and Varma, 2009).

The global importance of UCG has led to more and more countries keying into the necessary groundwork that will lead to the full establishment of this Clean Coal Technology (CCT). UCG-based associations or groups have been formed to provide focused leadership. The World Coal Association (WCA), World Energy Council, International Energy Association (IEA) Clean Coal Centre, Eurocoal, etc., continue to drive the CCT discourse and actions globally.

The Underground Coal Gasification Association (UCGA), one of such associations, promotes clean coal utilization by providing independent information and representation on all aspects of UCG. It aims to accelerate the safe commercial development of UCG globally. It has over 50 members including oil & gas, national governments, regional agencies, banks, accountants, lawyers, providers of UCG services, universities, energy associations, coal associations, etc. There are 22 countries represented, namely: Argentina, Australia, Bangladesh, Belgium, Botswana, Brazil, Canada, Chile, China, Hungary, Indonesia, Ireland, Japan, Netherlands, Norway, Poland, Slovakia, South Africa, Thailand, UK, USA and Vietnam (Lauder, 2014).

Table 6 provides information on global UCG activities up till 2012. Non-UCGA member countries involved engaged in

UCG activities at different levels – site identification, major trials, licensing, R&D - include Colombia, Czech Republic, India, New Zealand, Pakistan, Romania, Russia, Serbia, Slovenia, Spain, Turkey and Uzbekistan. Currently, there are four long running pilot plants, two in Australia, and one each in South Africa and China. None has progressed yet to commercial scale. Australia has the most advanced UCG projects in Chinchilla and Bloodwood Creek. There is one commercial site in operation in Angren, Uzbekistan for over 50 years. The apparent slow progress in UCG development has been attributed to its lack of inclusion in national energy policies and research objectives worldwide. This is believed to hamper the formation of regulations, licensing criteria, national and local planning guidelines and operational frameworks (Lauder, 2014). Nevertheless, MOUs have recently been signed and/or projects are underway in China, India, Indonesia, Poland, South Africa, Tanzania, UK, USA and Vietnam. Research projects are on-going in China, Japan, Pakistan, Poland, Romania, Vietnam and USA.

On the African continent, from the foregoing progress reports, South Africa is clearly the leader. ESKOM, South Africa's energy giant, has been developing UCG for over 10 years and in 2014 it invested a further US\$94 million in research, and expects the green light for UCG to be ruled out by 2019. They believe that it is a cost-competitive technology. UCG is expected to produce power at around US\$5-6 per kilo Joule, less than half the cost of importing the rival LNG. Also, the great potential and short-term need for UCG research and development has been recognised by South Africa's North West University, Potchesfstrom. They have created a coal research group engaging 40 post graduate students (20 PhDs and 20 Masters') researching on UCG with strong national and international collaboration. In Tanzania, an Australian company, Linc Energy has signed an MOU to build a 400MW UCG plant. Botswana and Morocco have shown more than passing interest in developing UCG as an energy source.

3. DISCUSSION AND RECOMMENDATIONS

Access to energy, especially electricity is a driving force for economic and social development. Coal utilization is a key component in the global energy mix. Coal does not presently contribute to Nigeria's electricity generation in spite of its abundant deposits. The Nigerian government approach, and indeed public opinion on coal utilization in Nigeria has been one-dimensional, mainly anchored on traditional coal mining. As mentioned earlier, in this document, given the 600 million tonnes proven coal reserves, it is a wonder that the level of Nigeria's coal utilization is so low, indeed almost zero. Energy remains critical to sustainable development – building stronger communities with hospitals and schools, and supporting business and industry, all precursors for the delivery of sustainable employment and economic growth. It is believed that coal will be the bedrock on which energy access is built (WCA document, 2013; IEA World Energy Outlook, 2011).

A recent study (IEA World Energy Outlook, 2011) considered the situation in sub-Saharan Africa and suggested that for the region to attain moderate access to energy, where electricity generation capacity is around 200-400MW per million of population, the region would need around 374GW of installed capacity. This represents about 12 times the current capacity in sub-Sahara Africa today. To achieve that level of capacity, the study estimated that an annual growth rate in electricity of around 13% would be needed for the next 20 years. In the past 20 years, the average has been only 1.7%. The inadequacy of energy supply is evident in Nigeria today, with fluctuating generation capacities between 2000 and 5000 MW, which, at 0.005MW per million people, falls woefully short of the requirements for sustainable development. In comparison, South Africa currently has around 800MW of installed capacity

per million people, yet it is still challenged to meet the energy needs of its people. India's capacity stands at 130MW per million people while the USA and Europe stand at about 2826MW and 1733MW respectively. There has to be a drastic and dramatic transformation of electricity supply in Nigeria.

Recent efforts by the Nigerian government to turn things around have yielded mixed results, but supply remains grossly inadequate. Many extenuating circumstances have been blamed for the continued shortfall, like acts of sabotage on gas pipelines. This notwithstanding, it may be suggested that the mono dependence on oil and gas and the total neglect of other potential energy sources has remained the bane of energy supply in the country. In particular, given proven coal reserves, it is highly disappointing that coal mines have remained shut for over 10 years. The national electricity grid is in place and can be further developed to ensure better distribution. The government needs to understand that, as obtains in other climes, all energy sources have some role to play in feeding these grids, including hydro and renewable energy sources. From the foregoing discussion, coal remains ostensibly the most affordable, safest and most reliable source to achieve genuine access to modern electricity services. Coal is, and will continue to be, the backbone of global electricity generation, and fundamental to expanding generating capacity in many developing countries (WCA document, 2013). Nigeria must key in. Developing, or rather, revisiting and re-developing, Nigeria's Coal Utilization Potentials requires a monumental paradigm shift. It's realizable, little steps at a time. Perhaps the best model in the step-wise approach would be a reappraisal of the country's coal potentials. The supervising ministries, departments and agencies must be given this mandate to provide information on capacities of coal fields, and the resources characterized for their appropriate utilization. The research findings, new and existing, in this regard must be made available in a database.

Global demands for safety and environmental concerns must guide whatever technology is embraced. This document is focused on underground coal gasification technology, which represents zero emission. A structured and patient approach must be adopted to maximize the advantages of this clean coal technology. And it must be championed and promoted by government. To imitate the successes of countries like South Africa, it is imperative that government indicates or selects research and tertiary institutions in the proximities of the known or proven coal reserves and gives full support to research and development to bring the UCG technology to reality. In addition, professional bodies like Materials Science and Technology Society of Nigeria (MSN), Nigerian Society of Chemical Engineers, Nigerian Metallurgical Society must also take up the mantle of creating awareness of new technologies such as UCG and other clean coal technologies, through seminars, workshops, lectures, symposia and publications, in synergy with the coal industry, research institutions and universities.

The WCA and IEA model is recommended as key to the development of Nigerian coal utilization which demands that:

- Government and people must have the ambition to achieve real energy access in the country, and believe it is possible.
- The right policy frameworks must be put in place, both on a national and international basis, to support effective energy institutions and business models that support the deployment of a comprehensive energy infrastructure where it is needed most.
- These frameworks will encourage access to finance from all sources, public and private, domestic and international (Foreign Direct Investment, FDI). This will provide the right level of investment to build the energy infrastructure that is so badly needed.

- It must be recognised, and accepted, that all sources of energy are necessary to meet the vast potential demand for electricity. Nigeria must diversify.

4. CONCLUSION

Developing Nigeria's coal utilization potential is a prerequisite for effectively addressing the country's energy challenges, and promoting sustainable economic development. Worldwide coal utilization is moving from traditional coal mining methods to clean coal technologies, in keeping with global demands to reduce environmentally harmful emissions. Underground coal gasification (UCG) technology has been established as technically feasible clean coal technology, in which coal is converted into gaseous products with higher heating value through controlled combustion with oxygen/air and gasification with steam. The UCG product gas, syngas, mainly a mixture of CO, H₂, CH₄ and CO₂, can be used as fuel for heating, power generation, hydrogen production or the manufacture of key liquid fuels such as diesel fuel or methanol. The UCG process will enable the diversification of Nigeria's resource development and provide the platform for sustainable economic development.

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CHEMICAL ANALYSIS OF LEPIDOLITE OBTAINED FROM OGBOMOSHO IN OYO STATE, NIGERIA

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ABSTRACT

The work reports the elemental and mineral compositions of the mineral lepidolite obtained from Ogbomosho in Oyo State, Nigeria. The lepidolite sample is a lilac-purple solid with silvery coloured mica, it is crystalline in texture with no observable smell. It is insoluble in cold and warm water, dilute and concentrated HCl, dilute and concentrated HNO₃. Flame test indicated that the mineral contains lithium and sodium. Classical analysis of the sample showed that it contains Al³⁺ and F⁻. X-ray fluorescence spectroscopy indicated that the sample contains gold (0.1819%), Al (8.2840%) and Li₂O (3.0%), Si (18.4046%), K (5.5939%), Fe (1.175%), Sb (0.6569%), Sn (0.5871%), Mn (0.3314%) and some other elements in trace amount. Analysis using XRD indicated quartz (SiO₂) as the dominant mineral phase with the presence of associated minerals such as muscovite (KAl₂(AlSi₃O₁₀)(OH)₂), and lepidolite (KLi₂AlSi₄O₁₀(F,OH)₂). The chemical analysis result indicated that the sample is Potassium alluminate mineral called Polyolithionite containing other impurities. The high level of Si and Al in the mineral and the presence of lithium (used for the treatment of bipolar disorder and enhancement of bone healing) in the mineral, calls for more focus on the exploration and extraction of the mineral in large scale. The potential of the ore for industrial and medical applications can serve as foreign exchange earnings for Nigeria.

Key words: Mica, Quartz, Lepidolite, Muscovite, Lithium, Bone healing

Introduction

A mineral can be identified by several physical properties, some of which are sufficient for full identification without equivocation. In other cases, mineral can only be classified by more complex optical, chemical or X-ray diffraction analysis (Chestermann and Lowe, 2008).

Lepidolite and spodumene are the common minerals that contain lithium. Commercial quantities of these two minerals are in special igneous rock deposit called pegmatites. Lepidolite is a lilac-gray or rose-coloured member of the mica group (Adebayo *et al.*, 2000). It is a secondary source of lithium and is used industrially for lithium storage batteries, smelting of aluminum ores, reduction of shattering in glass; in heat transfer processes due to its highest specific heat capacity; in rocket motors due to its high resistance to metal fatigue (Cerny, 1991, Oyinloye, 1997). Li⁺ has proved to be useful as a mood-stabilizing drug in the treatment of bipolar disorder in humans in order to enhance bone fracture healing (Hurlbut *et al.*, 1985).

Notable occurrences of lepidolite include Brazil, Ural Mountains, Russia, California, United States, Tanco Mine, Bernic Lake, Manitoba, Canada, Madagascar and Nigeria (Ekiti State, Nassarawa State, Oyo State). Studies of metals in pegmatites located in Nigeria have been carried out (Matheis and Emofurieta, 1987; Garba, 2003; Okunlola and Jimba, 2006; Olusiji, 2011).

This study assesses some physical and chemical properties of lepidolite obtained from Oyo State, Nigeria in order to focus more attention on the solid mineral sector of the Nigerian economy

Materials and Methods

Sample collection

The samples obtained from Ogbomosho in Oyo State, Nigeria were collected from the Nigerian Geosciences Research Laboratories (NGRL), Kaduna in March, 2016. It was identified to be a pegmatite containing lepidolite ore. It was then separated into the ore and the pegmatite (rock). It was then ground to powder with a motorized agate mortar to a fine powder with the grains passing through a 300 mesh screen.

Physical test

Appearance: A 1.0 g amount of the ground sample was collected with a spatula into a test tube, the colour, texture and odour was then observed.

Solubility test: This was carried out using distilled water, then in dilute HCl, concentrated HCl and later in concentrated HNO₃.

Test of pH: The pH of the solution of the sample or the filtrate was determined with litmus paper.

Flame test: A 0.3 g amount of the sample was collected using a spatula and placed in the flame of bursen burner to observe the colour of the flame.

Systematic analysis for metallic and non-metallic ions in the Lepidolite solution

Test for group I metallic chlorides of Pb, Ag or Hg

A 2 cm³ portion of the sample solution was transferred into a test tube, then 5 drops of 2M HCl was added, the formation of precipitate was observed, then one more drop of 2M HCl was added to ensure complete precipitation.

Test for group II metallic sulphides of Bi, Cu, Cd, Sn, Sb

To a 5 cm³ solution of the lepidolite, 10 drops of 6M HCl was added. Then 15M NH₃ was added to make it basic. Then 2 cm³ of the mixture was pipetted into a test tube and excess drops of H₂S bubbled into distilled water was added drop wise for formation of precipitation, the mixture was boiled to remove H₂S completely. Then 3 drops of 15M HNO₃ was added and boiled for one minute, then the mixture was transferred to a test tube and about 0.1 g of solid NH₄Cl was added. 15M NH₃ was added drop wise until the solution is basic. Then H₂S/H₂O was added drop wise until precipitate is complete.

Test for group III metallic hydroxides of Fe, Cr, Al

A 2 cm³ of the lepidolite solution was transferred into a clean crucible, and boiled completely to remove H₂S. Then 0.5 cm³ of 3M H₂SO₄ was added and stirred. The formation of precipitate was observed.

Test for group IV metallic sulphides of Ni, Co, Mn, Zn

To 5 cm³ of the solution, NH₄OH and (NH₄)₂CO₃ was added, and precipitate observed.

Qualitative Test for Anions in the Lepidolite

The action of heat on the lepidolite: A 0.1 g amount of the sample Lepidolite was put into test-tube. This was heated gently at first, then strongly. The evolution of any gas, melting, temporary or permanent colour change was noted. The action of dilute HCl on the lepidolite: The action of dilute HCl on the lepidolite in the cold or warm was carried out, the evolution of any gas was identified. The action of concentrated H₂SO₄ on the lepidolite: This was carried out in the cold and warm.

Sample Preparation for X-ray Fluorescence (XRF)

A 10 g amount of the powdered lepidolite sample was mixed with 1 g of stearic acid (organic binder) and the mixture was thoroughly homogenized in an agate mortar. The mixture was then transferred to a 40 mm diameter hardened steel disc and pressed into a pellet at a pressure of 25 tonnes using hydraulic pressure press. The pellet was then used for XRF analysis. Minipal 4 EDXRF made by JiangSu Skyray Instrument Co., Ltd was used for the analysis.

Sample preparation for X-ray Diffractometry (XRD) analysis

The powdered sample was placed into a sample holder with a powder press piston. The pressed powder inside the sample holder was then loaded into the X-ray diffractometer (XRD) with CuK α (1.54Å) radiation generated and 40kV and 30mA.

The X-ray fluorescence (XRF) and X-ray diffraction (XRD) analysis of the lepidolite ore sample was carried out at NASENI Centre of Excellence, Nanotechnology and Advanced Material, Akure, Ondo State, Nigeria, using the standard operating procedure of the machines.

The measurement conditions for the mineral sample analysis were Lithium target operated at 4kV and 30mA, with a continuous scan mode with scan range of 2 to 80 degrees and drive axis of theta -2- theta. Empyrean XRD spectrometer was used for the analysis.

Results and Discussion

Physical test

The lepidolite sample is a lilac-purple solid with silvery coloured mica, it is crystalline in texture with no observable smell. The sample solution was not soluble in cold water and was also not soluble when warmed. It was also not soluble in dilute and concentrated HCl likewise in HNO₃. And the lepidolite sample was neutral to litmus paper. The flame test, resulted to a red coloured flame. This indicates the presence of lithium.

Systematic Analysis of Metallic Ions in Lepidolite Solution

Group I: No precipitate was observed inferring the absence of Pb²⁺, Ag⁺ and Hg⁺. Likewise Group II CuS and PbS was absent. When ammonium chloride and ammonium hydroxide were added to a solution of lepidolite, a gelatinous white precipitate was observed which inferred that Al³⁺ was present and absence of reddish brown and green precipitate indicated the absence of Fe²⁺, Fe³⁺ and Cr³⁺. However, no visible reaction was observed which inferred the absence of Zn²⁺, Ni²⁺, Co²⁺, and Mn²⁺ of Group IV.

Qualitative Analysis of Anions in Lepidolite

The sample did not melt when heated, no gas was evolved and no colour change was observed. The action of dilute HCl on lepidolite: No visible reaction was observed which inferred that CO₂ from carbonate, S²⁻ from sulphide, or NO₂ from nitrate was absent. The action of concentrated H₂SO₄ on lepidolite: A colourless gas which had no effect on litmus paper was observed which inferred the presence of Cl⁻, Br⁻, F⁻, NO₃⁻ or C₂O₄²⁻. The action of acidified AgNO₃ on lepidolite: No visible reaction was observed when HNO₃ was added and a clear

solution was observed when AgNO₃ was added to the solution of the lepidolite which inferred that F⁻ was present and Cl⁻, NO₃⁻ and C₂O₄²⁻ were absent.

The action of BaCl₂ and KMnO₄ on lepidolite: No visible reaction was observed which inferred that CO₃²⁻, SO₃²⁻ and S²⁻ ions were absent. The group analysis of metallic ions revealed that the lepidolite contains aluminium, potassium, lithium and the analysis of anions revealed that fluoride ion was present in the lepidolite.

XRF and XRD results

The result from the elemental analysis (XRF) of the sample indicates that the sample is a potassium alluminate mineral containing elements like: Silicon, Aluminium, Phosphorus, Sulphur, Potassium, Calcium, Vanadium, Chromium, Manganese, Iron, Nickel, Copper, Zinc, Gold, Silver, Niobium, Molybdenum, Tin and Antimony (Table 1).

Table 1: XRF RESULT FOR THE LEPIDOLITE SAMPLE

Voltage(KV)	40.0	
Current(μA)	350	
Element	Intensity	Content
Mg	0.0000	0.0000
Al	0.0381	8.2840
Si	0.1689	18.4046
P	0.0028	0.1282
S	0.0044	0.2908
K	0.0687	5.5939
Ca	0.0079	0.1388
Ti	0.0000	0.0000
V	0.0001	0.0062
Cr	0.0001	0.0022
Mn	0.0043	0.3314
Co	0.0000	0.0000
Fe	0.0115	1.1752
Ni	0.0009	0.0503
Cu	0.0019	0.0448
Zn	0.0031	0.1060
As	0.0000	0.0000
Pb	0.0000	0.0000
W	0.0000	0.0000
Au	0.0003	0.1819
Ag	0.0000	0.0000
Rb	0.2907	4.0274
Nb	0.0020	0.0195
Mo	0.0016	0.2053
Cd	0.0000	0.0000
Sn	0.0032	0.5871
Sb	0.0053	0.6569

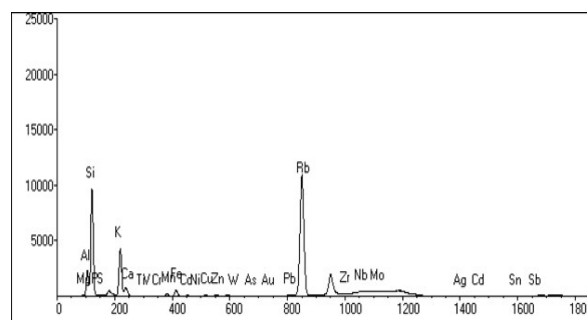


FIGURE 1: XRF RESULT FOR THE LEPIDOLITE SAMPLE

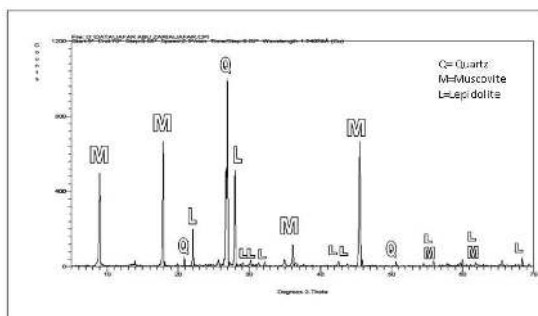


FIGURE 2: XRD RESULT FOR THE LEPIDOLITE SAMPLE

From Figure 1, the lepidolite sample from Ogbomosho, Nigeria contains: 8.2840% Al, 18.4046% Si, 0.1282% P, 0.2908% S, 5.5939% K, 0.1388% Ca, 0.0062%V, 0.0022% Cr, 0.3314% Mn, 1.1752% Fe, 0.0503% Ni, 0.0448% Cu, 0.1060% Zn, 0.1819% Au, 0.0195% Nb, 0.2053% Mo, 0.5871% Sn, and 0.6569% Sb respectively. The element with the highest percentage composition was silicon being 18.4046% while the one with least percentage composition is chromium with 0.0022%. This result conforms with the findings that pegmatite is one of the classical sources of broad spectrum of rare earth elements including Sn, Nb, Ta, U, Th (Cerny, 1994; Patrick De, 1999). Also, the oxides in the lepidolite samples were in the following percentages: SiO₂ 43.02, TiO₂ 0.26, Al₂O₃ 20.84, Fe₂O₃ 2.03, FeO 10.76, MnO 3.32, MgO 0.24, Li₂O 3.00, CaO 0.04, Na₂O 0.19, K₂O 10.24, Rb₂O 0.75, F 7.11, H₂O+ 0.81, H₂O- 0.10: K (Al_{0.9} Li_{0.9} Fe_{0.8} Mn_{0.2}) (Si_{3.1} Al_{0.9}) (OH)_{0.4} F_{1.6}" (Table 1).

The mineralogical analysis of the Lepidolite sample by X-ray diffraction (XRD) in Figure 2 gives the mineral phases present in the ore. As indicated in Table 2, 3 and 4, the sample contains Quartz (SiO₂), (KAl₂(AlSi₃O₁₀)(OH)₂), and Lepidolite (KLi₂AlSi₄O₁₀(F,OH)₂) with Quartz mineral as the dominant specie.

From the X-ray diffractogram (Figure 2) Quartz give one principal peak at 9.900 Å with 100% intensity, the Muscovite gives three principal peaks at 3.34 Å, 5.98 Å and 18.90 Å with intensities of 50%, 65% and 64.5% respectively and finally lepidolite gave two principal peaks at 9.5 Å and 10.3 Å with intensities of 19.65% and 45% respectively and other peaks in trace amounts.

Conclusion

From the result obtained, the lepidolite sample obtained from Ogbomosho in Oyo State, Nigeria contains several elements which are of variety of importance like: lithium, potassium, aluminium, silicon, sulphur, phosphorus, potassium, calcium, vanadium, chromium, manganese, gold and rubidium and their oxide forms which also have their own uses and applications, and even their carbonate forms. The XRD analysis also

revealed the presence of some minerals like; Quartz, Muscovite and the Lepidolite.

In an era of diversification of Nigerian economy, it can then be concluded that the presence of various metals of industrial and medical benefits are present in lepidolite. So exploration of lithium and other elements from lepidolite at large scale can serve as foreign exchange earnings for Nigeria.

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INVESTIGATION OF THE EFFECT OF GLUTAMINE AND GLUTATHIONE ON THE SHELF LIFE OF KUNU ACHA

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ABSTRACT

Acha (*Digitariaexilis* and *DigitariaIburua*) is a cereal crop which is grown across West Africa countries, is specified in Nigeria as an oldest crop. The grains are rich in methionine, an essential amino acid that is lacking in many major cereals. Acha is processed into Kunu (KunuAcha), which is a traditional non-alcoholic beverage widely consumed in the Northern parts of Nigeria especially during the dry season. There are many other types of kunuAcha which includes: Kununzaki, Kunungyada, Kununakamu, Kununtsamiya, Kununbaule, Kununjiko, Amshau and Kunungayamba. Generally, the shelf life of the above listed kunu including KunuAcha is two or three days under warm temperature. The effect of the biochemical preservatives used (Glutamine and Glutathione) is to increase the shelf life of KunuAcha. These preservatives limit the growth of microbes which contribute to the spoilage of nonalcoholic beverages Kunu Acha. From the result showed, 0.5g of Glutamine and 4.5 of Glutathione in 340g of KunuAcha has the lowest microbial loads. The preservatives even though show effectiveness in limiting the growth of all the microbes analysed in the KunuAcha, the effect is much seen in the control of *Sacchara* by eliminating it completely and limit other species. The least effect of Glutamine and Glutathione in controlling the growth of microbes is seen in *Bacilli* specie growth.

KEY WORDS: Kun, -acha, glutamine, glutathione, preservatives

INTRODUCTION

Digitariaexilis and *DigitariaIburua* which is also known with other names such as Fonio, Findi, Fundi, Pom, and Kabug, in different West African countries and Acha in Nigeria has been reported as the oldest West African cereal (NRC, 1996). Annual production in West Africa, grown on about 380,000ha, is estimated to be about 250, 000tons (Cruz, 2004). In Nigeria, annual yields of 3,098 metric tons, 112,000mt and 126,000mt have been reported (Abdullahi and Luka, 2003). The two Acha species, *Digitariaexilis* and *DigitariaIburua* grains are rich in methionine, an essential amino acid that is lacking in many major cereals (Temple and Bassa, 1991). The diets have relatively low free sugar and low glycemic content and this makes it adequate as a suggested diet of diabetic patients.

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Acha is processed into Kunu (KunuAcha), which is a traditional non-alcoholic fermented beverage widely consumed in the Northern parts of Nigeria especially during the dry season (Temple and Bassa, 1991). Other types of Kunu processed and consumed in Nigeria includes; Kununzaki, Kunungyada, Kununakamu, Kununtsamiya, Kununbaule, Kununjiko, Amshau and Kunungayamba. Much research had been done on other types of KunuZaki and none has been done on KununAcha (Fonio) which is what agitated this research or investigation on the shelf life of the Kunu (Acha) using preservatives Glutamine (GA) and Glutathione (GT).

- Deterioration of KunuAcha starts from two to three days after production, thus the necessity to extend the shelf life for commercial production and economic enhancement cannot be over emphasized.
- KununAcha also serves as an alternative food beverages for diabetes patient because of its low sugar contents.

- The spent, Glutamine and Glutathione used as preservatives in the kunuAcha can lead to neural improvement and reduction of toxicity in human body. (www.benefitsofGlutamine.mobi)

The aim of this work is for the “Investigation of the Effect of Glutathione/Glutamine of the Shelf Life of KunuAcha through the following objectives:

- ❖ Production of KunuAcha.
- ❖ Variation of independent variables (Concentration of Glutamine/ Glutathione) on fixed quantity of KunuAcha.
- ❖ Measurement of the microbes in the controls and the treated samples.
- ❖ Comparing and contrasting the effect of the preservatives in the treated samples and that of the controls.

MATERIALS AND METHODS:

Preparation of Kunu Acha

The raw materials for the preparation of the KunuAcha; Acha (*Digitariaexilis*), honey and ginger (*Zingiberofficinale*) were purchased from Nasarawa Market in Nasarawa State of Nigeria. The preservatives, Glutamine and Glutathione were purchased from Skye lack pharmacy, Wuse. The raw Acha was pre-cleaned by removing sand and other impurities through physical sorting, then about 300g was soaked for about 3min in clean water and washed through decantation to further remove any suspended particles and sand. About 1.7g of ginger was put in the soaked Acha and grinded to paste form. The paste was divided into two portions, small and large. Hot water (100 °C) was added into the large portion and stirred thoroughly and allowed to cool to about 60°C. The other portion was then added and stirred to reduce the viscosity of the mixture and allowed to cool for 6-7hrs. About 450 ml of honey was added as the source of sugar to finally produced kunuAcha. The process flow diagram is shown in Figure 1

Experimental design and treatment of the samples.

Eight sample bottles were sterilized using autoclave at temperature of 150°C maintained for the period of two hours. Control samples of kunu (without glutamine and glutathione), SC-1, SC-2 and SC-3 were then prepared according to the setup in Table 3.1 and filled into three sterilized capped plastic bottles respectively. The microbial analysis of sample SC-1 was carried out immediately after kunu production. Control sample container cap of SC-2 was punched while that of SC-3 was not punched. The two samples SC-2 and SC-3 were left at room temperature for ten days after which microbial analysis were

performed. Base on literature review, the biochemical preservatives, Glutamine and Glutathione were used in various quantities which were dissolved in 6ml of distilled water and added to 340grams of kunu placed in five punched capped bottles and left for ten days at room temperature after which microbial analysis was carried out. The samples with bottle's cap punched were repeated as shown Table 1.

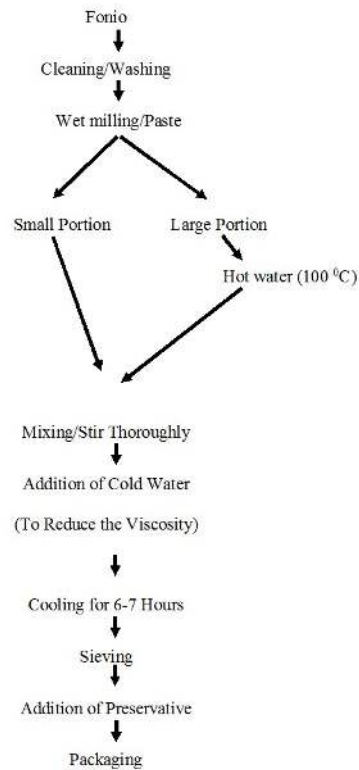


Figure 1: Process Steps of Producing KunuAcha.

Table 1 Control Samples Setup without Glutamine and Glutathione.

S/N	Sample	GA (g)	GT (g)	Days Kunu Acha of 340g kept At Room Temperature	Container Cap
1	SC-1	0	0	0	NA
2	SC-2	0	0	10	P
3	SC-3	0	0	10	NP

NB: GA mean Glutamine, GT mean Glutathione, NA mean Not Applicable, P mean Punched and NP mean Not Punched.

Table.2: Experimental Samples Setup with Glutamine and Glutathione and Bottles' Caps Punched.

S/N	Sample	GA (g)	GT (g)	Days Kunu Acha of 340g kept at Room Temperature
1	SA-1	0.5	4.5	10
2	SA-2	1.0	3.5	10
3	SA-3	1.5	2.5	10
4	SA-4	2.0	1.5	10
5	SA-5	0.5	2.0	10

RESULTS AND DISCUSSION

Table 3: Results of Microbial Analysis of Controlled Samples

S/ N	Sam ple	Sacri na	Flavobace rium Sp.	Lactoba cilli Sp.	Bac illi Sp.	Microc occi Sp.
1	SC-1	0	4	4	10	8
2	SC-2	246	360	330	760	880
3	SC-3	195	280	240	620	750

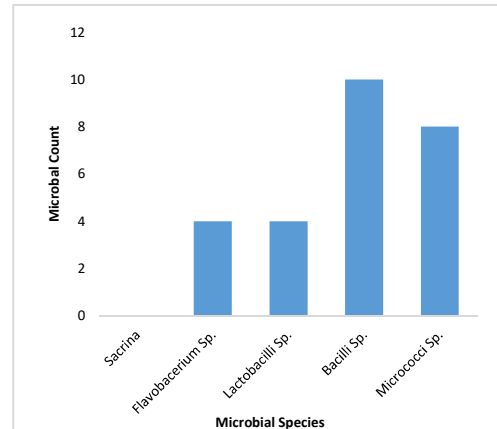


Figure 2: Variation of Microbial Count of Freshly Prepared Kunu Acha

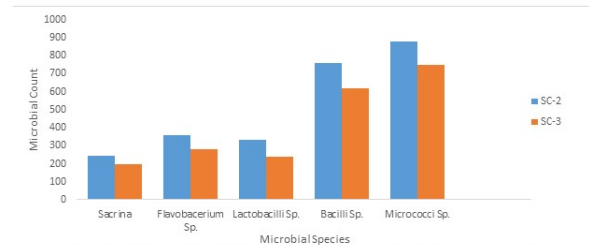


Figure 3: Variation of Microbial Count of Control Samples (Punched and Unpunched)

Table 4: Result of Microbial Analysis of Samples Treated with Glutamine and Glutathione and Containers' Caps Punched.

S/ N	Sam ple	Flavobacer ium Sp.	Lactoba cilli Sp.	Baci lli Sp.	Microco cci Sp.
1	SA-1	1	4	7	6
2	SA-2	2	5	8	7
3	SA-3	3	7	9	6
4	SA-4	5	8	8	9
5	SA-5	4	4	10	8

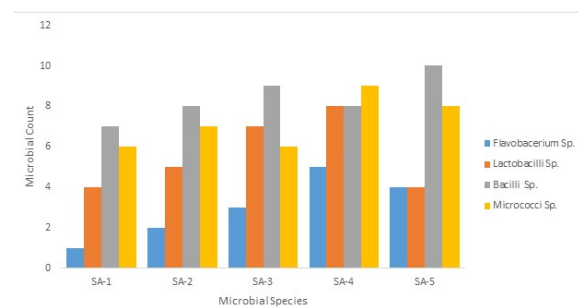


Figure4: Variation of Microbial Count of Treatment Samples

Discussion of results.

From the results of control analysis shown in Table 3, Figure 2 and Figure 3, sample SC-1 which is freshly prepared kunu has the minimum microbial level ranging from 0 to 10. The microbial load seen in this sample could be attributed to contamination of the raw material and also handling process. Control sample SC-2 and SC-3 as shown in Figure 4.2 have high microbial loads ranging from 246 to 880 and 195 to 750 respectively. These high counts of microbes could be attributed to the metabolic processes taking place inside the kunu by the microbes that were already present in these samples. However, the high degree of microbial loads in sample SC-2 compared to sample SC-3 could be attributed to the fact that bottle's cap of sample SC-2 was punched hence allowing continuous influx of microbes in air into the kunu sample in the bottle.

The results of microbial analysis shown in Table 4. and Figure 4. for samples treated with glutamine and glutathione shows a significant departure from the results obtained for control left at room temperature. This shows Glutamine and Glutathione effect in limiting the growth of microbes in non-alcoholic beverage such as kunuAcha. However, the effect of glutamine and glutathione in all the treated samples is much seen in Sacrina by eliminating the microbial loads and limiting the other species. SA-1 which has concentration of 0.5g Glutamine and 4.5g Glutathione in 340g of kunuAcha has the least microbial loads. Generally, sample SA-1 has the highest dosage of Glutathione, 4.5g which shows that Glutathione has the highest effect in controlling microbial growth

CONCLUSIONS AND RECOMMENDATIONS:

From the results and discussions, the following conclusions could be drawn:

1. There is significant growth of microbes in kunuAcha kept at room temperature for ten days without any preservatives added to it.
2. Glutamine and glutathione which is more of biological method of preservation can be safely adopted to preserve and extend the shelf life of non-alcoholic beverage such as kunuAcha.
3. The most effective dosage of glutamine and glutathione is 0.5g and 4.5g respectively per 340g of kunuAcha.
4. The preservatives even though show effectiveness in eliminating the microbial loads of Sacrina and limiting the growth of other species.

For future research, the following recommendations could be made:

1. The current research was carried out to study the impact of glutamine and glutathione in the microbial growth at the end of ten days. For further research, it is recommended the glutamine and glutathione effect in limiting the growth of microbes at one month, two months, three months or even a year should be investigated.
2. The effect of higher dosage of glutamine and glutathione outside the range studied in this project should be investigated.
3. The efficacy of extract of glutamine and glutathione from locally available resources in the control of

microbial growth in non-alcoholic beverages such as kunuAcha should be investigated.

4. This project should be repeated in the preservation of dried powder of Acha.

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CHEMICAL SURFACE MODIFICATION OF CORN COBS AND ITS' SORPTION CAPACITY FOR ACID BLACK 210 DYE REMOVAL FROM AQUEOUS SOLUTION

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ABSTRACT

Dye application processes produce waste waters possessing unacceptable environmental risk. Many synthetic dyes are known as organic pollutant with toxic effects on many organisms. Adsorption through agricultural products such as rice husk, sugarcane bagasse, soybean hull, sawdust, coconut shell, groundnut shell, apple waste, fly ash, corn cob etc. has been demonstrated to be a useful alternative to the conventional treatment systems for removal of dyes and toxic metals such as chromium, mercury(Hg), copper (Cu), nickel (Ni), etc. from aqueous solution. It could be considered as an eco-friendly device to the existing relatively more expensive treatment technologies. This work investigated the effect of various chemical treatments on the adsorption properties of corn cob for use as low cost adsorbent for removal of acid black 210 dye from aqueous solution. The chemical treatments used in this study were Alkali treatment (5% NaOH), Benzoyl treatment with (10% Benzoyl chloride) and silane treatment (1% Phenyl triethoxysilane). Scanning Electron Microscope (SEM) and FTIR analyses were used to examine the changes that occur between the chemically surface modified corn cob and the unmodified corncob. The adsorption capacities of these adsorbent towards this dye has been evaluated by determining the amount of dye adsorbed and the percentage removal efficiency. Treatment of corncob with silane reagent was found to improve the adsorption capacity of corn cob and treatment of corncob with benzoyl chloride decrease the adsorption capacity of corncob.

Keywords: Corn cob, adsorption, Scanning electron microscope, Acid black 210 dye, Chemical modification

Introduction

A corn cob is a major part of the corn waste. It is estimated that 40-50% of corn is corn cob. The corn cob fibre contain 30-40% cellulose, 20-36% hemicellulose, 16% lignin and 8% other materials. Hemicellulose and cellulose have a hydroxyl and carbonyl groups which can be used for the attachments of other functional groups (Muchlisyam, 2014). This high cellulose and hemicellulose contents of a corn cob makes it to possess the potential of being an adsorbent for dye removal. One attractive feature of lignocellulosic fibres is their chemical composition with a large amount of relatively easily accessible hydroxyl unit that can be used for the attachments of a variety of functional group (satyanarayana 2009).

Several researches were conducted for the removal of different classes of dyes from industrial effluents such as chemical precipitation, ion exchange, adsorption on activated carbon, coagulation, flocculation and advanced oxidation/reduction, along with the biological ones. Many of these techniques, even if very effective, can be expensive due to their initial and operational high cost, generating sludge, requiring additional treatment and causing disposal problems (El-Maghraby, 2011).

To reach the full objectives of zero pollution, adoption of alternative technologies which suit the situation of low capital availability, minimum man power and limited energy consumption are necessary. Adsorption through agricultural products such as rice husk, sugarcane bagasse, soybean hull, sawdust, coconut shell, groundnut shell, apple waste, fly ash, corn cob etc. has been demonstrated to be a useful alternative to the conventional treatment systems for removal of dyes and toxic metals such as chromium, mercury(Hg), copper (Cu), nickel (Ni), etc. from aqueous solution. It could be considered as an eco-friendly device to the existing relatively more expensive treatment technologies (Swami, 2006).

This work has investigated the effects of various chemical treatments on the adsorption properties of corn cob for use as low cost adsorbent for removal of acid black 210 dye from aqueous solution. Adsorbent samples were pre-treated in aqueous NaOH solution to activate the hydroxyl groups transforming them into alkoxides, facilitating the subsequent reaction with benzoyl chloride and silane and also increases the

accessibility of the reagent to the interior of the corn cob fibre resulting in the modification of the cellulosic fibre.

Materials and Methods

Materials

Corn cob were obtain from a maize farm in Giwa local government area of kaduna state, Sodium hydroxide (Loba chemie labrich), Hydrochloric acid (Aldrich), Phenyltriethoxysilane (Aldrich), Benzoyl chloride (BDH), Acetone (JDH), Acetic acid (JDH), Ethanol (Ideal SMA Canada), Acid black 210 dye. All chemical are of analytical grade.

Methodology

Preparation of Corn Cob

The corn cobs were washed, dried under sun light, chopped in to small pieces, ground to fine powder and placed in an air tight container for further use.

Alkali treatment

30g of corn cobs powder was added to 5% NaOH solution at room temperature for one hour and filtered through filter paper to remove the lignin. The residue was rinsed with distilled water and washed with dilute HCl solution to neutralize the alkali. They were made alkali free by rinsing with water and finally with distilled water. The washed corn cobs powder was dried by exposure to sun light (velmurugan, 2012).

Benzoyl treatment

10g of the alkali treated corn cobs powder was suspended in a mixture of 10% NaOH and benzoyl chloride and stirred for 15min. the residue was filtered and soaked in ethanol for 1hour to remove excess benzoyl chloride. It was finally rinsed with distilled water and dried in an oven at 80°C (Joseph, 2000 and kalia, 2011).

Silane treatment

1% phenyltriethoxy silane solution in acetone was prepared acetic acid was added to the solution to maintain a pH of 4 and stirred for 10mins. 10g of the dried alkali treated corn cobs powder was soaked in the solution for 1h. They were removed

from the solution by filtration and dried in hot air oven at 80°C (Uma, 2012).

FT-IR Analysis

FT-IR analysis was conducted using FTIR machine (Cary 260 of Agilent technology) to determine the changes in the structure of the untreated, alkali treated benzoyl and silane treated corn cobs powder by revealing the functional groups present.

Scanning Electron Microscope (SEM)

The untreated and treated corn cobs powder was observed under different magnifications using phenom proX super scanning electron microscope to examine the changes in their surface morphology.

Adsorption experiment

An accurately weighed quantity of acid black 210 dye was dissolved in distilled water to prepare the stock solution 100mg/L. 100ml of the dye solution was added to 2.5g of untreated, alkali treated, silane treated and benzoyl treated corn cobs powder in 250ml conical flask. This was done at room temperature (32°C). The mixtures were then stirred on a rotary orbital shaker at 160rpm. The kinetics of adsorption was determined by analysing the adsorptive uptake of the dye from aqueous solution. Therefore, samples were withdrawn from the shaker after every 30min, the adsorbents were separated from the solution by filtration and the absorbance value of the supernatant solutions were measured before and after adsorption at 460nm with UV Visible spectrophotometer (model UV0906) until equilibrium was reached.

The amount of dye adsorbed by the adsorbents (Q_e in mgg^{-1}) was calculated using the following formula

$$Q_e = \frac{V}{M} (C_0 - C_e)$$

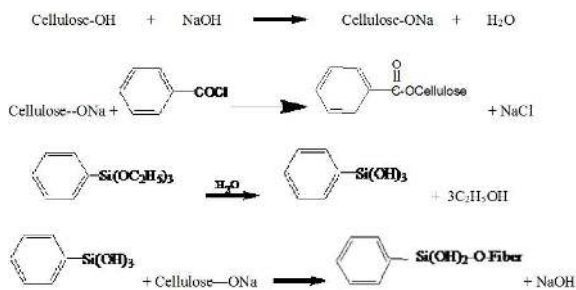
Where, C_0 and C_e are the initial and equilibrium adsorbate concentration respectively in (mg/L), V is the volume of the solution in (L) and M is the mass of dry adsorbents used in (g). The percentage removal efficiency of the dye was calculated as

$$\% \text{ removal efficiency} = \frac{(C_0 - C)}{C_0} \times 100$$

Where, C_0 is the initial concentration, C is the solution concentration after adsorption at any time.

Result and Discussion

Corn cob is an agricultural lignocellulosic by-product composed of cellulose hemicellulose and lignin (Carol and somerville, 2009). The objective of alkaline treatment is to degrade and dissolve away the lignin and leave behind most of the cellulose and hemicellulose in form of particles. Treatment of corn cobs with NaOH decreases the strength of the hydrogen bond, decreases the quantity of lignin and consequently leads to a cellulose increase (Sahare and Rajkumar, 2012). **Scheme 1** is the representation of the chemical surfaces modifications that takes place at the surface of the adsorbent.



Scheme 1: Reactions of the corn cobs with chemicals to modified the surface of the adsorbent

Kim & Holtzaple (2005) reported that NaOH mechanistically cleaves the alpha-aryl ester bonds from its polyphenolic monomers along with weakening of hydrogen bonds which in turn promotes the swelling of cellulose and mediated delignification of cellulignin have also postulated the consequence of alkali treatment, is the saponification of ester bonds resulting in swelling of wood which enhances the penetration of reagents in to the cell wall fine structure. Chemical treatment of corn cobs by benzoylation decreases the hydrophilic nature of the corn cob cellulose as benzoylation prevent hydrolyses of cellulose, whereas, chemical treatment of corn cobs by silanization improves the wetting behaviour of cellulose and also produce a tough and, flexible layer on the surface of the cellulose.

FT-IR Spectral Analysis

The FTIR spectra of the untreated, alkali treated, benzoyl and silane treated were analysed to determine the changes in the structure of cellulose, hemicellulose and lignin by revealing the functional groups present in the adsorbents. Figure 1a-d shows the FTIR band spectra of the treated and untreated corn cob. Figure 1a which is the untreated spectrum of corn cob shows peaks around 3336cm^{-1} corresponding to OH stretching vibration and 2926cm^{-1} due to the stretching vibration of the C-H group on the aromatic rings, in the spectrum of the alkali treated corn cob (figure1b), the OH peak increase to 3345cm^{-1} this was attributed due to the decrease in lignin of low OH group content with respect to cellulose and degradation of hydrogen bonds between OH groups. Also, the relative absorbance of C-H vibration decreased to 2896cm^{-1} this is due to the dissolution of lignin and hydrolysis of $-\text{OCH}_3$ groups to phenolic groups.

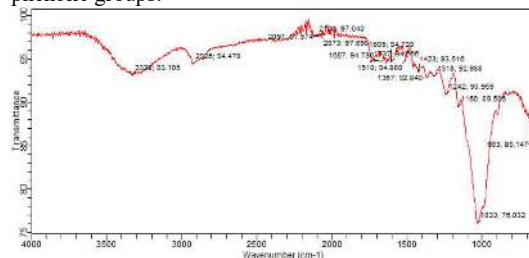


Figure 1a: FTIR spectrum of untreated corn cob

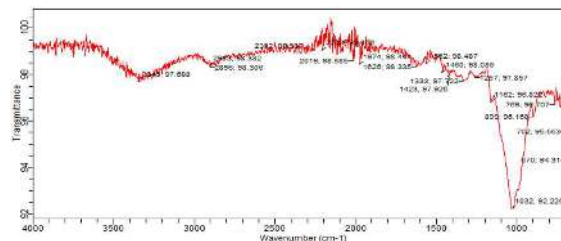


Figure 1b: FTIR spectrum of Alkali treated corn cob

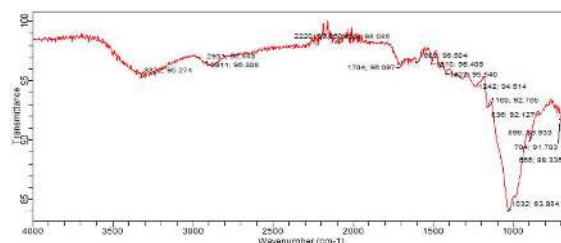


Figure 1b: FTIR spectra of Silane treated corn cob

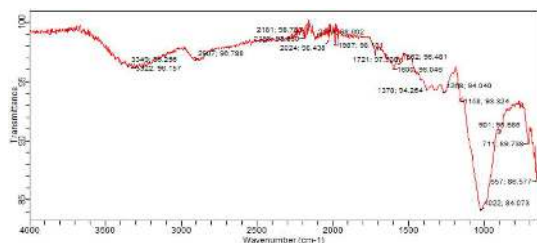


Figure 1c: FTIR spectrum of benzoyl treated corn cob

Important modifications were observed due to the appearance of a band at 1737 cm^{-1} which is a characteristic of $\text{C}=\text{O}$ stretching of unconjugated hemicellulose in the spectrum of untreated corn cob. The disappearance of this band and the appearance of a band at 1460 cm^{-1} in the alkali treated corn cob spectrum were reported to be $\text{C}-\text{H}$ deformation in lignin. Also the appearance of a peak at 1721 cm^{-1} is for $\text{C}=\text{O}$ stretching of the benzoyl carbonyl group in the benzoylated fibre and the appearance of a band at 1704 cm^{-1} correspond to $\text{C}=\text{O}$ stretching vibration for conjugation with phenyl group in the silane treated fibre.

From the FTIR spectra of the adsorbents after dye adsorption Figure 2a and 2b, it has been observed that there was a significant shifting of peaks in the OH group of all the adsorbents except for benzoyl treated adsorbents which shows little changes, indicating that significant amount of dye was adsorbed in all the adsorbents but little amount of dye was adsorbed in the benzoyl treated adsorbents since only little or negligible changes were observed in their spectra.

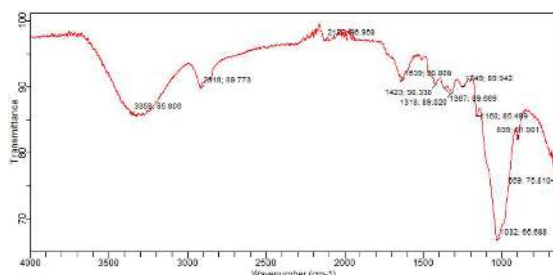


Figure 2a: FTIR spectra of silane treated corn cob after adsorption

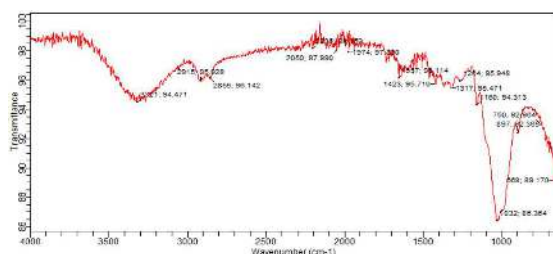


Figure 2b: FTIR spectra of benzoyl treated corn cob after adsorption

Important changes were observed due to the disappearance of certain peaks at 1737 cm^{-1} in the untreated adsorbent spectra, 1460 cm^{-1} in the alkali treated adsorbents spectra, 1704 cm^{-1} in the silane treated adsorbents spectra after adsorption and appearance of peaks at 1639 cm^{-1} which may be due to the adsorbed OH and conjugated $\text{C}-\text{O}$ in all the adsorbents spectra except for benzoyl treated adsorbents after adsorption.

Scanning Electron Microscope (SEM)

Scanning Electron Microscope (SEM) was used to examine the surface morphology of the treated and untreated adsorbents and the results obtained shows variation in their morphology. Figure 3a-3d shows the SEM photo micrograph of the

untreated, alkali treated, silane treated and benzoyl treated corn cob.

Figure 3a which is the untreated corn cob shows surface hardness (strong) and absence of pores indicating the presence of lignin, as lignin is responsible for providing the sturdy structure of plants.

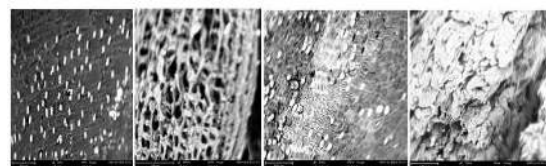


Figure 3: Photomicrograph of a) Untreated corn cob b) Alkali treated corn cob c) Silane treated corn cob d) Benzoyl treated corn cob

Figure 3b of the alkali treated corn cob showed a soft and porous surface. The soft and porous surface topography in the alkali treated adsorbents was due to the removal of lignin. This is in accordance with the work of (Sahare and Rajkumar 2012) which reported that NaOH heat produce a porous flat surface area apparently eliminating the rough external surface, the conformation of the fibre expands, the structure become loose, and the surface area of the fibre increases.

Figure 3c of the silane treated adsorbents shows a very clean and rougher surface. Their surface topography shows the absence of impurities which were present in the untreated fiber. Similar morphology was also observed in plate 1d of the benzoylated corn cob.

Adsorption experiment result

The adsorption efficiency of corn cob towards the dye before and after alkali treatment, benzoyl and silane treatments were shown in table 1.

Table 1: Adsorption efficiencies of the modified and unmodified adsorbents

samples	Absorbance	C_0 mg/ml	C_e mg/ml	Q_e mg/g	% removal efficiency
Stock solution	1.1731	0.10	0.10	0.00	00
Untreated corn cob	0.4344	0.10	0.038	2.48	62
Alkali treated Corn cob	0.4200	0.10	0.036	2.56	64
Silane treated corn cob	0.2637	0.10	0.034	3.12	78
Benzoyl treated corn cob	1.0032	0.10	0.090	0.40	10

From table 1, it was observed that the adsorption capacity of untreated adsorbents increases after alkali treatment, this may be due to the increase in the surface area of the adsorbent and accessibility of the adsorbent pores toward the dye. It may also be due to the fact that alkali treatment increases the amount of cellulose exposed on the fibre surface, thus increasing the number of possible reaction sites. It was also observed that the adsorption capacity of the untreated and alkali treated adsorbents decreases markedly after treatment with benzoyl chloride this may be due to the fact that benzoylation prevent hydrolysis of cellulose, or may be due to the presence of contaminated by-products and benzoyl ($\text{C}_6\text{H}_5\text{C}=\text{O}$) which attributed to the decrease in hydrophilic nature of the treated fibre. This can be supported with the work of (Sundman, 2015), which reported that any colour appearance (specifically yellow) on benzoyl treated fibre strongly indicates that the products are contaminated with by products. However, the most commonly by-products are benzyl alcohol and benzyl

ether, both of which are uncoloured. It is therefore not known what exactly causes the yellow colour.

On the other hand, the adsorption capacity of alkali treated corn cob increases markedly after silane treatment this may be due to the fact that silane improves the wetting behaviour of cellulose. And it was pointed out that the absorption properties of lignocellulosic materials are strongly dependent on the wetting behaviour of single cellulosic fibre (Satyanarayana, 2009). Or it may be due to the fact that silane usually dissolve impurities which may affect the adsorption capacity of the fibre or as a result of silane being a chemical coupling agent, makes the silane treated adsorbent possesses certain functions like reaction with functional group of the dye through covalent or hydrogen bonding which consequently promote the adsorption capacity.

Conclusion

Treatment of corn cob with alkali, benzoyl and silane modified the surface of the corn cob fibre. Chemical surface modification of corn cobs powder with silane coupling agent was found to increase the adsorption capacity of corn cob while chemical surface modification of corn cobs powder with benzoyl chloride was found to decrease the adsorption capacity of corn cob. Silane treated adsorbent with the highest percentage removal efficiency of (78% corn cob) was found to be a promising material for the removal of acid black 210 dye from aqueous solution.

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A DISCONNECT BETWEEN POLICY AND PRACTICE IN DEVELOPING COUNTRIES: MANAGING E-WASTE MATERIALS IN NIGERIA

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Abstract

There are insufficient management functions that begins with planning, institutional arrangements, and handling of e-waste materials in Nigeria. Modern trends, like recycling, still fall short of global practices. This study examined Waste Electrical and Electronic Equipment (WEEE) management strategies in South Eastern Nigeria with a view to suggesting appropriate implementable measures. The research concept was driven by the Pongrácz's theory of waste management. It used investigative approach through questionnaire administration. Twenty local government areas were purposively selected from 5 mutually exclusive strata of states. Data from 36 government agencies/offices were analyzed using percentage and linear multiple regression. Results revealed that WEEE management strategies are inadequate ($\beta = -1.024 < p = 0.657$ and $\beta = 0.608 < p = 0.764$). The study concluded that WEEE management strategies are inapt and poorly implemented. Regulatory bodies are therefore urged to urgently embrace and domesticate appropriate management strategies; conduct periodic inventory of WEEE types and quantity; as well as encourage the set-up and enforcement of frontier standards for modern facilities designated for the disposal of e-waste materials.

Key Words: E-waste; Waste Electrical and Electronic Equipment (WEEE); Recycling; Waste Management Theory; South Eastern Nigeria

1.0 Introduction

Several reported incidents of uncontrolled transboundary movements of hazardous wastes, some of which declared as economic goods, have its final stop in developing countries (Basel Convention, 2011). E-waste materials or Waste Electrical and Electronic Equipment (WEEE) are some of the closest source for generated hazardous wastes in Nigeria and other West African nations (Öko-Institut and Green, 2010). The global concerns about WEEE arose following its proliferation in recent decades and the rapid growth in quantities that requires disposal throughout the world. These countries are now facing huge challenges in managing WEEE which are either internally generated or imported illegally (GFMECD, 1995). Reports have shown that most consignments of Used Electrical and Electronic Equipment (UEEE) are a combination of less than 25% of functional UEEE and over 75% of WEEE (Ayodeji, 2011). Anecdotal evidences have supported the claims that innovation and rapid changes in technology, planned obsolescence of Electrical and Electronic Equipment (EEE), and low initial cost of near End-of-Life EEE have resulted in the fast-growing surplus of WEEE around the globe. In particular, the quick growth in the ICT sector has led to an improved capacity of EEE and simultaneously decreased products' lifetime, such that the quantity of waste produced is increasing by 10% (Ayodeji, 2011; Basel Convention, 2011).

The provisions of the National Environmental (Sanitation and Wastes Control) Regulation S.I.28 of 2009 stipulates that part of the management strategies should be to promote available policies, strategies, legislations, acts, regulations and guidelines for solid waste (WEEE) management through establishment of baseline studies, public health criteria, and a need for comprehensive monitoring programme incorporating an early warning system for the down-stream users (NESREA, 2011). Subjective evidences suggests that there is inadequate action of management functions that starts with strategic planning, institutional arrangements, directing and control of WEEE activities in Nigeria (Basel Convention, 2011; NESREA, 2011). The extent of WEEE generation, collection, storage, treatment and final disposal in different regions in Nigeria appears uncertain. This has invariably informed the kind of strategies put in place or executed for its control and hence this article. Formal recycling, still fall short of global

practices (ESWAMA, 2004; Basel Convention, 2011). Therefore, this study assess WEEE management strategies in South Eastern Nigeria and suggest appropriate implementable measures.

2.0 Contemporary Approaches for E-Waste Management in Nigeria

WEEE Management Strategies are tied to resolving e-waste problem through, strategic planning, legal and regulatory framework, public education and participation, Institutional arrangements, funding of scheme, WEEE generation and handling, as well as technical planning and design of WEEE management systems (Okorhi, 2015). Currently, the plan of action for WEEE management strategies in Nigeria is anchored on any or a combination of four significant regulations namely: the Harmful Waste (Special Criminal Provisions) Act Cap H1 LFN 2004; the National Environmental Protection (Waste Management) Regulations S.I.15 of 1991; the National Environmental (Sanitation and Wastes Control) Regulation S.I.28 of 2009 and the National Environmental (Electrical/Electronics Sector) Regulations S.I. No. 23 of 2011 (Basel Convention, 2011). There exist, in each state, established structure for collecting and disposal of waste. Under this structure, a state, through its "Agency" would collect solid waste (WEEE) under the classified scheme (Federal Environmental Protection Agency (FEPA), 1999; ESWAMA, 2004; Basel Convention, 2011).

3.0 A Conceptual Model and Theory for WEEE Management

Essentially, developing a viable strategy is developing a broad formula for how an "Agency" is going to deliver on its mandates, what is the limit of its goals are, and what policies will be needed to carry out those goals (Porter, 1998). Such strategy may have been developed clearly through a planning process or it may have evolved tacitly through the activities of its various functional sectors. Waste management theory therefore proposes tools to be applied to achieve set objectives (GFMECD, 1995; Antony and Pamela, 2013). This research concept was driven by the Pongrácz's theory of Waste Management which is based on an arranged expectations such that the management of waste would avert that waste to protect human health and the environment (Pongrácz, 2002).

Therefore, through the practice of waste management, there would arise the avoidance of resources' losses. On this premise, the authors attempt to develop a framework to address the issue of e-waste. It was followed with a discussion on major contextual issues that influences the WEEE policy making process, as well as its partly application as the assessment tool for WEEE management strategies in South Eastern Nigeria.

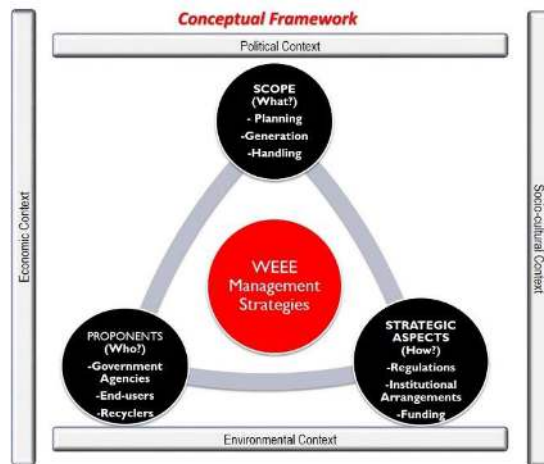


Figure 1: Conceptual framework for WEEE Management Strategies (Adopted from Okorhi (2015), Assessment of WEEE Management Strategies in South Eastern Nigeria

To attain sustainable environment and a healthier population, a methodological approach for the effective management of WEEE and its developmental strategies must go beyond purely technical considerations to formulate specific objectives and implement appropriate measures with regard to political, institutional, social, financial, economic and technical aspects of e-waste management (Schübeler *et al*, 1996). The authors adopted a conceptual framework (Figure 1) giving the models for WEEE management, and identifying strategies and principles that normally guide WEEE management system development.

4.0 Methodology

The study was carried out in South Eastern Nigeria. The study area comprises five states namely: Abia, Anambra, Ebonyi, Enugu and Imo States. Together, there are 95 local government areas (LGAs) in these states. The region, was first divided into five mutually exclusive strata of states. Four LGAs were purposively selected from each stratum. The approach of the survey was investigative through questionnaire administration. The research instrument comprised questions delineated to 40 personnel from the Monitoring and Control Agencies of EEE/WEEE. The agencies surveyed are the National Environmental Standard and Regulation Enforcement Agency (NESREA); Standards Organisation of Nigeria (SON); the Nigeria Customs Service; Enugu State Waste Management Authority (ESWAMA); Abia State Environmental Protection Agency (ASEPA); Anambra State Waste Management Authority (ASWAMA); Ebonyi State Environmental Protection Agency (EBSEPA); the Imo State Bureau for Sanitation & Transport; as well as LGAs Environmental Health Offices. The data collection instrument was subjected to face validity, content validity and pre-testing. The survey considered the strategies for managing WEEE in South Eastern Nigeria in line with the four prominent National Environmental Regulations on e-wastes. The study specifically assessed the measures employed as management strategies for generated WEEE in-line with best practices. Also, innovative approaches drawn from these regulations for sustainable management of

WEEE were measured. In the test of our hypothesis, we used all questions on management/disposal method to be dependent variable and all questions to do with laws/legislatures, policies and regulations on e-wastes to be independent.

5.0 Results and Discussion

It is pertinent to mention that the survey revealed that the Nigeria Customs Service in South Eastern Nigeria had mandates that are insensitive to flows of WEEE. Hence, four (4) of the questionnaire administered to the Agency's offices were returned incomplete, and only thirty-six (36) completed questionnaire from other government agencies at federal, state and local government levels were used for this article. In the furtherance of this study, this section presents and discuss data collected on major aspects giving both descriptive and inferential analyses. Table 1 presents the descriptive analysis of the study; Table 2 depicts the inferential analysis.

5.1 Component 1: WEEE Legal and Regulatory Framework

The promotion of sustainable strategies, policies, legislations, acts, regulations and guidelines for WEEE management is an inclusive aspect of the planning process. From Table 1, a total of 19(54.29%) respondents agreed that government promulgates edicts to enforce protection policies against illegal disposal of WEEE. Although results from field - 54.29% showed that government supports this process, about half - 16(45.57%) of the respondents also agreed that government actually prepared and developed working and management plans for WEEE to assist stakeholders. Likewise, only 11(31.43%) respondents slightly agreed that the execution of management provisions of the workman's plan to cater for WEEE is been implemented. Together, the strategies for implementation were considered inappropriate by 25(71.43%) respondents (from a breakdown reflecting 8(22.86%) to small extent, 13(37.14%) to very small extent and 4(11.45%) not at all).

5.2 Component 2: Strategic Planning for WEEE

The National Environmental (Electrical/Electronics Sector) Regulations, 2011 clearly provides e-waste management tenets in written codes. However, evidence from field suggested that only 4(11.45%) respondents strongly affirmed to be acquainted with the rules of engagement. This is most worrisome when - 16(45.57%) WEEE managers at state and local government level complained of vague knowledge and the existence of e-waste guidelines like the National Environmental (Electrical/Electronics Sector) regulations. Most peculiar with this were the Environmental Health Officers who oversees waste management activities at grassroots level. It is noteworthy to mention that the collection, collation, processing and storage of statistics on generated e-waste in the region is impracticable - 22(62.86%). Such information would promote sustainable strategies that would identify seasonal waste and projected periodic volume. This can also be collaborated with 18(51.43%) respondents whom affirmed that the periodic documentation on e-waste quantity and budgeting to support the management process are inadequately carried-out.

5.3 Component 3: Institutional Arrangements

As part of the value-chain for WEEE management strategies, the institutional arrangements covers coordination of WEEE activities, manpower development and support services, as well as government supervisory roles on the implementation and evaluation processes. 15(42.86%) respondents strongly disaffirmed the existence of any established competent body or unit for the specific implementation of e-waste management strategies. More interestingly, field results -25(71.45%) respondents suggested that there are no provisions for training facilities for e-waste management personnel. A total of 20(57.14%) respondents affirmed government's provisions on

support services to control illegal e-waste importation and distribution practices in the study area, but then it rarely monitor the sources of e-waste into the region. In addition, the coordination of activities for municipal e-waste collection and final disposal was poorly implemented -21(60%) respondents. 28(80.00%) respondents agreed that, on the long term, government do not maintain abandoned land-based e-waste dump.

5.4 Component 4: WEEE Generation and Handling

Part I – General Provisions, Section 2, Sub-section 3 of the National Environmental (Electrical/Electronics Sector) Regulations S.I. No. 23 of 2011 demands that the principles of these regulations should be anchored on the 5Rs which are: Reduce, Repair, Re-use, Recycling and Recover as the primary drivers of the sector and should encompass all the categories and Electrical and Electronic Equipment listed in Nigeria. Together, 26(74.39%) respondents affirmed that government encouraged management methods like the Reuse, source Reduction, Recycling, Repair, Recovery, Landfilling and Incineration of WEEE. Nonetheless, 20(57.14%) respondents disagreed on the existence of formal Recycling facilities for e-waste in parts of South Eastern Nigeria. Moreover, Part III: E-waste – Control, Section 34, Sub-section 4, of the regulations emphasized on the establishment and manage e-waste Recycling facilities for the collection and treatment of WEEE, 25(71.43%) respondents said that the government is yet to build such facilities or acquire relative technologies for the purpose of e-waste disposal in the study area. Again, field results (20(57.14%) respondents) suggested that governments have setup and enforced standards for modern facilities for the disposal of e-wastes, observations showed that WEEE is managed together with other municipal solid wastes. Only 6(17.14%) respondents agreed that government provided technical advice to generators of e-wastes on appropriate intermediate conversion techniques/technologies and 15(42.86%) respondents said that the collection, segregation and final disposal activities for e-waste are ineffectively managed by the existing system. Also, 18(52.43%) respondents attested to the non-existence of arrangements for the specific collection and final disposal of WEEE.

6.0 Inferential Analysis (Multiple Linear Regression)

Table 2 showed analysis on hypothesis H_0 : WEEE management strategies in South Eastern Nigeria are adequate. A linear multiple regression test was carried out on questions relating to the legal and regulatory framework, strategic planning, institutional arrangements, WEEE generation and handling. The comparable values for regression inferential statistics are the Standardized Coefficients (Beta, β) which results for H_0 are $\beta_1 = 0.838$, $\beta_2 = -1.024$ and $\beta_3 = 0.608$. We deduce results for two of the three questions are insignificant since the calculated Beta coefficient values, $\beta_2 = -1.024$ and $\beta_3 = 0.608$ respectively, are less than the p-values tabulated. Hence we accept the alternative hypothesis H_1 : WEEE management strategies in South Eastern Nigeria are inadequate. This finding agrees with the Basel Convention Report: Where are WEEE in Africa? (Basel Convention, 2011).

7.0 Conclusion and Policy Recommendations

The tested hypothesis has proven that the monitoring and control agencies relied mostly on poorly structured management strategies supposedly meant for municipal solid wastes in managing WEEE. Therefore, the study concluded that WEEE management strategies in Nigeria are inapt and poorly implemented. From the findings generated, the following recommendations were made: First, the regulatory bodies should urgently embrace and domesticate appropriate management strategies contained in the recent National Environmental (Electrical/Electronics Sector) Regulations S.I.

No. 23 of 2011. Secondly, it is recommended that during the implementation process, the adopted management strategies should be separated from those used for general municipal solid waste, and e-waste should be categorized. This is because, e-waste is classified as hazardous waste and therefore needed to be strategically handled and disposed. Finally, government should set-up and enforce standards for frontier facilities (recycling plants, landfills, incinerators etc.) for the disposal of e-wastes.

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Table 1: Policy Instrument for WEEE by Monitor and Control Agencies

	Q/N	Policy instrument:	To Very Great Extent		To Great Extent		To Small Extent		To Very Small Extent		Not At All	
			N		N		N		N		N	
		Does your agency:	N	%	N	%	N	%	N	%	N	%
LEGAL AND REGULATORY FRAMEWORK	1	Promote strategies/policies/legislations/acts/regulations for WEEE management	6	17.14	19	54.29	8	22.86	0	00.00	2	05.71
	2	Promulgate edicts to enforce protection policies against illegal disposal of WEEE	7	20.00	12	34.29	2	05.71	7	20.00	7	20.00
	3	Enact appropriate legislation on grading rules, waste minimization and so on to back e-waste management strategies	6	17.14	13	37.14	8	22.86	2	05.71	6	17.14
	4	Has the provisions of Harmful Wastes Act, promulgated after the Koko waste saga in 1988 been an effective legislative instrument for the control of flow of e-waste in South Eastern Nigeria.	0	00.00	9	25.71	1	02.86	17	45.57	8	22.86
	5	Does the political system during strategy implementation affect the implementation process?	1	02.86	12	34.29	11	31.43	5	14.29	6	17.14
	6	Are the strategies for implementation appropriate?	2	05.71	8	22.86	8	22.86	13	37.14	4	11.45
STRATEGIC PLANNING	1	Provide e-waste management tenets in written codes	4	11.45	4	11.45	5	14.29	5	14.29	17	45.57
	2	Prepare and develop working and management plans to stakeholders	6	17.14	17	45.57	10	28.57	1	02.86	1	02.86
	3	Execute management provisions of the workman's plan	1	02.86	11	31.43	9	25.71	7	20.00	7	20.00
	4	Carry out periodic inventory surveys on types of e-waste generated in the region	1	02.86	3	08.57	5	14.29	16	45.71	10	28.57
	5	Collect, Collate, Process and Store statistics on generated e-waste	3	08.57	1	02.86	0	00.00	10	28.57	22	62.86
	6	Have adequate periodic documentation on e-waste quantity and budgeting to support management process	1	02.86	3	08.57	3	08.57	10	28.57	18	51.43
	7	Monitor and protect the environment against illegal e-waste dumping	9	25.71	11	31.43	3	08.57	4	11.45	8	22.86
PUBLIC EDUCATION & PARTICIPATION	1	Educate the public on e-waste management scheme	7	20.00	11	31.43	2	05.71	2	05.71	13	37.14
	2	Are all sectors of the populace adequately carried along during implementation of strategies?	2	05.71	9	25.71	14	40.00	5	14.29	5	14.29
	3	Does all sectors always comply with the strategies employed?	0	00.00	2	05.71	9	25.71	15	42.86	9	25.71
INSTITUTIONAL ARRANGEMENTS	1	Establish a competent body to implement e-waste management strategies	4	11.45	4	11.45	8	22.86	4	11.45	15	42.86
	2	Improve management capability of special waste (e.g. E-waste) unit through training and manpower development	2	05.71	6	17.14	7	20.00	4	11.45	16	45.71
	3	Provide training facilities for e-waste management personnel	3	08.57	7	20.00	0	00.00	0	00.00	25	71.43
	4	Provide support services to control illegal e-waste importation and distribution practices	7	20.00	13	37.14	5	14.29	5	14.29	5	14.29
	5	Take punitive action against defaulters	17	45.57	8	22.86	4	11.45	3	08.57	3	08.57
	6	Monitor the sources of e-waste into South Eastern Nigeria	2	05.71	8	22.86	5	14.29	6	17.14	14	40.00
	7	Coordinate environmental sanitation activities on generators (especially EIA and EAR)	1	02.86	4	11.45	4	11.45	5	14.29	21	60.00
	8	Maintain abandoned land-based e-waste dump	1	02.86	3	08.57	1	02.86	2	05.71	28	80.00
	9	Carry out Environmental Impact Assessment (EIA) on existing or abandoned dumpsites	0	00.00	6	17.14	3	08.57	11	31.43	15	42.86
FUNDING OF SCHEME	1	Provide monetary support for e-waste management	0	00.00	2	05.71	1	02.86	7	20.00	25	71.43
	2	Assess the adequacy of monetary support to take care of logistics	2	05.71	1	02.86	0	00.00	11	31.43	21	60.00
WEEE GENERATION AND HANDLING	1	Establish and manage e-waste Recycling facilities	3	08.57	4	11.45	2	05.71	6	17.14	20	57.14
	2	Encourage the Reuse; source Reduction, Recycling, Repair, Recovery, Landfill and Incineration of waste electrical/electronic equipment (WEEE or e-waste)	7	20.00	19	54.29	3	08.57	0	00.00	6	17.14
	3	Efficiently manage e-waste collection, segregation and final disposal activities	3	08.57	7	20.00	4	11.45	6	17.14	15	42.86
	4	Provide technical assistance in the evacuation and final disposal of e-waste	3	08.57	13	37.14	5	14.29	6	17.14	8	22.86
	5	Provide technical advice to generator of e-wastes on appropriate intermediate conversion techniques/technologies	2	05.71	4	11.45	7	20.00	6	17.14	16	45.71
	6	Coordinate the activities of municipal refuse (special waste) collection and final disposal	5	14.29	11	31.43	0	00.00	1	02.86	18	51.43
	7	Set-up and enforce standards for modern facilities for the disposal of e-wastes	6	17.14	14	40.00	7	20.00	5	14.29	3	08.57
	8	Build recycling plants, landfill, incinerators and acquire technologies for the purpose of e-waste disposal	2	05.71	7	20.00	0	00.00	1	02.86	25	71.43
	9	Control dumpsites activities and locations for disposal of e-waste	4	11.45	13	37.14	1	02.86	3	08.57	14	40.00

(Total Number (N) of respondents = 36); Source: Field Survey based on Okorhi (2015), Assessment of WEEE Management Strategies in South Eastern Nigeria

Table 2: Summary of Statistical Test for Hypothesis H₀**REGRESSION**

/MISSING LISTWISE

/STATISTICS COEFF OUTS R ANOVA

/CRITERIA=PIN(.05) POUT(.10)

/NOORIGIN

/DEPENDENT PromoteStrate4WEEEmgt

/METHOD=ENTER ExeMgtProvOfDWorkmanPlanmpromMgtCapaOfSpeciWasteUnitThroTrainNManpDev
BuiLandfIncineNAdeqTechnoForDPurpOfEwastDispo.**Regression****Variables Entered/Removed^a**

Model	Variables Entered	Variables Removed	Method
1	Build landfill, Incinerators & Adequate technologies for the purpose of e-waste disposal?, Execute Management Provision Of the Workman's Plans?, Improve management capability of special waste unit through training & manpower development	.	Enter

a. Dependent Variable: Promote strategies for WEEE management?

b. All requested variables entered.

Model Summary

Model	R	R Square	Adjusted R Square	Std. Error of the Estimate
1	.693 ^a	.481	-1.077	10.68693

a. Predictors: (Constant), Build landfill, Incinerators & Adequate technologies for the purpose of e-waste disposal?, Execute Management Provision Of the Workman's Plans?, Improve management capability of special waste unit through training & manpower development

ANOVA^a

Model		Sum of Squares	Df	Mean Square	F	Sig.
1	Regression	105.789	3	35.263	.309	.830 ^b
	Residual	114.211	1	114.211		
	Total	220.000	4			

a. Dependent Variable: Promote strategies for WEEE management?

b. Predictors: (Constant), Build landfill, Incinerators & Adequate technologies for the purpose of e-waste disposal?, Execute Management Provision Of the Workman's Plans?, Improve management capability of special waste unit through training & manpower development

Coefficients^a

Model		Unstandardized Coefficients		Standardized Coefficients	t	Sig. (p)
		B	Std. Error	Beta		
1	(Constant)	3.759	12.482		.301	.814
	Execute Management Provision Of the Workman's Plans?	1.700	1.799	.838	.945	.518
	Improve management capability of special waste unit through training & manpower development	-1.825	3.052	-1.024	-.598	.657
	Build landfill, Incinerators & Adequate technologies for the purpose of e-waste disposal?	.518	1.332	.608	.389	.764

a. Dependent Variable: Promote strategies for WEEE management?

Okorhi (2015) based on assessment of WEEE Management Strategies

CHARACTERIZATION OF KULUKI WOLFRAMITE ORE DEPOSIT FOR ITS BENEFICIATION

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Abstract

The Characterization of Kuluki Wolframite ore in Bauchi, Nigeria was carried out in this project work. The study runs a sieve analysis process to investigate the particle size distribution, it also determined the liberation size of the valuable mineral (WO_3) and major gangue mineral (Fe_2O_3). XRF, XRD and SEM were used. The mesh of the grind was found to be 209.4 μm , and the liberation size of the valuable mineral, WO_3 was established to be -250+180 μm sieve size having the highest percent of WO_3 of 53.2% and that of the major gangue Fe_2O_3 was also established to be +250 μm having the highest percent of 28.61%. The XRD analysis also revealed the presence of, Hematite, thereby confirming that it is an iron manganese tungstate that is intermediate between Ferberite (Fe^{2+} rich) and Hubnerite (Mn^{2+}).

Introduction

The role and importance of mineral to the economic and political development of a nation cannot be overemphasized. Nigeria is endowed with metallic and non-metallic mineral resources, however, owing to the low level of exploration of the mineral deposits most of the known mineral occurrences are yet to be evaluated for their reserves and grade (Usaini, 2010).

Nigeria is a nation blessed with rich human and natural resources. It has been discovered that there are about thirty-four (34) different solid minerals among which includes large deposits of iron ore along the Kogi-Benue through, Agbaja iron ore deposits (which is the largest iron ore deposit in Nigeria with about one billion tones in reserve). Reserves of good quality coal low in sulphur and ash are about over two and half million tons (Federal office statistics, 2003).

Tungsten is a hard rare metal under standard conditions when uncombined, it is found naturally on earth almost exclusively in chemical compounds. It has the highest melting point of all elements and its high density is 19.3 times that of water. China is the major producer of tungsten, producing about 61,800 tonnes in 2011. Approximately, half of the tungsten is consumed for the production of hard materials with the remaining major use being in alloys and steels (Lassner, 1999).

Wolframite is not scientifically classified as an individual mineral species by the IMA (international mineralogical association). However, it is universally recognized as a mineral series, with the Huebnerite and Ferberite being its end members. Huebnerite is the manganese rich end member, and Ferberite is the iron rich end member. The term wolframite can be used generally to describe unspecified members of this group or to describe the intermediary member of this series. Wolframite is named for its tungsten content, since wolfram means tungsten in German (www.mineral.net, 2016).

There are deposits of wolframites in Kano, Kaduna, Bauchi and Niger states of Nigeria. However, they have not been majorly exploited but they show great advantages if they are ventured into on the basis of this and in line with the government policies of diversifying the economy through the encouragement of investors in the solid minerals subsector of the economy, this work set out to characterize kuluki wolframite ore. The research work was aimed at characterizing Kuluki wolframite ore deposit, Bauchi State Nigeria.

Materials and Methods

The materials/ reagent and equipment used in this research are:

Kuluki wolframite ore sample, stearic acid, XRF machine, XRD machine, sieve shaker and a range of sieves, scanning electron microscope (SEM).

Experimental Procedure

320g sample of the ore was crushed and ground to fine particle size ranges and subjected to sieve analysis. The arrangement of the sieves were done using a sieve scale in which the ratio of the aperture widths of the adjacent sieves is the square root of two ($\sqrt{2}=1.414$). Sieve sizes from 250 μm to 63 μm were arranged in a stack with the coarsest sieve on the top and the finest at the bottom. A tight fitting pan was placed below the bottom sieve to receive the final undersize and a lid was placed on the top of the coarsest sieve to prevent escape of the sample. The arranged sieves were placed in a sieve shaker which vibrates the materials vertically. At the end of twenty minutes, the nest was taken apart; the amount of material retained on each sieve was weighed. To determine the liberation size the small percentage of the weight retained on each sieve during sieve analysis was taken and XRF examination was carried out on each to determine the size fraction with the highest percent of tungsten. 10g of the powder sample was mixed with 1g of stearic acid (binder) and thoroughly homogenized in an agate mortar the mixture was then transferred into a 40mm diameter hardened steel disc and pressed into a pellet at a pressure of 25ton using a hydraulic pressure press. The pellets were then used for XRF analysis to determine the chemical composition of the Kuluki wolframite ore sample. 10g of the sample is placed in the jaw holder of SEM and analyzed for its morphology, crystal orientations and structure. The same procedure for the preparation of the sample for XRF analysis was used for the preparation of the sample for XRD. The prepared sample was analyzed for its mineralogical compositions.

Results and Discussion

Results of various laboratory experiments and analysis carried out are presented and discussed below.

Sieve analysis and Liberation studies of Kuluki wolframite ore

It was observed from the size analysis test results presented above that 179.6 g of the total weight (320g) was retained on the 250 μm sieve size, 56.35 g on 180 μm , 43.50 g on 125 μm , 15.74 g on 63 μm and 22.9 g on -63 μm . From the table, the mesh of grind was calculated to be 209.4 μm .

180 μm $\longrightarrow$ 74.17%

X $\longrightarrow$ 80%

using Gaudin Schumann method to calculate the 80% passing, we have;

$$X = \left(\frac{80}{74.17} \right)^2 \times 180 = 209.4\mu\text{m}$$

Table 4.1: Sieve Analysis of Kuluki Wolframite Ore

Sieve Range (μm)	Weight (g)	Weight (%)	Nominal (μm) aperture size	Cumulative undersize (%)	Cumulative oversize (%)
+250	179.60	56.46	250	43.54	56.46
-250+180	56.35	17.71	180	25.83	74.17
-180+125	43.50	13.67	125	12.16	87.84
-125+63	15.74	4.95	63	7.21	92.79
-63	22.90	7.19	-63	0.02	99.98

X-ray fluorescence of Kuluki Wolframite Ore

Figure 4.1 and 4.2, presents the size and assay analysis results of the ore sample. The result showed that both the valuable mineral WO₃ and the major gangue mineral Fe₂O₃ were averagely distributed in all sieve sizes. This phenomenon indicates that WO₃ and Fe₂O₃ were normally distributed and the weight of the minerals decreased as the sieve size decrease, except for -63μm, which deviated a bit and increased in mass. This trend compared favorably also with Weiss (1985), where similar trends was observed.

Table 2, shows the chemical composition of the various sieve sizes of the Kuluki wolframite ore as revealed by XRF. It shows that at +250μm sieve size, the percentage of WO₃ is 44%, at -250+180μm, 53.2%, at -180+125μm, 53.1%, at -125+63μm, 43.1%, at -63μm, 52.7%. Hence, the liberation size of the valuable mineral, WO₃ is -250+180μm since it has the highest percent of WO₃, 53.2%. It also shows that at +250μm sieve size, the percentage of Fe₂O₃ is 28.61%, at -250+180μm, 26.99%, at -180+125μm, 26.64%, at -125+63μm, 22.98%, at -63μm, 26.99%. Based on this, the liberation size of the major gangue mineral, Fe₂O₃ is +250μm, since it has the highest percent of Fe₂O₃, 28.61%. This trend compares favorably with works done by Weiss (1985), where they also observed similar trends.

Scanning Electron Microscopy of the head sample of Kuluki Wolframite Ore

Plate 1, 2 shows the micro-structural morphology of the wolframite ore. The gray patches represent the tungsten ore, which shows that it is opaque, non-fluorescent and sub metallic. It also shows that the darker patches between the tungsten ore represent iron.

This microstructure can also be used to find the liberation size of the ore from the scale of the structure.

$$100\mu\text{m} \longrightarrow 2.6\text{cm}$$

$$X\mu\text{m} \longrightarrow 5.3\text{cm}$$

$$X\mu\text{m} = \frac{100 \times 5.3}{2.6}$$

$$X = 203.85\mu\text{m}$$

This is in line with the liberation size gotten from the sieve analysis, which is -250+180μm.

XRD Analysis of Kuluki wolframite ore

Table 3, present the result of XRD analysis of the ore sample. The result revealed the presence of Chrysotile, Hematite, Nacrite, Riebeckit, and Quartz.

It can be deducted from this result that the wolframite, (Fe, Mn) WO₄, is an iron manganese tungstate mineral that is intermediate between Ferberite (Fe²⁺ rich) and Hubnerite (Mn²⁺ rich) from the literature review of this work.

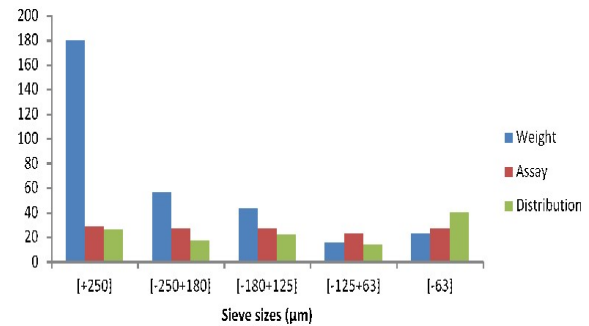


Figure 1: Size Distribution of the WO₃ in the Kuluki Wolframite Ore Matrix

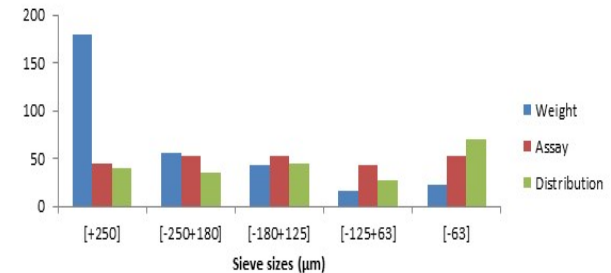


Figure 2: Size Distribution of the Fe₂O₃ in the Kuluki Wolframite Ore Matrix

Table 4.2: XRF result for Kuluki Wolframite ore in compound form

Compound	(+250μm)	(-250+180 μm)	(-180 +125μm)	(-125+63 μm)	(-63 μm)
Al ₂ O ₃	0.4	-	-	0.66	-
SO ₃	-	0.42	0.42	-	0.39
K ₂ O	0.12	0.12	0.14	0.15	0.19
CaO	0.282	0.688	0.598	0.591	0.767
Sc ₂ O ₃	0.01	0.028	0.027	0.025	0.037
V ₂ O ₅	0.049	0.064	0.046	0.049	0.064
Cr ₂ O ₃	0.007	-	-	-	-
MnO	3.73	4.38	4.46	3.68	4.52
Fe ₂ O ₃	28.61	26.99	26.64	22.98	26.99
SrO	-	9.6	11	12	10
Ag ₂ O	2.01	3.74	2.31	2.11	2.69
La ₂ O ₃	0.19	-	0.10	-	-
Yb ₂ O ₃	0.65	0.61	0.66	0.51	0.66
TiO ₂	-	0.15	0.13	0.13	0.19
WO ₃	44	53.2	53.1	43.1	52.7
LOI	19.942	0.01	0.369	14.015	0.802

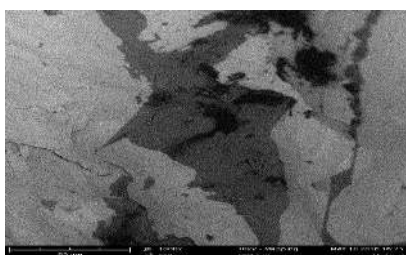


Plate 1: SEM image of head sample (x1000)

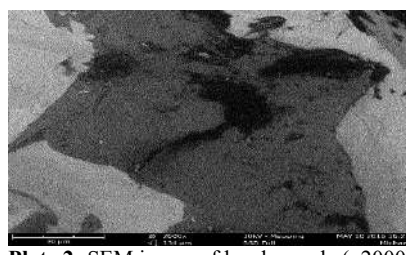


Plate 2: SEM image of head sample (x2000)

Table 3: XRD Analysis Result of the head sample

No	Card	Chemical formula	Chemical name	Mineral Name	Wt%	S.G
1	25-0645	$Mg_3[Si_2-XO_3](OH)4-4x$	Magnesium Silicate Hydroxide	Chrysotile	0.669	0.209
2	33-0664	Fe_2O_3	Iron Oxide	Hematite	0.657	0.175
3	16-0613	$MgX(Mg, Fe)_3(Si, Al)_4(OH)_2 \cdot 4H_2O$	Magnesium Iron Aluminum Silicate Hydroxide	-	0.658	0.165
4	16-0606	$Al_2Si_2O_5(OH)_4$	Aluminum Silicate Hydroxide	Nacrite-2/IT	0.684	0.163
5	31-0794	$(Mg, Al)_9(Si, Al)_8(OH)_{10} \cdot 10H_2O$	Magnesium Aluminum Silicate Hydroxide	-	0.456	0.161
6	13-0092	$Fe_2O_3 \cdot H_2O$	Iron Oxide Hydrate	-	0.373	0.156
7	19-1061	$(Na, Ca)_2(Fe, Mn)_3Fe_2(Si, Al)_8(OH)$	Sodium Iron Silicate Hydroxide	Riebeckite	0.557	0.139
8	46-1045	SiO_2	Silicon Oxide	Quartz	0.401	0.134
9	16-0351	$(Mg, Fe, Al)_6(Si, Al)_4(OH)_8$	Magnesium Aluminum Iron silicate Hydroxide	-	0.620	0.129
10	29-1016	$KMg_2Al_3(Si_{10}Al_2)O_{30}$	Potassium Magnesium Aluminum Silicate	-	0.504	0.122

Conclusion

The characterization of Kuluki wolframite ore was carried out from the results obtained. The mesh of the grind was found to be 209.4 μ m. The liberation size of the valuable mineral, WO_3 was established to be -250+180 μ m sieve size having the highest percent of WO_3 of 53.2%. The liberation size of the major gangue Fe_2O_3 was also established to be +250 μ m having the highest percent of 28.61%. The XRD analysis also revealed the presence of chrysotile, hematite, nacrite, riebeckite, quartz, establishing that it is an iron manganese tungstate that is intermediate between Ferberite (Fe^{2+} rich) and Hubnerite (Mn^{2+}).

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SUSCEPTABILITY OF KULUKI WOLFRAMITE ORE DEPOSIT TO MAGNETIC AND GRAVITY CONCENTRATION TECHNIQUES

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ABSTRACT

The developed world is rapidly running out of minerals. To address this, attention is steadily shifting to Africa and other less developed continents to supply the necessary ores to help save it. The beneficiation of Kuluki wolframite ore, Bauchi state, Nigeria was aimed at being one such saving effort. This research investigated and compared the efficiency of the two most important beneficiation techniques for tungsten ores (gravity and magnetic separations). The methodology employed includes; sample collection, liberation size determination and separation. Water was used as separating medium in gravity separation. For magnetic concentration however, a low intensity separator was used. Adopting a liberation size of -250+180µm, the results obtained revealed that gravity separation yielded a better concentrate (65.3% W) than magnetic concentration (63.5% W). The calculated recoveries were 93.68% for concentrate, 5.88% for tailings as against the 38.53% (concentrate) and 19.63% (tailings) calculated for magnetic method.

Introduction

The role and importance of minerals to the economies of nations cannot be overemphasized. This is because for a nation to develop technologically, its mineral resources must be judiciously harnessed. Indeed, since pre-historic times, human race has passed through various civilizations for which minerals have served as the backbone. As a result, tags such as Iron Age, Bronze Age, etc. have not been uncommon in academic writings (Indian Bureau of Mines, 2013). Although it is no secret that Nigeria is endowed with a lot of minerals, among which are wolframite and other tungsten ores as listed by Umar *et al.* (2011), poor exploration has hampered the development of its mining sector (Usaini 2010). With its recent economic challenges which have forced the government into a diversification move however, prospects for the sector remain bright. In the words of Burt (1996), wolframites low-cost, easy-to-control and eco-friendly processes of beneficiation are comparative advantages not shared by many minerals. With a rising global demand for wolframite due to increasing need for alloys (Dongfang *et al* 2015), the burden on Nigeria to develop its huge deposits has never been more obvious. In line with this, the present study was aimed at investigating the susceptibility of kuluki wolframite ore deposit to magnetic and gravity concentration techniques

Materials and Methods

The materials/ equipment used in this research are: Kuluki wolframite ore sample, sieve shaker and a range of sieves, gravity separation machine, magnetic separator.

Sieve Analysis

So that particles of sample could be distributed into a range of sizes (ultimately to determine the best one for liberation), a sieve analysis trailed the collection of sample. Several sieves (of aperture sizes between 250µm and 63µm) were arranged (in order of decreasing coarseness) in the stack of a sieve shaker. Below them (acting as a 'cap') was placed a tight fitting pan. All of sample was poured into the topmost

sieve (which almost immediately was sealed prevent a loss in sample mass). A shaking time of 20 minutes was set using an automatic timer. Machine was then activated. During shaking; particles (majorly undersized) fall through successive sieves until they arrive at ones with apertures slightly smaller than their diameters. There they are retained and later weighed. Where such apertures are not to be found however, particles are collected in the plain bottom pan.

Separation Tests

Following the discovery of size of liberation, separation processes aimed at removing tungsten from sample mix were carried out. As stated earlier, only two of the extant processes were used. Gravity separation (which was carried out as outlined). Machine was cleaned and made reasonably free of contaminants. Slope of deck was measured and carefully adjusted. Product collecting pans were arranged into position. Adequate care was taken during arrangement so that wrong fixes are avoided. Machine was switched on and along with it the flow of water. Sample was introduced into feed box and then slowly into flowing water. At end of process, products collected in pans were dried and weighed. While process last, successive currents of water, penetrated the sample and expectedly separated its constituents into several groups mainly according to density. Magnetic separation (which was done as listed below) machine was lightly cleaned. Sample was loaded into machine hopper and made to pass through a rotating disc via a vibrating plate. Products (collected in different containers) were at end of separation weighed.

Results and Discussions

Sieve Analysis

As can be seen from table, the results obtained indicate an interesting and consistent drop in retained weight alongside a decrease in sieve aperture. While 250µm captured the largest chunk (179.60g), 180µm, 125µm as well as 63µm held 56.35g, 43.50g and 15.74g respectively. In apparent deviation to trend however, plain pan (-63µm) retained 22.90g.

Table 1: Results from Sieve Analysis of Kuluki Wolframite Ore

Sieve Range (µm)	Weight (g)	Weight (%)	Nominal (µm) aperture size	Cumulative undersize (%)	Cumulative oversize (%)
+250	179.60	56.46	250	43.54	56.46
-250+180	56.35	17.71	180	25.83	74.17
-180+125	43.50	13.67	125	12.16	87.84
-125+63	15.74	4.95	63	7.21	92.79
-63	22.90	7.19	-63	0.02	99.98

Chemical Analysis

Table 2: Compound Composition of the Different Size Fractions

Compound	(+250 μ m)	(-250+180 μ m)	(-180 +125 μ m)	(-125+63 μ m)	(-63 μ m)
Al ₂ O ₃	0.4	-	-	0.66	-
SO ₃	-	0.42	0.42	-	0.39
K ₂ O	0.12	0.12	0.14	0.15	0.19
CaO	0.282	0.688	0.598	0.591	0.767
Sc ₂ O ₃	0.01	0.028	0.027	0.025	0.037
V ₂ O ₅	0.049	0.064	0.046	0.049	0.064
Cr ₂ O ₃	0.007	-	-	-	-
MnO	3.73	4.38	4.46	3.68	4.52
Fe ₂ O ₃	28.61	26.99	26.64	22.98	26.99
SrO	-	9.6	11	12	10
Ag ₂ O	2.01	3.74	2.31	2.11	2.69
La ₂ O ₃	0.19	-	0.10	-	-
Yb ₂ O ₃	0.65	0.61	0.66	0.51	0.66
TiO ₂	-	0.15	0.13	0.13	0.19
WO ₃	44	53.2	53.1	43.1	52.7
LOI	19.942	0.01	0.369	14.015	0.802

Table 3: Percentage Composition of Elements in the Different Size Fractions

Element	(+250 μ m)	(-250+180 μ m)	(-180 +125 μ m)	(+125-63 μ m)	(-63 μ m)
Al	0.212	-	-	0.349	-
S	-	0.168	0.168	-	0.156
K	0.099	0.099	0.116	0.124	0.158
Ca	0.201	0.491	0.427	0.422	0.548
Sc	0.007	0.018	0.017	0.016	0.024
V	0.027	0.036	0.026	0.027	0.036
Cr	0.005	-	-	-	-
Mn	2.89	3.393	3.455	2.851	3.501
Fe	20.03	18.89	18.65	16.09	18.89
Sr	-	8.12	9.31	10.15	8.46
Ag	1.87	3.48	2.15	1.96	2.51
La	0.162	-	0.085	-	-
Yb	0.571	0.536	0.579	0.448	0.579
Ti	-	0.09	0.078	0.078	0.114
W	34.90	42.19	42.11	34.18	41.80
O	18.84	22.07	22.16	19.03	22.08

Tables 2 and 3 present the compositions of the constituents of kuluki wolframite in compound and elemental forms. From them, the following can be deduced:

- Element of interest (W) has its highest composition (42.19%) at 180 μ m. Associated with it are 18.89%Fe, 3.393%Mn, 3.48%Ag, 22%Ag, 8.12%Ar, 0.536Yb, 0.09%Ti, 22%O, 0.0168%S, 0.099%K, 0.491%Ca, 0.018%Sc, 0.036%V.
- Major gangue (Fe) gets its best composition at 250 μ m (20.03%). W interestingly however has one of its lowest compositions (34.90%) at same size.
- Prior to analysis in search of individual elements, constituents had greater compositions as compounds (ex. W; which was 53.2% total sample at 180 μ m in compound form reduced considerably to 42.19% at same size range when elemental analysis was carried out)

To achieve best separation/concentration results possible, liberation size for mineral of interest could safely be taken as 180 μ m.

Separation Tests

Results obtained upon separation of kuluki wolframite are presented in tables 4 and 5.

It could be easily gleaned from these results that:

- Gravity separation retains a greater weight of concentrate (60.50g) than magnetic concentration (12.80g).

- Heavy weight losses are unavoidable in gravity concentration. (Some 10% of total feed should be expected).

Chemical analysis which (as stated earlier) closely followed separation revealed the elemental composition of concentrates as well as tailings (to be) as shown in Tables 6 and 7.

Table 4: Result Obtained From Magnetic Concentration

Sieve Size (μ m)	Products	Weight (g)	Weight (%)
-	Feed	50.00	100.00
250+180	Concentrate	12.80	25.60
	Tailings	37.20	74.40

Table 5: Result Obtained From Gravity Concentration

Sieve Size (μ m)	Products	Weight (g)	Weight (%)
-250+180	Feed	100.00	100.00
	Concentrate	60.50	60.50
	Tailings	29.50	29.50
	Losses	10.00	10.00

Table 6: Elemental Composition of Concentrates

Elements	Concentrate (Magnetic) (%)	Concentrate (Gravity) (%)
Si	3.948	6.454
S	0.534	0.488
P	3.473	1.721
Cl	0.154	0.131
K	0.154	0.216
Ca	0.808	0.551
Ti	0.427	0.193
Mn	4.288	2.334
Fe	22.253	21.946
Zr	0.013	0.023
Nb	0.027	0.039
Mo	0.047	0.068
Cd	0.013	0.011
Sn	0.020	0.017
Sb	0.033	0.017
W	63.500	65.331
Au	0.147	0.182
Bi	0.160	0.278

Table 7: Elemental Composition of Tailings

Elements	Concentrate (Magnetic) (%)	Concentrate (Gravity) (%)
Si	55.731	61.246
S	1.300	2.111
P	4.230	3.124
Cl	4.710	5.351
K	1.810	1.216
Ca	6.400	5.551
Ti	0.127	0.133
Mn	1.460	0.994
Fe	10.253	6.047
Zr	0.011	0.023
Nb	0.005	0.036
Mo	0.012	0.058
Cd	0.015	0.012
Sn	1.075	0.917
Sb	1.023	0.015
W	11.132	8.243
Au	0.196	0.522
Bi	0.510	3.923

Table 8: Metallurgical Balance with Emphasis on Metal Content

Products	Weight (g)		Weight (%)		Assay (%)		Metal Content	
	Gravity	Magnetic	Gravity	Magnetic	Gravity	Magnetic	Gravity	Magnetic
Feed (F)	100.000	50.000	100.000	100.000	42.190	42.190	4219.000	2109.000
Concentrate (C)	60.500	12.800	60.500	25.600	65.331	63.500	3952.526	812.800
Tailing (T)	29.500	37.200	29.500	74.400	8.423	11.132	248.479	414.110
Loss (L)	10.000	-	10.000	-	-	-	-	-

Table 9: Recovery for Element of Interest

Products	Recovery (%)	
	Gravity	Magnetic
Feed	-	-
Concentrate	93.684	38.530
Tailing	5.889	19.631

Conclusion

From results obtained, it can be seen that magnetic separation is a less effective separation technique than gravity concentration (for Kuluki wolframite). Although, it does conserve/save more weight in the final concentrates, the tungsten content of its concentrate (63.50%) alongside recoveries of 38.53% and 19.63% are 'mocked' by the gravity process (which 'boasts' of a tungsten content of 65.33% in its concentrate and recoveries of 93.68% and 5.88%).

A metallurgical balance for these results is presented in Tables 8 and 9 below;

$$\text{Weight (\%)} = 100\%$$

$$\text{Concentrates} = (C \div F) \times 100$$

$$\text{Concentrate (Magnetic)} = (12.800 \div 50.000) \times 100 = 25.600\%$$

$$\text{Concentrate (Gravity)} = (60.500 \div 100.000) \times 100 = 60.500\%$$

$$\text{Tailings} = (T \div F) \times 100$$

$$\text{Tailing (Magnetic)} = (37.200 \div 50.000) \times 100 = 74.400\%$$

$$\text{Tailing (Gravity)} = (29.500 \div 100.000) \times 100 = 29.500\%$$

$$\text{Loss (Gravity)} = (L \div F) \times 100 = (10.000 \div 100.000) \times 100 = 10.000\%$$

$$\text{Metal Content} = \text{Weight (g)} \times \text{Assay (\%)}$$

$$\text{Feed (Magnetic)} = 42.190 \times 50.000 = 2109.000$$

$$\text{Feed (Gravity)} = 42.190 \times 100.000 = 4219.000$$

$$\text{Concentrate (Magnetic)} = 63.500 \times 25.600 = 1625.600$$

$$\text{Concentrate (Gravity)} = 65.331 \times 60.500 = 3952.526$$

$$\text{Tailing (Magnetic)} = 11.132 \times 74.400 = 828.221$$

$$\text{Tailing (Gravity)} = 8.423 \times 29.500 = 248.479$$

$$\text{Recovery (\%)} = (Cc \div Ff) \times 100$$

$$\text{Concentrates (Magnetic)} = ((63.500 \times 12.800) \div (42.190 \times 50)) \times 100 = 38.530\%$$

$$\text{Concentrates (Gravity)} = ((65.331 \times 60.5) \div (42.19 \times 100)) \times 100 = 93.684\%$$

$$\text{Tailings} = (Tt \div Ff) \times 100$$

$$\text{Tailings (Magnetic)} = ((11.132 \times 37.200) \div (42.190 \times 50)) \times 100 = 19.631\%$$

$$\text{Tailings (Gravity)} = ((8.423 \times 29.500) \div (42.190 \times 100)) \times 100 = 4.976\%$$

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MECHANICAL PROPERTIES AND THERMAL STABILITY OF Sn ALLOY PROCESSED BY EQUAL CHANNEL ANGULAR EXTRUSION¹

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Abstract

This study investigated the compressive strength, strain and modulus; hardness and thermal stability of Sn-alloy due to severe plastic deformation, via equal channel angular extrusion (ECAE). The as-received work piece was forced through a specially designed die with an external angle of $\psi = 0^\circ$ and internal angle $\phi = 90^\circ$. The test piece was extruded such that its geometry remained unchanged even after two consecutive passes. The unextruded and extruded sections of the samples were subjected to metallographic examination and observed under an optical microscope. Compression tests were carried out on the samples using Instron universal testing machine operated at a constant rate of 0.02 mm/sec while microhardness tests were conducted on all the samples. The compressive modulus (stiffness) and hardness of the Sn alloy increased with the number of ECAE passes. The strength and strain decreased marginally after the second ECAE pass. The modulus was found to be 8.4 times higher after the second ECAE pass while the hardness value increased by only 12.2%. The increased mechanical properties are thought to be due to high level of dislocations generation and multiplication that may have resulted in strain hardening as the material passed through the sharp angles of the die. A small hump was observed on each of the heating and cooling enthalpy curves in all the samples. However, the samples were found to be consistently thermally stable without regard to the ECAE passes.

Keywords: Extrusion, compressive properties, DSC, Tin alloy.

1.0 INTRODUCTION

Tin, as a metallic material, is often underused for various manufacturing purposes as a result of its low strength identified in its inability to withstand stress. Different methods have been employed to improve the strength of tin alloy and other materials which may alter the shape. Equal channel angular extrusion (ECAE) has proven as one of the Severe Plastic Deformation (SPD) methods that allows very high deformations to be imparted without change of the orientation of the processed material (Luis et al., 2012; Segnal et al., 1981 and Segnal, 1999). The higher the deformation applied to the billet processed by ECAE, the more dislocations, and, hence, the smaller the achieved grain size and the higher the mechanical improvement (Baik et al., 2003). The yield strength was first observed to be inversely proportional to the grain size (Hall, 1951; Petch, 1953). The mechanical properties of material are practically influenced by the change in grain size.

Equal channel angular extrusion (ECAE) is one of the mostly used SPD processes. In this process, the material is extruded through two channels (entrance and exit) that intersect at internal angle ϕ and external angle ψ of a die. The cross section of these channels is of approximately the same. The ECAE process can be used to introduce severe plastic deformation within a part in order to reduce the grain size and thus, improve the mechanical properties of the processed material (Stolyarov et al., 2001). Plastic deformation is not uniformly distributed across the surface and the length of the billet (Osinkolu, et al., 2006). The bulk grain refinement of materials by severe plastic deformation using equal channel angular extrusion (ECAE) started in the early 70's by Segal and his co-workers (Segnal et al., 1981 and Segnal, 1999).

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were extensively used to investigate the amount of plastic deformation and how it affects the grain size distribution of materials processed by ECAE (Hall, 1951; Petch, 1953; Pereira et al., 2009; Xue et al., 2006). Several researchers have also modeled strain and stress

distributions in the work piece after one or more passes using Finite Element Modeling (FEM) techniques (Xue et al., 2006). The microstructural generation, and grain size distribution in copper and other alloys have been well documented even after several successive passes in equal channel angular extrusion. Optical microscopy carried out by Katarina and co-workers estimated the grain size of the extruded copper to be approximately 3 μm after the 10th ECAE pass (Katarina et al., 2009). It has been reported that the first few passes are the most efficient in grain refinement while the microstructure becomes gradually more uniform as the number of passes increases (Beyerlein et al., 2005; Li et al., 2004). Other techniques such as electron backscatter diffraction have been used to reveal the texture development in materials subjected to equal channel angular extrusion. Pereira and his co-workers investigated the effect of ECAE on the lattice spacing of a magnesium alloy using peaks from XRD. They reported a shift in 2θ values towards lower angles after one ECAE pass, indicating an increase of about 0.05% to 0.1% of the lattice planes of the Magnesium alloy (Pereira et al., 2009). Distribution of equivalent plastic strain along various paths on cross sections of pure aluminum subjected to ECAE has been carried out by FEM calculations (Zhang et al., 2009). However, this work investigated the compressive strength, strain and modulus; hardness and thermal stability of Sn-alloy due to severe plastic deformation, via equal channel angular extrusion (ECAE). This is with a view to ascertaining the suitability of this method of severe deformation for n alloys.

2.0 EXPERIMENTAL DETAILS

Three samples of as-received Sn alloy rod were machined to the required dimensions for Equal Channel Angular Extrusion (ECAE) of 12 mm in diameter and 75 mm long. The first sample was extruded through one pass, the second through two passes leaving a no pass as the control. Figure 1 shows the ECAE mould used for the extrusion. The extrusion process was carried out at room temperature with well lubricated channels. The unextruded and extruded samples were cut from the middle, surface grinded and polished. The well-polished

¹ Being a paper presented at the Nigerian Materials Congress 2016 (NIMACON-2016) held at the Ahmadu Bello University between November 21 and 25, 2016.

surfaces were then etched with Nital (Nitric acid) before the microstructure was examined on an optical microscope.



Figure 1: ECAE mould showing well-lubricated channels

A small portion of mass 8.7 mg was cut from both the control and extruded samples. The extruded samples were cut at the sharp end where the billets made contact with the die (i.e the point where there was maximum effective plastic strain/deformation, shown by Δ in Figure 2), which was verified by the FEA simulation of the ECAE process.

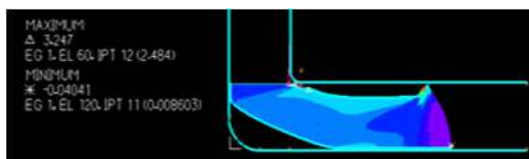


Figure 2: Point (Δ) showing max effective strain in the billet

The melting behavior, phase formation and the activation energy at each heating / cooling cycle were determined for all the samples by Differential Scanning Calorimetry (DSC) (Netzsch 404PC). The heating and cooling rate was 5°C min^{-1} and each sample was heated up to 240°C . The samples were also quenched from the liquidus with the cooling rate estimated as 50°Cs^{-1} .

Compressive specimens 10 mm in diameter and 10 mm gauge length were machined from the Equal Channel Angular Pressed (ECAPed) and control samples on a lathe machine. Compression tests were then carried out on the control and extruded samples. Compression tests were carried out at room temperature using Instron 3369 universal testing machine operated at a constant strain rate of 0.02 mm/sec. The maximum compressive stress, strain and modulus were then obtained.

The hardness tests were conducted on the extruded and unextruded samples using the Brinell Hardness tester. A steel ball 15 mm in diameter was applied with a relatively large force as an indenter on the samples. The Brinell hardness number was obtained by dividing the applied force, P , in kg, by the actual surface area of the indentation which is a segment of a sphere as shown in Equation 1.

$$BHN = H \quad \frac{P}{\pi D t} = \frac{2P}{\pi D [D - \sqrt{D^2 - d^2}]} \quad (1)$$

where D is the diameter of the ball in mm, t is the indentation depth from the surface in mm, and d is the diameter of the indentation at the surface in mm, the internal diameter (d) of the indented material was measured using a vernier caliper.

The extrusion process was also carried out theoretically applying a modelling technique of Finite Element Analysis (FEA), using a commercial software (Automatic Dynamic Incremental Nonlinear Analysis, ADINA) and the result was compared with the experimental outcome.

3.0 RESULT AND DISCUSSION

3.1 Metallographic analysis

The physically observed extruded samples showed surface cracks which, after cutting the specimen for optical microscopy observation showed that the cracks did not penetrate the extrudate. The microstructure of both extruded and unextruded samples (Sn alloy) as obtained by optical microscopy is shown in Figure 3. It was observed that even after the 2nd ECAE pass no signs of cracks or fracture could be found in the interior part. There appeared to be evidence of grain size redistribution from coarse to finer grains from no-pass to two ECAE passes.

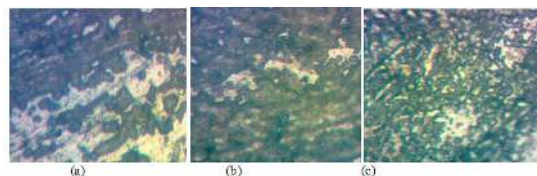


Figure 3: Micrographs of samples (a) before extrusion (b) after the 1st pass, (c) after 2nd pass

3.2 Mechanical properties

Figure 4 showed the compressive stress against compressive strain for Sn alloys. The modulus (stiffness) was found to be 8.4 times higher after the second ECAE passes. The compressive modulus value was 287.62 MPa for no pass which increased extensively to 2362.25 MPa after the second pass. The increase in compressive modulus are thought to be due to high level of dislocations generation and multiplication that may have resulted in severe strain hardening as the material passed through the sharp angle of the die.

The compressive strength decreased with increase in the number of ECAE passes. The no-pass compressive strength of 57.7488 MPa decreased to 42.70632 MPa after two passes. In like manner, compressive strain at maximum stress which had a value of 0.41471 MPa for no pass, decreased to 0.28770 MPa after two ECAE passes. The hardness test result indicated a marginal increase from the initial value of 69 HBR when unextruded to 88 HBR after second ECAE pass.

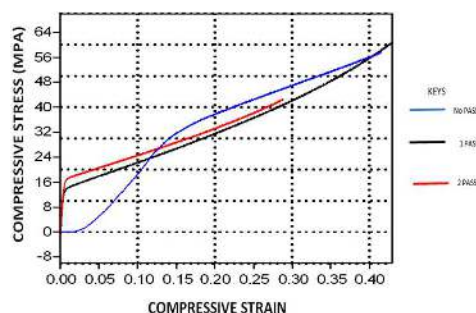


Figure 4: Stress-strain curves for combined samples.

3.3 Thermal Properties

The DSC curves for unextruded and extruded Sn alloy obtained during heating and cooling cycles are as presented in Figure 5 (a-c). The presence of small peaks during the heating and cooling cycles may indicate presence of some trace compounds within the alloy (Ajao, 2009). The temperature at which these small peaks appeared tended to reduce from 175.7 to 174.5 and 173.7 for no pass, one pass and two passes extrusions respectively. However all the endothermic and exothermic peaks for the three cases showed that the samples were consistently thermally stable. There were no observable unusual thermal changes in the materials due to ECAE in Sn alloy.

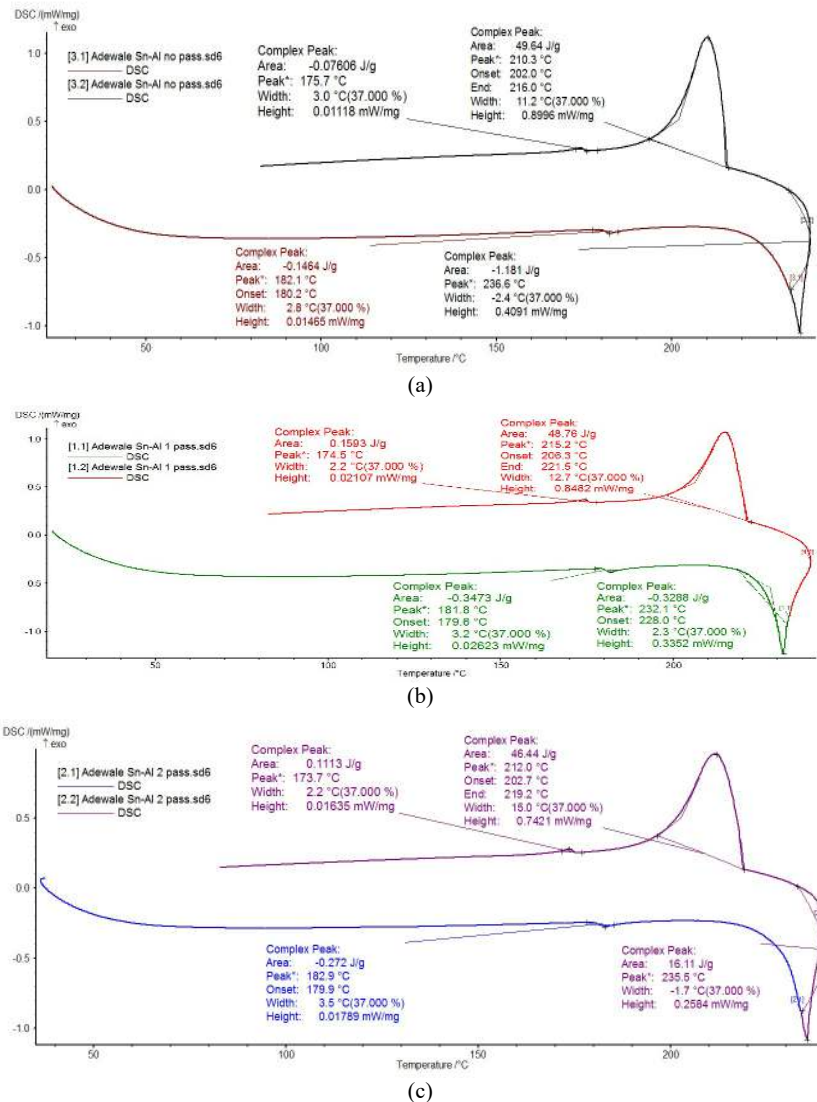


Figure 5: The DSC scans for ECAE (a) no pass, (b) one pass and (c) two passes.

3.4: Finite Element Analysis

Distributions of plastic deformation after one ECAE pass for some time intervals was carried out theoretically by finite element method (FEA) via automatic dynamic incremental non-linear analysis (ADINA) as shown in Figure 6 (a-c). The Figures showed that plastic deformation is non-uniformly distributed along the cross-section and the length of the specimens. Along the workpiece length, the plastic deformation was divided into three areas. The head, where there was non-uniformity of plastic deformation caused by non-uniform material flow between the vertical and horizontal channel. The body, where there was steady state plastic deformation and the tail, where the non-uniformity of plastic deformation was related to the uncompleted pressing of specimen at the exit channel. The non-uniformity of plastic deformation concentrated at the bottom part of the workpiece had previously been observed to increase plastic deformation with increased number of ECAE presses (Kvačak et al., 2007; Kočiško et al., 2009; Leo et al., 2007).

CONCLUSION

It can be concluded from this study that compressive modulus and hardness of Sn alloy increased with increased number of ECAE passes while the compressive strength and strain decreased. The modulus of the alloy increased by 8.3 times from no pass to two ECAE passes. However, the samples were found to be thermally stable without regard to the number of ECAE passes. Small peaks were observed on both the endotherm and exotherm scans which were thought to indicate the presence of some trace compounds within the alloy.

From the theoretical observation, plastic deformation of Sn alloy was found to be non-uniformly distributed along the cross-section and also the length of the specimens. Also, deformation increased with the number of ECAE steps.

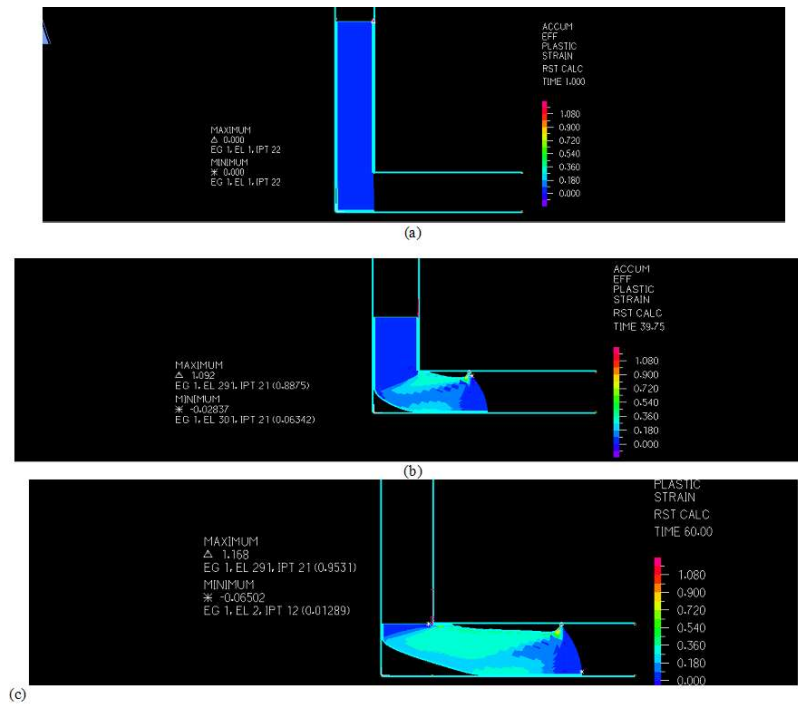


Figure 6: Distribution of plastic deformation (a) at the 0 s, (b) after 40 s and (c) after 60 s extrusion.

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DESIGN, FABRICATION, AND TEST-RUN OF A PILOT PLANT FOR PRODUCTION OF ALUMINIUM HYDROXIDE

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ABSTRACT

The design, fabrication and test run of a pilot-scale reactor for the production of aluminium hydroxide from aluminium sulphate derived from Kankara Kaolin was investigated. XRD, XRF and BET techniques were carried out on the aluminium hydroxide prepared from the pilot scale reactor. The kinetics of the reaction for precipitation of aluminium hydroxide was found to be pseudo first order. The activation energy and pre-exponential factor of the precipitation reaction were found to be 102kJ/mole and 1.5×10^{14} /sec respectively. MATLAB was used for the design of the reactor with a conversion of 99.98% obtained. The product from the pilot-scale reactor was found to be a mixture of crystalline and amorphous phases for the first run, and as purely crystalline mix of Bayerite and Boehmite for the second run. The BET surface area of the product was found to be 97.73m²/g for the first run and 227.779m²/g for the second run.

Keywords: Kinetics, Design, Aluminium hydroxide, Kankara kaolin, Test-run

1.0 Introduction

Aluminium hydroxide Al(OH)₃ is found in nature as the mineral gibbsite and its three rare polymorphs which are bayerite, doyleite and nordstrandite. There are also two close relatives AlO(OH) which differ only by the loss of water. Freshly precipitated aluminium hydroxide forms gels, which is the basis for application of aluminium salts as flocculants in water purification. This gel crystallizes with time. Aluminium hydroxide is mainly used as a feedstock for the production of aluminium oxide (alumina) that is used in the manufacture of aluminium metal. Other major uses of aluminium hydroxide include the manufacture of: specialty calcined aluminas, aluminium sulphate, polyaluminium chloride, aluminium chloride, zeolites, sodium aluminate, activated alumina, and aluminium nitrate. Aluminium hydroxide powder which has been heated to elevated temperatures under carefully controlled conditions is known as active alumina and is used as a desiccant, an adsorbent, in gas purification, as a Claus catalyst support, water purification, and as a component in the synthesis of zeolite catalysts. Virtually all aluminium hydroxide used commercially is manufactured by the Bayer process which involves dissolving the mineral Bauxite in sodium hydroxide at temperatures up to 270°C (Hind *et al.*, 1999). The by product, red mud, is hazardous (Lang, 2010), thus precipitating the need for alternative safer routes. Other methods of commercial production include the production of gelatinous aluminium hydroxide, involving the neutralization of aluminium sulphate or ammonium alum by ammonia or sodium hydroxide, or by the neutralization of a sodium aluminate solution by acids, NaHCO₃ or CO₂. The aim of this work is to design, fabricate, and test run a pilot scale reactor for the production of aluminium hydroxide from Kankara kaolin via chemical precipitation using sodium hydroxide.

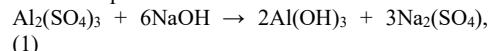
2.0 Materials and methods

The materials used for this work were Al₂(SO₄)₃ solution obtained from the dealumination of activated Kankara kaolin (Aderemi *et al.*, 2009), sodium hydroxide solution, barium chloride, stainless steel (grade 304), plastic tanks, plastic valves, plastic flow meters, electric motor, Teflon rod, Teflon plates and stainless steel rod. Aluminium hydroxides were prepared from aluminium sulphate obtained from Kankara kaolin. A 50wt% sodium hydroxide solution was introduced at a rate of 10ml/min into the continuously stirred Al₂(SO₄)₃ solution at different time intervals for three temperature conditions. A plot of temperature against concentration was then made and subsequently a plot of rate constant against

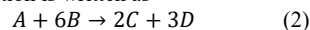
temperature was then made from the results obtained. The pilot semi-batch reactor was designed using numerical methods (MATLAB software). The operating conditions were taken to be as follows: reaction temperature of 79°C, pressure of 1 atm, flow rate of NaOH of 0.3225 l/hr, volume of Al₂(SO₄)₃ of 32.2469l, activation energy of 102.2373kJ/mol and pre-exponential factor of 1.153509×10^{14} sec⁻¹. The pilot scale reactor was drawn for construction using AUTOCAD 2013 version. The pilot scale reactor was fabricated using stainless steel of grade 304 for external surfaces and polypropylene for the internal reactor tank. Plastic fittings and pipes were chosen all through the reactor. A pre-fabricated electric motor was installed on the reactor top. A reinforced Teflon rod was used as the shaft of the impeller with Teflon impeller blades. The pilot scale reactor was test run in two batches, for 30 minutes each. The operating conditions were taken as those used for the reactor design. The aluminium hydroxide powders produced were then analysed by X-ray diffraction (XRD) on a PANalytical Empyrean diffractometer using nickel filtered Cu K α radiation in the range 2 θ -10⁰-75⁰. The composition of the aluminium hydroxide powders were determined using a PANalytical Minipal 4 Spectrometer. The surface area of the aluminium hydroxide powders produced were determined using a GAPP V-Sorb 2800P BET surface area analyser after undergoing outgassing for 16 hours.

3.0 Results and discussion

Using the power law model for homogenous reactions, from the Stoichiometric equation:



The reaction is written as



The rate law is

$$-r_A = k C_B^m C_A^n \quad (3)$$

For very large C_B that doesn't change appreciably i.e. C_B $\cong$ C_{B0},

Equation 3.4 can be written as

$$-r_A = k' C_A^n \quad (4)$$

Where $k' = k C_B^m$

Taking the natural log of both sides,

$$\ln(-r_A) = \ln\left(\frac{dC_A}{dt}\right) = \ln k' + n \ln C_A \quad (5)$$

Data for C_A with time was plotted using the polynomial fit by differential method of analysis to get -r_A, then ln(-r_A) was plotted with lnC_A to get n, and ln k'.

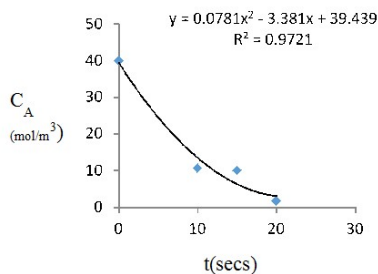


Figure 1a: Plot of concentration of $\text{Al}_2(\text{SO}_4)_3$ (C_A) with time (t) at 90°C (in water bath at 100°C)

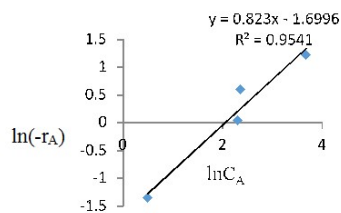


Figure 1b: Plot of rate with concentration on log-log scale at 90°C (in water bath at 100°C)

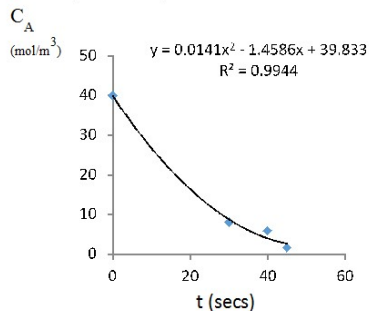


Figure 2a: Plot of concentration of $\text{Al}_2(\text{SO}_4)_3$ (C_A) with time (t) at 79°C (ambient environment, 25°C)

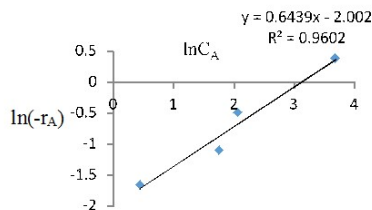


Figure 2b: Plot of rate with concentration on log-log scale at 79°C (ambient environment, 25°C)

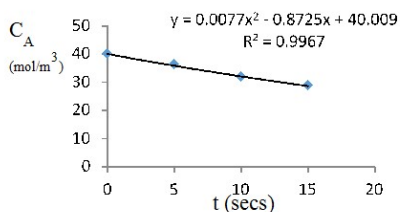


Figure 3a: Plot of concentration of $\text{Al}_2(\text{SO}_4)_3$ (C_A) with time (t) at 73°C (in water bath, 20°C)

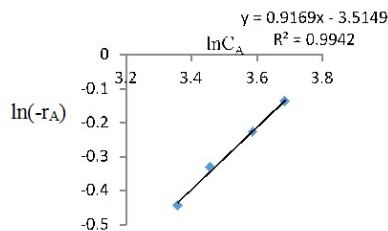


Figure 3b: Plot of rate with concentration on log-log scale at 73°C (in water bath, 20°C)

The kinetic data were obtained after processing the data gotten from laboratory bench scale experiments. From Figures 1b, 2b and 3b, using Equation (5), the values for $\ln k'$ were found to be -1.6996, -2.002, and -3.5149 respectively. Also, the values for n were found to be 0.823, 0.6439, and 0.9169 respectively. From Arrhenius equation

$$k' = Ae^{\frac{-E}{RT}} \quad (6)$$

Taking the natural log of both sides, it is written as

$$\ln k' = \ln A - \frac{E}{RT} \quad (7)$$

The plot of $\ln k'$ with $1/T$ is made and the slope was obtained as E/R with an intercept of $\ln A$

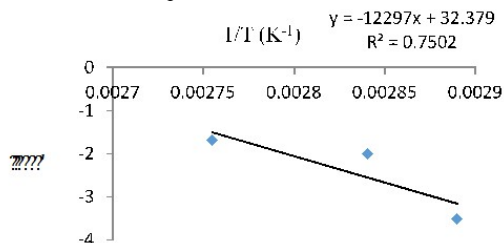


Figure 4: Plot of $\ln k'$ with temperature ($1/T$)

From the plot of $\ln k'$ against $1/T$, from Equation (7), and using $R = 8.314 \text{ J/molK}$, it was found out that

$$E_A = 102.237 \text{ kJ/mol}$$

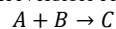
$$A = 1.153509 \times 10^{14} \text{ sec}^{-1}$$

$$n \cong 1$$

E_A = Activation energy
 A = Pre exponential factor
 n = Order of the reaction

Using a Basis of 10.448 Kg of $\text{Al}(\text{OH})_3$ per day (6 batches of 4 hours each)

From Fogler (2006), for an elementary liquid-phase reaction, take an irreversible reaction between A and B to give C:



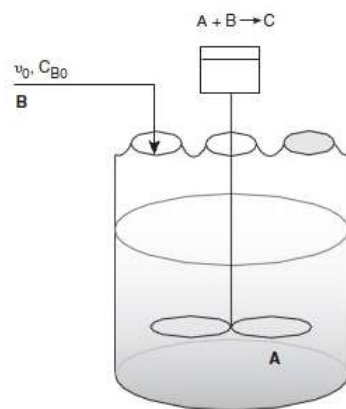


Figure 5: Semi-batch reactor

The rate equation can be written as:

$$\frac{dC_A}{dt} = r_A - \frac{v_0}{V} C_A \quad (8)$$

And for B it becomes

$$\frac{dC_B}{dt} = r_B + \frac{v_0(C_{B0} - C_B)}{V} \quad (9)$$

Substituting the rate law from Equation (4) in Equations (8) and (9) gives

$$\frac{dC_A}{dt} = -k' C_A^n - \frac{v_0}{V} C_A \quad (10)$$

$$\frac{dC_B}{dt} = -k' C_A^n + \frac{v_0}{V} (C_{B0} - C_B) \quad (11)$$

Similarly for C and D, it was gotten as

$$\frac{dN_C}{dt} = r_C V = -r_A V \quad (12)$$

$$\frac{dN_C}{dt} = \frac{d(C_C V)}{dt} = V \frac{dC_C}{dt} + C_C \frac{dV}{dt} = V \frac{dC_C}{dt} + v_0 C_C \quad (13)$$

Therefore,

$$\frac{dC_C}{dt} = k' C_A^n - \frac{v_0}{V} C_C \quad (14)$$

And

$$\frac{dC_D}{dt} = k' C_A^n - \frac{v_0}{V} C_D \quad (15)$$

The conversion of A is given as

$$X_A = \frac{N_{A0} - N_A}{N_{A0}} \quad (16)$$

Thus

$$X_A = \frac{C_{A0} V_0 - C_A V}{C_{A0} V_0} \quad (17)$$

For a constant density system,

$$V = V_0 + v_0 t \quad (18)$$

Equations (10), (11), (14), (15), (17), and (18) were then solved using the ODE solver in Matlab to get the values for C_A , C_B , C_C , C_D , X_A , V and t .

At a volume of 42.5 litres in the reactor, the conversion (X_A) was found to be 99.98%.

The time for the reaction was found to be 31.9 minutes.

The total volume of the reactor is 50 litres, allowing for 15% head space as recommended by Blaasel (1990).

To determine the mixer power required for the stirred tank reactor,

From Harry Silla (2003), since we are dealing with a liquid-liquid mixture

$$P_n = p V_r \quad (19)$$

where p = power factor and V_r = volume of the reactor mix

To determine the stirrer specification, using standard stirred vessel configuration (Beek *et al*, 1999) where D is the Diameter of vessel:

$$\text{Diameter of impeller (d)} = 1/3 \times D \quad (20)$$

$$\text{Width of impeller blade (w)} = d/5 \quad (21)$$

$$\text{Height of liquid in reactor (H)} = D \quad (22)$$

$$\text{Height of bottom of vessel from the impeller (L)} = 1/3 \times H \quad (23)$$

$$\text{Width of Baffles} = D/10 \quad (24)$$

$$\text{Length of impeller blade (l)} = d/4 \quad (25)$$

$$\text{Number of Baffles} = 6$$

$$\text{Number of impeller blades} = 4$$

Since the reaction is between two liquids,

Therefore $p = 5 \text{ hp}/1000 \text{ gal}$ and V_r = volume of the reactor mixture

But 1 gallon = 3.784 litres

Therefore for 42.5 litres reaction volume, we have

$$P_n = 5 \times 42.5 / (3.784 \times 1000) = 0.05616 \text{ hp}$$

To determine the stirrer and baffle specification from Equations 20 through 25:

Where D is diameter of reactor = 38cm, Height of reactor (H_r) = 55cm, Diameter of impeller (d) = 12.67cm, Width of impeller blade (w) = 2.534cm, Height of liquid in reactor (H) = 38cm,

Length of impeller blade (l) = 3.168cm

The pilot scale reactor was drawn using AUTOCAD (2013 version). Figure 5 is an x-ray projection of the drawn pilot scale reactor. The pilot scale reactor was constructed at HANIGHA in Kaduna, Kaduna State using the specifications obtained from the reactor design. Plate I is a pictorial view of the fabricated reactor.

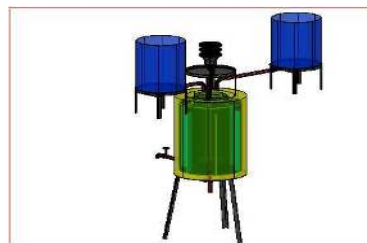


Figure 6: X-ray projection of aluminium hydroxide pilot scale reactor using AUTOCAD, 2013 version.



Plate I: Fabricated pilot scale reactor for the production of aluminium hydroxide from alum from Kankara kaolin.

The XRD patterns of aluminium hydroxide produced from the pilot scale reactor were determined.

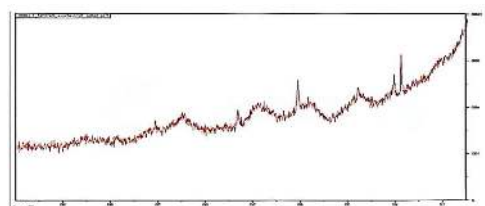


Figure 7: XRD pattern of aluminium hydroxide produced for run 1

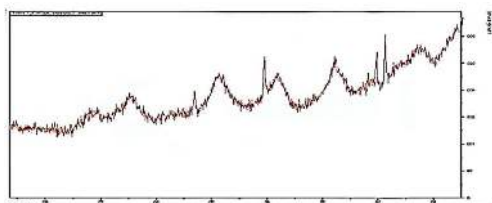


Figure 8: XRD pattern of aluminum hydroxide produced for run 2

From Figure 4.8, it can be seen that the characteristic diffraction peaks for boehmite at $2\theta = 27.86^\circ, 38.14^\circ, 48.68^\circ$, and 64.88° appear albeit dwarfed. The major diffraction peaks for bayerite could be seen at $2\theta = 18.62^\circ, 20.14^\circ, 40.34^\circ$ and 53.64° . From Figure 4.9, the characteristic diffraction peaks of boehmite at $2\theta = 14.24^\circ, 27.86^\circ, 38.14^\circ, 48.68^\circ$, and 64.88° were well identified. Also the major diffraction peaks for bayerite at $2\theta = 18.62^\circ, 20.14^\circ, 40.34^\circ$ and 53.64° . This showed that the product from the pilot scale reactor was formed between the pH of 7 and 8. For run 1, the transition from pH 7 to 8 is less advanced as that seen in run 2.

Table 1: Chemical composition of aluminium hydroxide obtained from alum from Kankara kaolin from the pilot scale reactor

Constituents	Run1	Run2
SiO ₂	4.97	3.32
Al ₂ O ₃	70.54	74.34
MoO ₃	3.00	1.86
SO ₃	13.3	15.78
CaO	0.500	0.335
TiO ₂	0.053	0.036
MgO	1.63	1.20
Cr ₂ O ₃	0.289	0.236
MnO	0.039	0.040
Fe ₂ O ₃	3.10	2.55
NiO	0.079	0.055
ZnO	0.19	0.18
CuO	0.039	0.041
Na ₂ O	2.18	1.96
K ₂ O	0.059	0.025
V ₂ O ₅	0.028	0.038

The probable percentage increase in yield noticed at pH of 7 due to a larger Al₂O₃ content than commercial value was also observed in the oxide content of the sample for Al₂O₃ at 70.54 for run 1 and 74.34 percent for run 2. V₂O₅ showed the lowest (0.028) percentage for run1 and (0.025) for K₂O for run 2 as was seen in Table 1. This findings are consistent with the report of Misra (1990) and are a pointer to highly crystalline nature of the samples obtained from the pilot-scale reactor. The surface areas of the two products of the pilot scale reactor were determined.

Table 2: BET-surface area analysis of aluminum hydroxide produced from pilot scale reactor setup

Sample ID	BET Surface Area (m ² /g)	Pore Volume (cm ³ /g)	Pore Size (nm)
Run 1	97.736	0.051	2.074
Run 2	227.779	0.113	1.980

The product of the pilot scale reactor setup yielded a much higher surface area of 97.73m²/g for Run 1 and 227.77m²/g for Run 2, as was seen from Table 4.5. Also, the values of the surface areas of the two runs in the pilot scale setup compared favourably with the reported values in the literature. However, the value of 97.73m²/g for the run1 in the pilot scale reactor setup further confirmed that the sample was partly amorphous and is consistent with the findings of Kosmulski (2009).

4.0 Conclusions

Aluminium hydroxide precipitated from Kankara kaolin by the reaction between aluminium sulphate and sodium hydroxide was found to obey *psuedo* first order kinetics. The conversion of Al₂(SO₄)₃ was found to be 99.98% from the numerical design. Aluminium hydroxide produced from the pilot scale reactor was found to mostly crystalline with major peaks for bayerite and boehmite clearly visible. The composition of the aluminium hydroxide produced from both runs with the pilot scale reactor also point to a crystalline material, with an increase for the value of run 2. Finally, the surface area of the first run was more than expected for amorphous material, but less than crystalline material, pointing towards a partly amorphous, partly crystalline product, while run 2 gave a distinctly crystalline value.

5.0 Acknowledgement

The authors are grateful to the Petroleum Technology Development Fund (PTDF) for their funding.

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FLEXURAL AND COMPRESSION STRENGTH AND STRAIN PROPERTIES OF SURFACE-TREATED SISAL FIBRE / COCOA-POD HUSK PARTICLES-FILLED HYBRID POLYESTER COMPOSITE

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ABSTRACT

This study reports the investigation of the effect of hybridising cocoa pod husk (CPH) particles with sisal fibre in unsaturated polyester composites with a view to assessing the effects of filler surface treatment on the small strain flexural and compression strength and strain properties. The fillers were surface treated with two coupling agents: sodium hydroxide (NaOH) and benzoyl peroxide (BP). The flexural and compressive strength and strain were compared for the untreated, NaOH- and BP-treated samples for filler concentrations of 2 – 12%w/w. Significant improvement in flexural strength/strain and reduction in compression strength/strain were recorded in all the composites prepared at 2%w/w concentration from each of the fillers due to surface treatment. The recorded significant improvement in properties due to surface treatment can be attributed to surface modification of the surface chemistry by the coupling agents used. This may have substantially improved filler – matrix bonding due to the removal of unwanted soluble cellulose, hemicellulose, pectin, lignin, etc on the surfaces. NaOH was found to be more effective in the surface treatment of CPH while benzoyl peroxide was better for sisal fibre. It can be concluded that the improved properties recorded at the low concentration soon disappeared at higher filler loading concentration. This study showed that combination of CPH as a particulate and sisal fibre as a fibrous filler a hybrid in polyester would only be applicable in light load-bearing situations since the improvement recorded at due to surface treatment at higher filler loading will only be good enough for materials saving and utilisation of the fillers in composite fabrication only.

Keywords: retting, surface treatment, hybrid fibre composites, cocoa pod husk powder, mechanical behaviour, polyester,

Introduction

Numerous naturally occurring fibrous and particulate materials of engineering interest abound in our environment. Many constitute environmental nuisance because they are considered as wastes for being post-agricultural harvest by-products among other reasons. Intense researches are going on these materials mostly in the developing countries of the world that are blessed with vast forest resources.

Common naturally occurring fibrous materials such as sisal (Durowaye *et al.*, 2014, Paul *et al.*, Joseph *et al.*, 1999), pineapple leaves (Asim *et al.*, 2015), hemp (Shanks and Quajai, 2006, Quajai, 2005), jute (Murali *et al.*, 2015), kenaf (Zampaloni *et al.*, 2007), bamboo (Dagang *et al.*, 2012), banana (Liu *et al.*, 2009) etc.; and particulates including saw dust, coconut shell ash (Imoisili *et al.*, 2012), wood base filler derived from oil palm wood flour (Gattenholm *et al.*, 1993, Fuad *et al.*, 1998), rice husk (Oyetola *et al.*, 2006, Ismail *et al.*, 2001, Martí-Ferrer, *et al.*, 2006, Joshi *et al.*, 2015), etc. have been intensely researched as fillers in polymeric based composites. These fillers introduce some advantages compared to traditional inorganic fillers, including their renewable nature, low density, nonabrasive properties, reasonable strength, and stiffness (Neus *et al.*, 1999).

CPH form about 70% of a cocoa fruit. The husks are generated after opening the pod for removing the cocoa beans (Ofori-Boateng and Lee, 2013). These wastes are largely unexploited and considered as a disposal problem. They are left to rot on the cocoa plantation producing foul odours and propagating diseases such as black pod rot (Vriesmann *et al.*, 2011).

Some scientists analysed the utilization of CPH as green solid base catalysts for trans-esterification of oils (Ofori-Boateng and Lee, 2013) as a source of proteins (Serra *et al.*, 1999), pectins (Vriesmann *et al.*, 2011; Vriesmann *et al.*, 2012) or other useful chemicals (Mansur *et al.*, 2014), as a catalyst in

bio-energy production (Amos *et al.*, 2016) and as a raw material of the densification process (Syamsiro *et al.*, 2012).

Sisal is a natural plant fibre with the botanical name *Agave sisalana* which belongs to a family of *Asparagaceae*. It has a 7-10 year life-span and typically produces 200-250 commercially usable leaves. Each leaf contains an average of around 1000 fibres (Chandramohan *et al.*, 2011). The fibre element, which accounts for only about 4% of the plant by weight, is extracted by a process known as decortication where leaves are crushed and beaten by a rotating wheel set with blunt knives, so that only fibres remain (Vilane *et al.*, 2014).

Sisal fibre possesses high specific strength and modulus as it is low priced, recyclable, easily available. Investigations of sisal fibre as reinforcement to make reinforced polymer composites has aroused great interest among materials scientists and engineers all over the world. In recent years, interest had been principally focussed on the mechanical properties of the composites in relation to the efficient way to improve the interfacial bonding properties between sisal fibre and polymeric matrices for improved load bearing capability. Sisal and many cellulosic based fibres have thus been investigated in this respect by treating the fibre surface with appropriate coupling agent for enhanced mechanical performance of the resulting composites among many other studies.

Retting is a chemical process of removing non-cellulosic material attached to fibres to release individual fibres from the natural biopolymer composites. Once the part is collected they are kept in the field or under water for about 2 to 3 weeks during which the pectinous substances that bind the fibres together with other plant tissues are made to ferment, soften and degraded by micro-organisms. The quality of fibres obtained is mostly determined by the retting condition and duration.

Natural fibres are rich in cellulose and they also are low-cost, easily renewable source as reinforcement or fillers in polymer composites. Cellulosic fibres are hygroscopic in nature;

moisture absorption can result in swelling of the fibres which may lead to micro-cracking and degradation of the composite. This problem can be overcome by treating fibres with suitable chemicals often referred to as coupling agents to decrease the hydroxyl groups which may be involved in the hydrogen bonding within the cellulose molecules (Vijay *et al.*, 2012). The major reason for surface treatment is to modify the surface chemistry of the fibre so as to improve the filler-matrix interface compatibility for proper wetting of the fibre.

Alkaline treatment or mercerization is one of the most used chemical treatments of natural fibres when used to reinforce thermoplastics or thermosets. The important modification done by alkaline treatment is the disruption of hydrogen bonding in the network structure, thereby increasing surface roughness. This treatment removes a certain amount of lignin, wax and oils covering the external surface of the fibre cell wall, depolymerizes cellulose and exposes the short length crystallites (Clemons *et al.*, 1994). The treatment changes the orientation of the highly packed crystalline cellulose order, forming an amorphous region (Chandramohan *et al.*, 2011). Apart from alkaline coupling agent treatment, silane and peroxides are also common in natural fibre surface treatment. Some reported works on sisal and other natural fibres especially in their use in composites include Joseph and Thomas, (1996), Joseph *et al.*, (1999), Oladele *et al.*, (2014) and Vijay *et al.*, (2012) among many others.

A hybrid composite consists of more than one filler or reinforcement fibres. In most cases, the motivation is to take advantage of the combined reinforcing effects of the fillers, which may be fibres or particulates or combined, in enhancing the various properties of the composites fabricated from either a thermoset or thermoplastic matrix. Previous works have been reported on efforts that have been made in this area some of which include Kalaprasao and Thornas (1995), Chikhradze *et al.* (2012), Gururaja *et al.*, (2012) and Vasanta *et al.*, (2013) among others.

This work reports the effect of surface treatment with NaOH and benzoyl peroxide on the flexural and compression strength and strain properties of sisal and CPH hybrid polyester composites with a view to ascertaining the possible different application areas for the new materials thereof thereby expanding their utilisation and adding more value as fillers.

Materials and Methods

The sisal leaves were collected and washed properly after which they were soaked in water for period of minimum of 21 days so as to allow fermentation to take place for easy removal of the fibres (retting). The resulting soft sisal fibres were then mechanically separated and again repeatedly washed in clean water. They were then sun-dried and kept safe in a safe dry place. The fibres were further oven dried at 80°C for about one hour before use.

The CPH was collected directly from the farm after harvesting during the cocoa season. The inner soft whitish layers that protect the cocoa beans were thoroughly scraped off. The hard shells were then broken into smaller parts and placed in an oven at low heat (120 - 150°C) for at least 18 – 24 hours till a constant dried weight was achieved. The dried samples were later pulverised and sieved into average particle size of 120 µm.

The unsaturated polyester was obtained from local suppliers with the required accelerator and catalyst. Polyvinyl acetate (PVA) was obtained from Fibre Glast (USA) was used as the mould release.

Filler surface Treatment Procedure

5% NaOH (Sigma Aldrich) solution was prepared as the alkali and 5% benzoyl peroxide (Alfa Aesar, USA) as the coupling agents. The fillers were dried at 60°C in an oven for 2-3 hrs prior to the surface treatment. They were soaked in the prepared solution for 3 hrs followed by a thorough washing in distilled water to remove excess NaOH. They were again dried for another 24 hrs.

The peroxide treatment was carried out on an alkali pre-treated fillers using benzoyl peroxide in acetone for 30 and 45 mins. After the treatments, the fillers were thoroughly washed with distilled water and dried in hot air oven at 80°C for 24 hours.

Composite Fabrication and Testing.

Tensile test pieces were fabricated in an aluminium mould in accordance with appropriate ASTM specification. The polyester was mixed with measured amount of the accelerator and catalyst and were properly mixed and allowed to settle for about 10 mins to initiate cross-linking and allowed the bubbles to clear. The mixture was then carefully poured into the mould which had been coated with a mould release (PVA) and allowed to cure before removal.

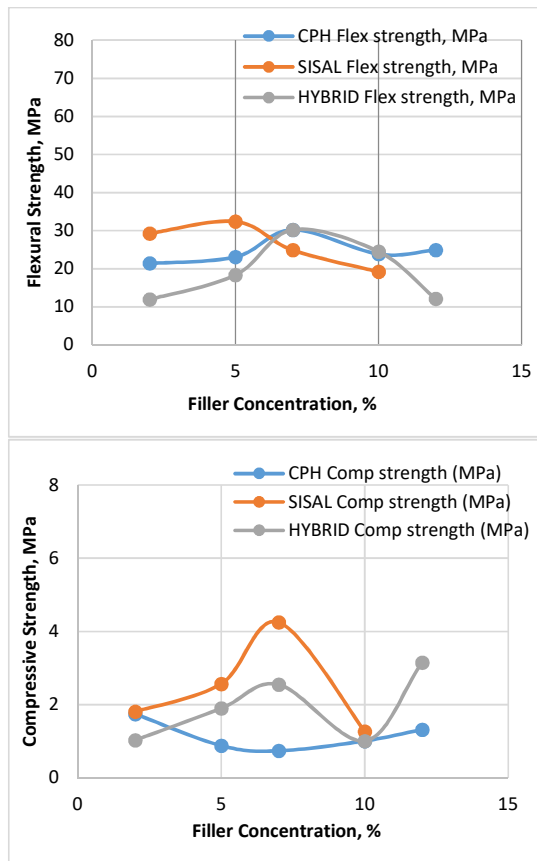
The procedure for the preparation of the single and hybrid composites followed that of the unfilled samples by adding the respective filler carefully ensuring even dispersal. The fillers were equally treated by soaking in the respective coupling agent as described in the previous section and then added to the prepared matrix and mixed thoroughly before carefully pouring into the mould.

In all, composite specimens of with 0, 2, 5, 7, 10, 12, and 15%w/w filler concentrations were prepared for flexural and compression tests. In this investigation, the ratio sisal:CPH filler for the hybrid fillers was 1:1. The flexural (3-point bending) and compression tests were carried out on the fabricated samples in a Universal Instron Testing machine. All tests were carried out at very low strain rate of 1.0 mm/min and at short time intervals to prevent severe deformation.

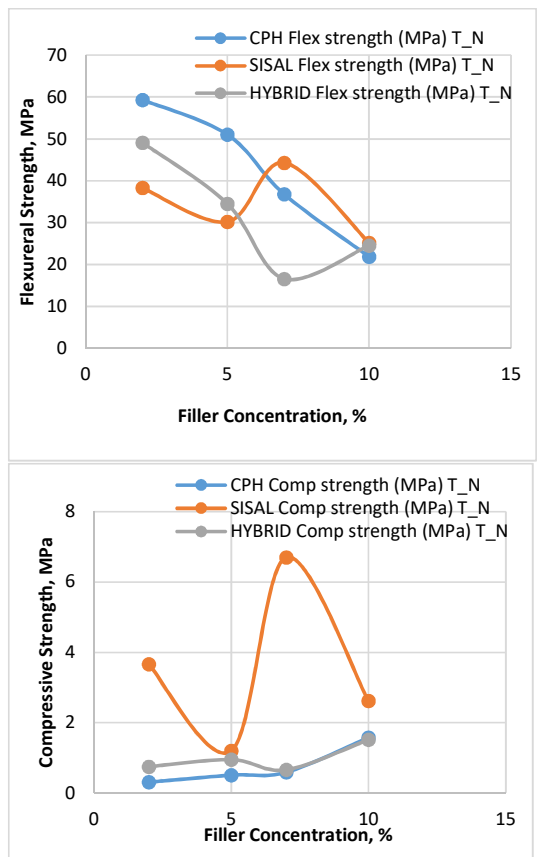
Result and Discussion

Figure 1 presents the plots of flexural and compressive strengths against concentrations of CPH particles, sisal and the hybrid when untreated (Figure 1a), NaOH-treated (Figure 1b) and benzoyl peroxide (BP) treated (Figure 1c). It can be seen that the flexural strength decreased from the values recorded at the 2% concentration as the filler concentration increased for each of the fillers. The initial response of CPH to surface treatment was the highest of the three fillers at the low filler concentration of 2% (Figure 1b). The response pattern in flexure due to surface treatment as the filler concentration increased generally followed a downward trend.

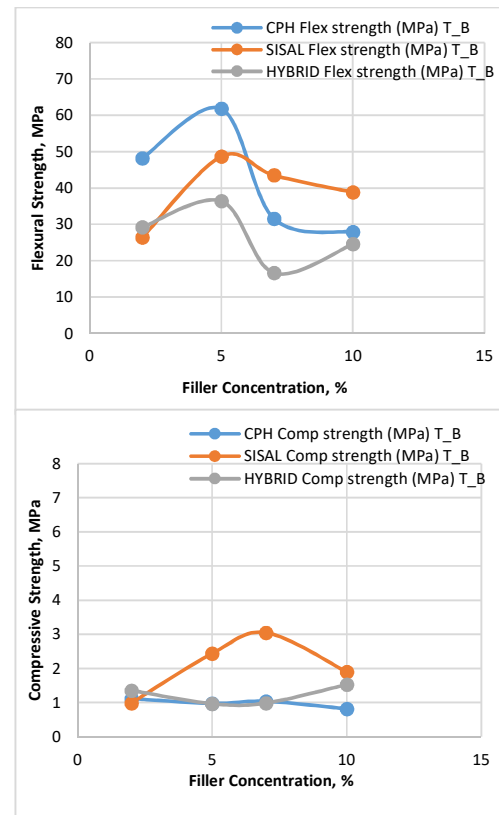
However, surface treatment had little or no significant influence on the compressive strength of CPH and the hybrid composites as the filler concentration increased whereas a consistent increase that recorded a maximum at 7% was recorded for sisal composite when BP-treated compared to NaOH treatment (Figure 1b).



(a) Untreated filler composites



(b) NaOH treated filler composites



(c) Benzoyl peroxide treated composites

Figure 1: The graphs showing the plots of the flexural and compression strengths for CPH, sisal, and hybrid composites when fillers were (a) untreated (b) NaOH treated and (c) BP treated.

It can be inferred from the plots that the flexural strength of the CPH filled composites increased sharply at 2% w/w after NaOH treatment decreasing steadily up to 10%. When BP-treated, the sharp increase at 2%w/w was less compared to NaOH-treated samples. It can also be seen that from about 7%w/w whether treated or not, the flexural strength was approximately the same through to 12%.

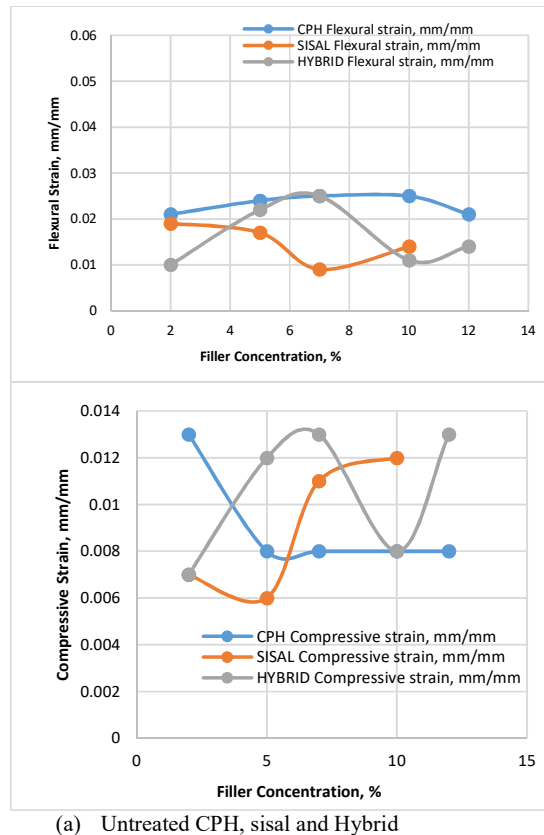
Figure 2 presents the plots of the flexural and compressive strains against the concentrations of CPH particles, sisal and the hybrid when untreated (Figure 2a), NaOH-treated (Figure 2b) and benzoyl peroxide (BP) treated (Figure 2c). At comparable filler concentrations, it can be observed that surface treatment resulted in a general increase in the strains. NaOH treatment resulted in a consistent decrease in the strain of the CPH and hybrid filled composites as the filler concentration increased when tested in flexure compared to BP-treated samples in the compression mode.

Conclusion

In this study, surface treatment of the fillers with the coupling agents (NaOH and BP) resulted in significant flexural strength increases, compressive strength decreases. NaOH was found to be more effective in the surface medication of CPH particles whereas the BP was more effective for sisal fibre.

Hybridisation of CPH particulate and sisal fibre in polyester composite under flexural and compression test conditions did not result in much significant improvement. Hybridisation mostly resulted in intermediate properties in the hybrid composites. This should be expected as the fillers are organic with properties that are unlikely to be able to transfer load to

the matrix being equally compliant under the test condition. The two fillers are usable in polyester in applications that require low bending strengths for matrix materials savings of between 7 and 10%. Value has therefore been added to the waste filler materials for their utilisation in composite fabrication in non-load-bearing applications in housing infrastructure.



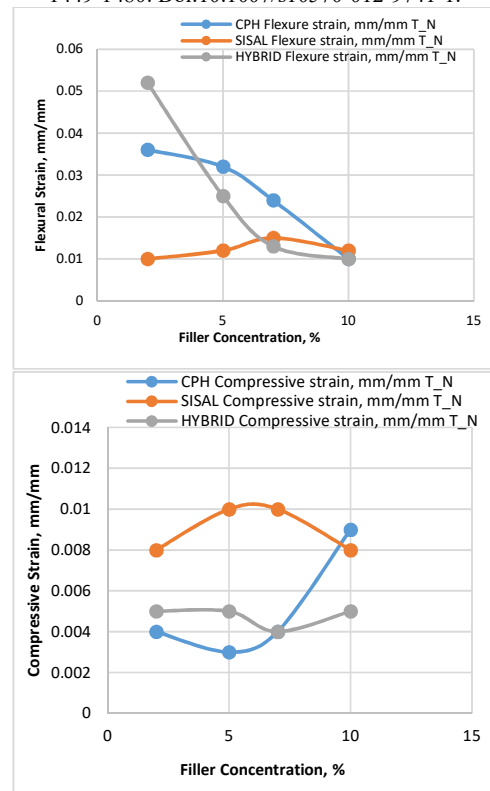
(a) Untreated CPH, sisal and Hybrid

Figure 2: The graphs showing the plots of the flexural and compression strengths for CPH, sisal, and hybrid composites when fillers are (a) untreated (b) NaOH treated and (c) benzoyl peroxide treated.

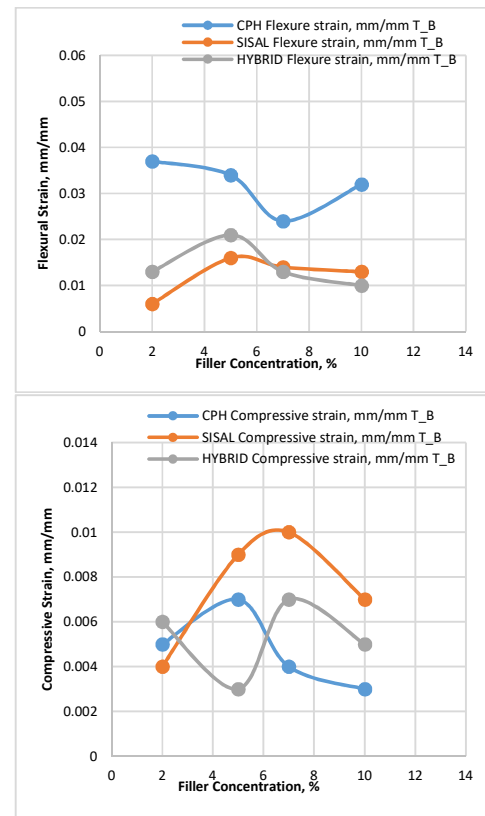
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(b) NaOH-treated CPH, sisal and Hybrid



(b) BP-treated CPH, sisal and Hybrid

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SYNTHESIS AND CHARACTERISATION OF CONDUCTING POLYMER BLEND – NIO NANOCOMPOSITES

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ABSTRACT

Poly N-vinyl carbazole (PVK) – Polyaniline (PANI) blend and - PVK-PANI-Nickel Oxide (NiO) nanocomposites have been synthesised from their monomers through chemical oxidation technique at different NiO nanocrystals concentrations of 5%, 10% and 15% . The spin-coated films were studied by X-ray diffraction (XRD), Fourier Transform Infrared (FTIR) and UV-visible spectroscopy while the 4-point probe electrical measurement and Scanning Electron Microscopy (SEM) were carried out. The XRD revealed the nanocrystalline nature of the synthesized NiO and the average crystallite size obtained was estimated to be 16 nm. Strong absorption UV region were observed for the blend and the nanocomposites. It was observed that beyond 5% NiO concentration, the band gap was insensitive to increase in the nanocrystals in the blends. The electrical conductivity was of the order $10^{-4} (\Omega \text{ cm})^{-1}$ for both the PVK-PANI blend and the nanocomposites. Scanning Electron Microscopy (SEM) revealed that PANI was not uniformly distributed within the PVK-PANI matrix, with identifiable phases and what appeared PANI clustering and uniformly dispersed nanocrystals within the PVK-PANI blend. The new nanomaterials are under investigation in this research program for their potential utilisation as active materials in optoelectronic devices that could eliminate the possibility of interface damage in multilayer device structures. This is expected to result in improved device lifetime where organic-organic and organic-inorganic materials are in direct contact.

Keywords: Synthesis, PVK, PANI, NiO nanocrystals, Polymer Blend, Nanocomposites,

INTRODUCTION

The need for cheap devices, light weight, flexible, large area of coverage, ease of processing, environmental friendly materials [1] have led to intense research on conductive organic materials. Conducting polymers have been used in wide range of applications in diverse areas such as organic light emitting devices, organic photovoltaic cells, energy storage devices and sensors among many others. These have in turn had positively affected humans in different areas ranging from medicine, environment, food security, biomedical engineering and energy, to mention a few. The conductivity of conducting polymers can further be enhanced by chemical manipulation of the polymer backbone, the nature of the dopant, the degree of doping and blending with other polymers [2].

Polyaniline, polypyrrole, poly (n-vinylcarbazole) and polythiophenes with their derivatives are few of the most widely investigated conducting polymers. Polyaniline (PANI) is one of the most studied conducting polymers and has shown promising applications due to ease of synthesis, low cost, high environmental stability, good redox properties and the ability to be electrically switched between its conductive and resistive states [3, 4]. Poly(n-vinylcarbazole) is a hole transport and light weight material which exhibits high thermal and chemical stability along with excellent electronic property, applicable in optical, electronics and solar devices [5, 6, 7].

Nickel Oxide (NiO) is an important class of p-type metal oxides [8] characterised with wide energy band gap [9] and excellent thermal stability [10]. Researchers are currently investigating NiO for various applications such as sensors, solar absorber, electrochromic devices, batteries, etc. [8]

Polymer blend is fast receiving great deal of attention due to the need to improve on the charge transport efficiency and reduction in degradation at the interface in multilayer system [11] thereby increasing the device life time and efficiency.

The conducting polymer composites and nanocomposites have been widely studied and many are already making tremendous impacts on the many organic electronic devices already in the market. A good example is poly(ethylenedioxythiophene) (PEDOT)/ polystyrene sulphonate (PSS) which has been used as a buffer layer [12]

and anode layer [27] in organic electronics devices. Though several works have been reported on polymer nanocomposites the reported increased photoconductivity of PVK/CdS nanocomposite [7] and improved conductivity and thermal stability in PANI with 30% NiO nanoparticles [13] were encouraging contributions.

This study is on the investigation of the effect NiO nanocrystals in PVK-PANI blend, the optical and electrical responses of the nanocomposite was carried out with a view to develop nanomaterials with potential for single layered deposition in devices thereby eliminating interfaces in the layered structure.

METHODOLOGY

Materials

Nickel chloride hexahydrate ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$) precursor for the nanocrystals, sodium hydroxide (NaOH), aniline monomer, N-vinylcarbazole (NVK), ferric chloride (FeCl_3), ammonium persulphate (APS), ethanol, chloroform, N,N-dimethylformamide (DMF) (all from Sigma-Aldrich) and distilled water.

Synthesis of NiO Nanocrystals: The sol gel method was employed for the synthesis of NiO nanocrystals at room temperature. $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and NaOH were both dissolved in absolute ethanol. The NaOH solution was added to the solution of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and the resulting mixture was stirred for about 2 hrs yielding a light green gel precipitate. This was filtered and washed thoroughly with distilled water and ethanol and was thereafter oven dried at 40°C for 24 hrs so as to remove water molecules. The dried precipitate was annealed at 400°C for one hour to obtain a black sample of NiO nanocrystals.

Synthesis of PVK-PANI Blend: FeCl_3 solution was added to the solution of NVK monomer, to initiate polymerization of PVK followed by immediate addition of the aniline and APS to the polymerizing NVK to the mixture. The resulting mixture was stirred continuously and five minutes later ethanol was added to precipitate the PVK and the resulting solution was stirred for about thirty minutes. After stirring for about 30 minutes the resulting mixture was left for 24 hrs. The

precipitate formed was filtered, washed with ethanol and dried in an oven at 40°C for 24 hrs.

Synthesis of PVK-PANI/NiO Nanocomposite: The concentration of the previously synthesized NiO nanocrystal was calculated and appropriate quantity equivalent to the required concentrations of the nanocrystals (5%, 10% and 15%) relative to the equivalent mass of the monomers was obtained. The FeCl₃ solution was added to the solution of NVK monomer to initiate the polymerization PVK followed by immediate addition of the NiO nanocrystals in the various percentages to the polymerizing PVK. Aniline monomer was then added to the mixture followed by the APS solution. The resulting mixture was stirred continuously followed by addition of ethanol to the solution which precipitate PVK and the resulting solution was stirred for about 30 min. The resulting mixture was left for 24 hrs. The precipitate formed was filtered, washed with ethanol and dried in an oven at 40°C for 24 hrs.

The characterisation was carried out by XRD (GBC eMMA XRD), FTIR (Schimadzu FT-IR 8300), scanning electron microscopy (SEM) with EDX (Phenom Pro X SEM 800-07334), UV-Vis spectrophotometry (Schidmazu 1800 series double beam) and Keithely 2400 Four point Probe system for resistivity and conductivity measurements.

RESULTS AND DISCUSSION

FTIR Analysis

Figure 1 presents the FTIR spectra of the synthesized samples. Band at 420 cm⁻¹ corresponding to Ni-O stretching vibration mode and broad absorption peak at 3466 cm⁻¹ which is attributable to the O-H stretching vibrations suggesting the presence of water molecules [14, 15]. This confirms the presence of NiO nanocrystals as synthesised. The peak wavenumbers of 744 cm⁻¹ of PVK-PANI corresponding to the 1, 2-disubstituted ring of out of plane deformation of C-H aromatic ring or ring deformation of substituted aromatic structure [16]. The band at 1156 cm⁻¹ corresponds to aromatic ring C-H in-plane deformation [17, 18] while the peak at 1222

cm⁻¹ is attributed to C-H in plane deformation of aromatic ring. The band at 1325 cm⁻¹ corresponds to CH₂ bending vibration due to the deformation of vinylidene group [16], the bands at 1452 cm⁻¹, 1483 cm⁻¹ and 1597 cm⁻¹ are attributed to the C=C stretching of the aromatic ring [16, 18, 19], the band at 2926 cm⁻¹ and 2966 cm⁻¹ are due to C-H aliphatic stretching vibrations due to CH₂ stretching vibrations, peak at 3046 cm⁻¹ corresponds to the =C-H asymmetric stretching vibrations of the aromatic structure [16, 19] and the band at 3452 cm⁻¹ is due to the presence of N-H stretching vibration (Saravanana, *et al.*, 2008). Figure (2–5) represents the spectra of the nanocomposites at different percentage of NiO nanoparticles. Notable shift in wavelength number was observed in the NiO having values at 416 cm⁻¹, 406 cm⁻¹ and 406 cm⁻¹ corresponding to 5%, 10% and 15% NiO nanoparticles present in the nanocomposite. Also a notable stretch was observed on the quinoid ring with wavelength band located at 1670 cm⁻¹ for the nanocomposites [20]. Table 1 is the summary of the dominant vibrational modes in the composites showed that the synthesised nanocomposites were indeed formed.

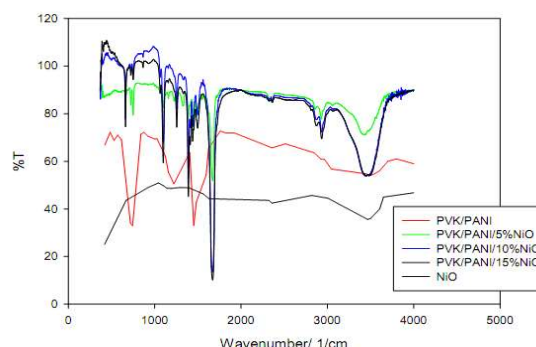


Figure 1. FTIR Spectrum of NiO, PVK/PANI and the Nanocomposites

Table 1: Table showing the relevant FTIR Bands for the synthesised nanocrystals, the blend and the PVK-PANI-NiO Nanocomposites.

Observed Wavenumber/cm-1					Assignments
NiO		PVK/PANI			
		5%	10%	15%	
420	-	416	406	406	ν (Ni-O) Stretching vibration
-	744	750	750	750	γ (C-H) of mono-substituted ring
-	1156	1157	1157	1157	γ (C-H)/ ν (C-N)
-	1222	1224	1225	1225	δ (C-H)
-	1325	1327	1334	1334	CH ₂ bending vibration
-	1452	1452	1440	1440	ν (C=C)
-	1482	1483	1496	1496	Benzenoid ring/ ν (C=C) of carbazole ring
-	1596	1670	1668	1670	Quinonoid ring/ ν (C=C) of carbazole ring
-	3452	3431	3448	3448	ν (N-H)
3466	-	-	-	-	ν (O-H) Stretching Vibration

δ in-plane deformation, ν stretching, γ out-of-plane deformation

X-ray Diffraction Studies

Figure 2 shows the XRD pattern of the NiO nanocrystals which exhibits three peaks at scattering angles of 37.25°, 43.305° and 63.10° indexed as (1 1 1), (2 0 0) and (2 2 0) crystal planes of the crystalline NiO respectively [21, 22]. The d-spacing was calculated to be 2.088 Å using the Bragg expression and the lattice constant, *a*, is 4.176 Å. The diffraction peaks were indexed to the cubic crystalline structure of NiO and the peak

positions and the relative intensity of the characteristic peaks matches with the ICDD, No. 04-0835 [23]. The XRD spectrum shows a significant amount of line broadening which is characteristics of nanocrystals [24]. The average crystallite size obtained is 16 nm from the most intense peak position using the standard Debye-Scherrer's formula.

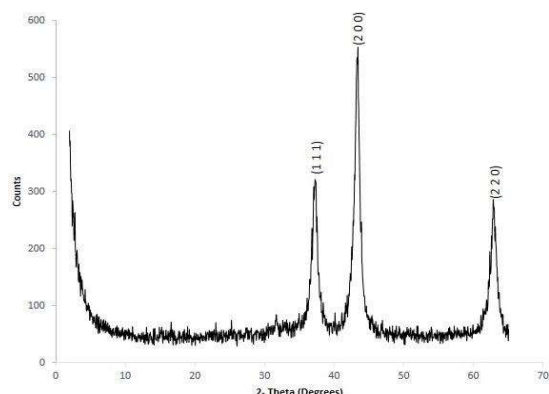


Figure 2: XRD Spectrum of NiO Nanoparticles

SEM and EDX Analysis

Figure 3 shows the SEM micrograph (2,500x) of the PVK/PANI blend (Figure 3(a)) and the PVK/PANI/10% NiO nanocomposite (Figure 3(b)). Figure 3(a) revealed identifiable phase spherical shape as PANI within the PVK/PANI blend. Figure 3 (b) shows that the NiO nanocrystals were agglomerated and averagely uniformly dispersed within the PVK/PANI.

The EDX spectrum shown in Figure 4 (a) confirms the presence of Oxygen, Carbon and Nitrogen for PVK/PANI blend and Figure 4 (b) confirms the presence Nickel, Oxygen, Carbon and Nitrogen for the polymer nanocomposite as the elements present in the films. It is noted that the substrate is a soda glass material which Ca, Si, and Na as dominant elements present. Also, the deposited films are in the nanometer thickness range, as confirmed in previous studies of this class of nanocomposite.

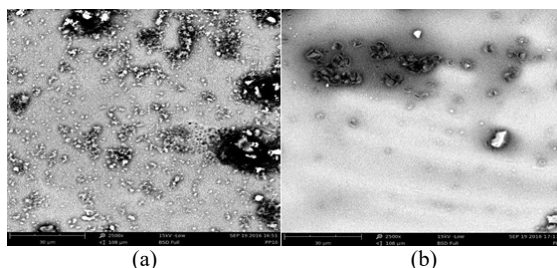


Figure 3 SEMmicrographs of (a) PVK-PANI Blend and (b) PVK/PANI/ 10%NiO nanocomposite

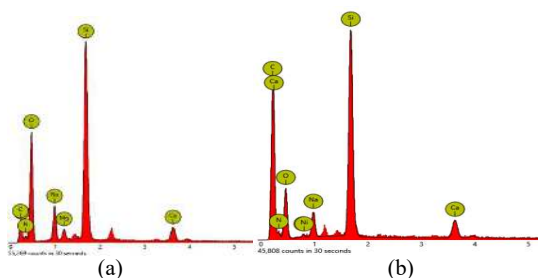


Figure 4: EDX spectrum of (a) PVK-PANI Blend and (b) PVK/PANI/ 10%NiO nanocomposite.

Optical Studies

The UV-visible spectroscopy of the synthesised NiO nanocrystals, the PVK/PANI blend and the 5, 10 and 15% NiO nanocomposites are as presented in Figure 5. The plots showed strong absorption in the UV region with absorption wavelength between 330 -375 nm for the synthesized thin films. It was observed that the absorption in the wavelength range of 420-

440 nm (blue light) [25] which is characteristics of PANI disappears in the PVK/PANI blend spectrum. The direct energy band gap of the thin films was estimated using the Tauc relation [26].

$$\alpha h\nu = A(h\nu - E_g)^n$$

where α is absorption coefficient, $h\nu$ is the photon energy, E_g is the band gap, $n=12$ for the direct transitions. The Plot of $(\alpha h\nu)^2$ versus $h\nu$ for the films was used to obtain optical band gap by extrapolating the straight line of the plot to $(\alpha h\nu)^2 = 0$.

Figure 6 shows the the energy band gap plots of NiO nanocrystals, PVK/PANI blend and the three PVK/PANI/NiO nanocomposites. It showed a band gap of 3.7 eV for the nanocrystals, 3.6 eV for the blend, 3.35, 3.34 and 3.30 eV for 5, 10 and 15% NiO concentration in the blend respectively. Meanwhile an energy band gap of 3.6 eV had previously been reported on NiO nanoparticles [27].

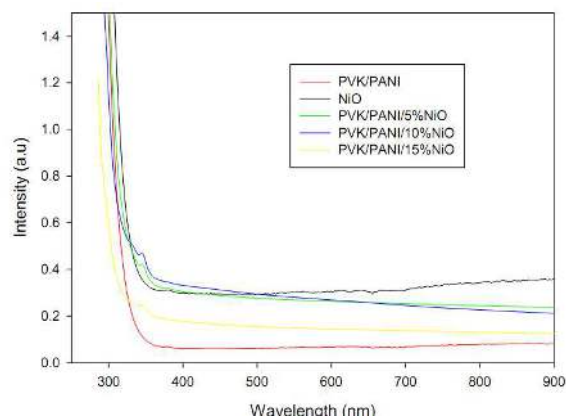


Figure 5 Absorbance spectra of NiO Nanoparticles and PVK-PANI Blend

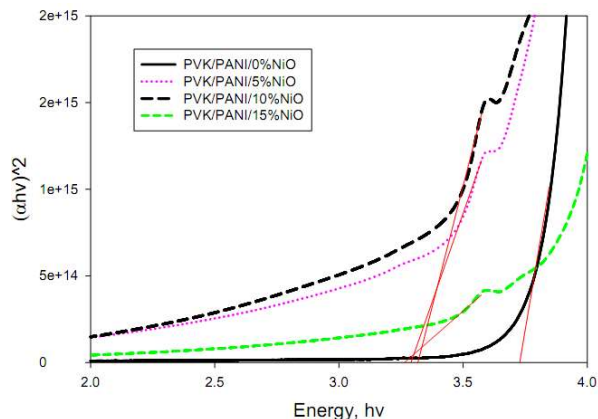


Figure 6 The Energy Band Gap plots for PVK/PANI blend and the 5, 10 and 15% NiO Nanocomposites.

Electrical Characterisation

Table 1 shows the summary of the obtained sheet resistance, resistivity and conductivity of the thin films. The electrical conductivity decreased upon addition of 5%NiO the nanocrystals which then began to rise when increased to 10% and eventually marginally rose to $3.66 \times 10^{-4} (\Omega \text{ cm})^{-1}$ from $3.32 \times 10^{-4} (\Omega \text{ cm})^{-1}$, a marginal increase of about 10%. This might be attributed to in ability of the charge carriers possessing sufficient energy to hop between favourable localized sites within the matrix of the blend [10].

Table 2: Sheet Resistance, Resistivity and Conductivity of PVK/PANI at different NiO Nanocrystal concentration.

Sample	Sheet Resistance	Resistivity (Ω cm)	Conductivity (Ω cm) ⁻¹
PVK-PANI	3.01 X 108	3.01 X 103	3.32 X 10⁻⁴
PVK-PANI 5%	3.21 X 108	3.21 X 103	3.11X 10⁻⁴
PVK-PANI 10%	3.08 X 108	3.08 X 103	3.24 X 10⁻⁴
PVK-PANI 15%	2.73 X 108	2.73 X 103	3.66 X 10⁻⁴

CONCLUSION

The PVK/PANI blend and PVK/PANI/NiO nanocomposite were synthesized via chemical oxidation approach. XRD analysis confirms the synthesis of NiO nanocrystals with size estimated to be 16 nm. The FTIR spectra obtained for all the synthesized samples confirmed presence of the associated functional groups and the presence of the nanocrystals in the nanocomposites. The optical characterization showed strong absorption in the ultraviolet region. The obtained direct energy band gap of PVK/PANI showed a decrease upon addition of 5%NiO nanocrystals and remained almost unaffected afterwards as (0% (3.60 eV); 5% (3.35 eV); 10% (3.34 eV); and 15% (3.30 eV)) NiO nanocrystals in the PVK/PANI blend can therefore be said not to have a significant effect on conductivity of the nanocomposite. The synthesised PVK/PANI blend could be a potential material for use in OLED but NiO nanocrystals of higher concentrations in the blend might result in much more significant and appreciable conductivity increase. This is expected to result in improved device lifetime where organic-organic and organic-inorganic materials are in direct contact.

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EFFECTS OF ALKALINE TREATMENT ON TENSILE, IMPACT AND MORPHOLOGICAL PROPERTIES OF OKRO BAST FIBRE/UNSATURATED POLYESTER RESIN COMPOSITES

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ABSTRACT

Composites of Okro bast fibres with unsaturated polyester resin were produced using the hand layup technique. The fibres were treated with NaOH solution of 5%, 10% and 15% concentrations, the fibres were then neutralized with 1% acetic acid and finally rinsed with distilled water. The composites were also prepared by adding different weight proportions of Okro bast fibres 5%, 10% and 15%. The composites were subjected to tests to evaluate their mechanical properties. Tensile strength, elongation and impact strength were found to increase with increase in filler content and NaOH concentration. The result obtained from scanning electron microscope indicates better adhesion for the treated OBF/UPR composites.

Keywords Okro fibre, unsaturated polyester resin, tensile strength, impact, and scanning electron microscope.

Introduction

Natural fibres (such as jute, hemp, sisal, palm, kenaf, ramie, luffa and flax) are utilized as fillers or reinforcing material for polymer-based matrices. Natural fibre are eco-friendly, light weight strong and low cost and can be used in a polymeric matrices to reinforce and achieve desired properties such as impact strength, stiffness, low density sound damping and texture together with eco-friendly characteristics in composites. This also decreases the amount of waste disposal problems and enhances reduction in environmental pollution (Kalia *et al.*, 2011).

Most bast fibres are characterized by fines and flexibility, which makes them quite strong and widely applicable in the manufacture of ropes and twines bagging materials and heavy-duty industrial fibres (Ajayi, *et al.*, 2000).

Okro (*Abelmoschus esculentus* (L.) Moench), also known as *Hibiscus esculentus* L., is a member of the mallow (Malvaceae) family, which includes hibiscus and cotton among other species, it can be found as a tall-growing, warm-season annual or perennial (in India and Africa) that is well suited to a wide range of soil types (Santulli *et al.*, 2014).

It represents the only vegetable crop in the Malvaceae family, whose products have significant use in the food sector. In several parts of the world it is known as Okro, Quingumbo, and Lady's finger, Gombo, Gumbo, Bamia, Kubewa, and Bhendi. The vegetable fibres are mainly composed of cellulose and non-cellulosic materials, such as hemicelluloses, lignin, pectin, waxes, and some water-soluble compounds. The lignin and pectin act as bonding agent (Muhanti *et al.*, 2005). The origin of Okro is disputable, but it seems to be native to the Abyssinian centre of origin of cultivated plants, an area that includes Ethiopia, Eritrea and the eastern part of the Anglo-Egyptian Sudan. It is currently grown throughout tropical Asia, Africa, the Caribbean and southern United States. (Santulli *et al.*, 2014). Okro can grow up to 2m tall and has leaves 10–20 cm long and broad, with lobes ranging from 5 to 7. It has white or yellow petals that constitute the flowers of diameters in the range of 4–8 cm, that are often characterized by a red or purple spot at the base of each petal. The seeds are contained in a capsule up to 18 cm long that shows 4 to 10 distinct ribs or ridge. The immature young seed pods are the edible part of this plant. Most okro cultivars produce green pods, but a few varieties produce yellow or dark red pods. These pods are harvested when immature and high in mucilage, generally within 2–6 weeks after flowering. In some countries the most interesting part of okro plant is represented by the seeds, which yield edible oil with a pleasant taste and odor, and high in

unsaturated fats such as oleic and linoleic acid. (Santulli *et al.*, 2014).

De Rosa *et al.*, 2009, in their study observed that the cross-sectional shape of okro fibre shows a polygonal shape that varies from irregular to a circular shape. Their diameter also varies in the range of about 40–180 µm. Each ultimate cell is roughly polygonal in shape with a central hole, or lumen like other natural plant fibres. The cell wall thickness and lumen diameter vary typically between 1 to 10 µm and 0.1 to 20 µm respectively. The considerable difference of the diameter values of the single fibre, lumen, and their rough shape strongly affects the mechanical and dimensional properties of okro fibres. The chemical composition Okro bast fibre, has been studied and in table 1.

Table 1; Composition of Okro bast fibre

Cellulose	60-70%
Hemicellulose	15-20%
Lignin	5-10%
Pectin matter	3.4%
Fatty and waxy matter	3.9%
Aqueous extract	2.7%

2.0 Methodology

2.1 Okro Fibre Extraction

The okro bark was in bundled ribbon form and immersed in water retting bath, little pressure was applied to the soaked bundle to ensure that the bark were fully submerged for a period of 10 days during which the cementing materials such as pectin, lignin, cellulose, and hemicellulose must have loosen and soften. On 10th day the retted ribbon was removed and washed with sufficient quantity of water until the pulp was completely detached from fibre, the fibres were shredded and combed to have a finer fibre. Then the fibres were allowed to dry at room temperature. After drying, the fibres were chopped into short length (5-10mm) which was used in this work for fabrication of the composites.

2.2 Fibre treatment

Sodium hydroxide solution by weight concentration of 5%, 10% and 15% were prepared using distilled water and sodium hydroxide. The fibre were soaked in the solution for a period of thirty minutes with continuous stirring. It was later removed from the solution and rinsed with water, then neutralized with 1% acetic acid and then finally rinsed with distilled water.

2.3 Preparation of the Composites Sample

Short okro fibre reinforced unsaturated composites were prepared by hand-lay-up method. The calculated amount of unsaturated polyester resin, accelerator (COBALT) and catalyst (MEKP) were weighed out and thoroughly mixed. The corresponding amount of okro fibres were weighed out and added to the UPR it was thoroughly mixed to ensure even distribution of fibres. The mixture was then poured in to a mould in a glass mould (200 x 120x80 mm) which foil paper has been laid for ease of removal of the fabricated composites. Similar procedure was used to prepare composites of different fibre loading of 5%, 10%, and 15%wt of fibre for both treated and untreated OBF/UPR. The fabricated composites were allowed to cure under laboratory conditions before subjecting them to morphological, physical and mechanical analysis.

2.4 Characterization of Composites

2.4.1 Tensile Testing

Tensile strength and elongation at break were carried out using Type Mosanto Tensometer machine at the department of MECH. ENG. ABU, Zaria. The test was performed according to ASTM D638. The test samples were clamped between the upper and lower jaw of the tensometer and the machine was started. The sample was stretched gradually with application of force until it reaches the breaking point. Reading of maximum load and elongation at break were taken accordingly. The test was repeated Three (3) times for each of the composites and the average values were recorded. The result is shown in figures 1 and 2 respectively.

2.4.2 Impact

The impact test was performed according to ASTM D256 standard using Cat Nr.412 Charpy Impact Testing Machine 15joules capacity. The composites samples were cut to a length not more than 10centimeter and a uniform width, the sample was placed on the machine and held tightly with the aid of knots, the ends are observed to be of equal length and a hammer of 15joules capacity was raised and then released to hit the sample. Work done on breaking the samples was recorded, test was repeated three times and an average was recorded.

2.4.3 Scanning Electron Microscopic Analysis

The composite samples were analyzed using Phenon SEM Machine Pro X model 10 KV the composites are not conductive to make it conductive ,samples surface

were coated with 5mm of gold using a sputter machine .the coated samples was placed on a sample holder and placed into the machine column then viewed through a navigating camera however ,adjustment was made before transferring into the electronic code .Viewing voltage was set using 10KV,magnification were increased and the sample morphology were stored in the electronic mode .the machine setting was changed from electronic mode to navigation camera before ejecting the samples from the machine.

3. Results and discussions

3.1 Tensile strength

Figure 1 shows that there is an increase in tensile strength at 15% alkali treatment and 15% filler loading with a value of 22.21Mpa, which is greater than all the samples .The maximum tensile strength for treated okro bast fibre /unsaturated polyester resin composites indicate that the alkali treatment has improved the adhesive characteristics of the fibre surface by removing the natural and artificial impurities there by producing rough surface topography. The treatments also leads to fibre fibrillation i.e. that is breaking down the fibre bundles into smaller fibres, this also increase the chance of effective surface area to be available for contact with the matrix.(sirgar *et al.*, 2013).A decrease was observed for 10% alkali treatment and the filler content of 5% to15% corresponding to17.86 to 8.74Mpa as show in figure 1respectively. There was similar observation for 5% alkali treatment at 5 to 15% filler content with a decrease corresponding to 19.82 to 8.25Mpa. The observed decrease could be attributed to improper fibre wetting due to increased tendency of fibre entanglement with increasing short fibre as well as the possibility of increasing fibre-rich and/or matrix-rich areas within the composite (Sumaila *et al.*, 2013)].

It was observed that values obtained for the untreated okro bast fibre / unsaturated polyester resin composites is lower than that the control sample and some treated okro bast fibre/ unsaturated polyester resin composites values obtain are 17.64,14.79 and 15.09Mpa.The observed decrease in strength of the untreated okro fibre UPR composites could be attributed to the presence of the cementing material which lead to poor fibre/ matrix adhesion, and could also be due to micro cracks formation at the interface under loading and non uniform stress transfer due to fibre agglomeration in the matrix (Sanjay 2009).

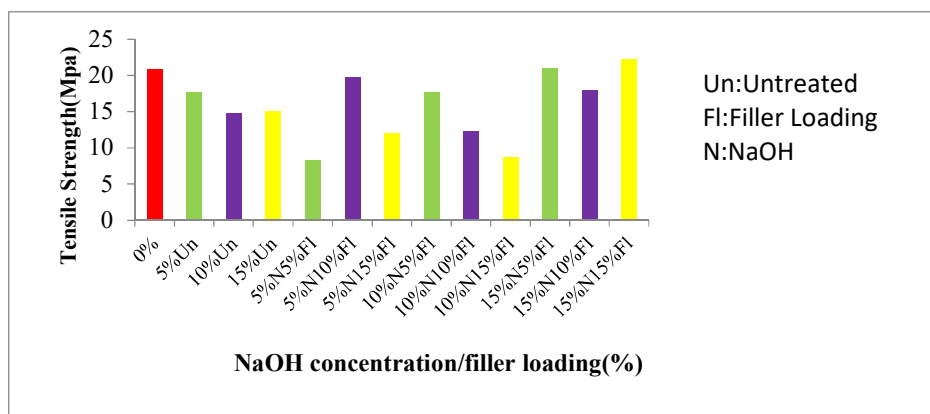


Figure1. Tensile strength versus filler loading of treated and untreated OBF/UPR composites

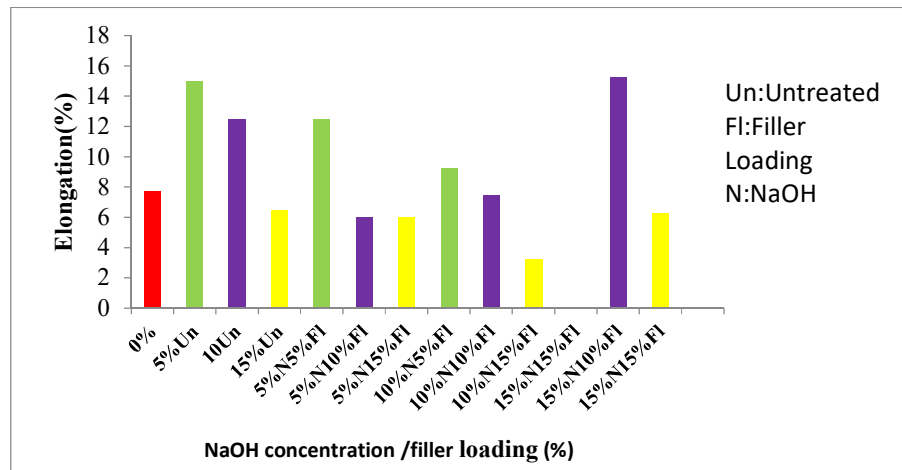


Figure 2: (%) Elongation versus filler loading of treated and untreated OBF/UPR Composites

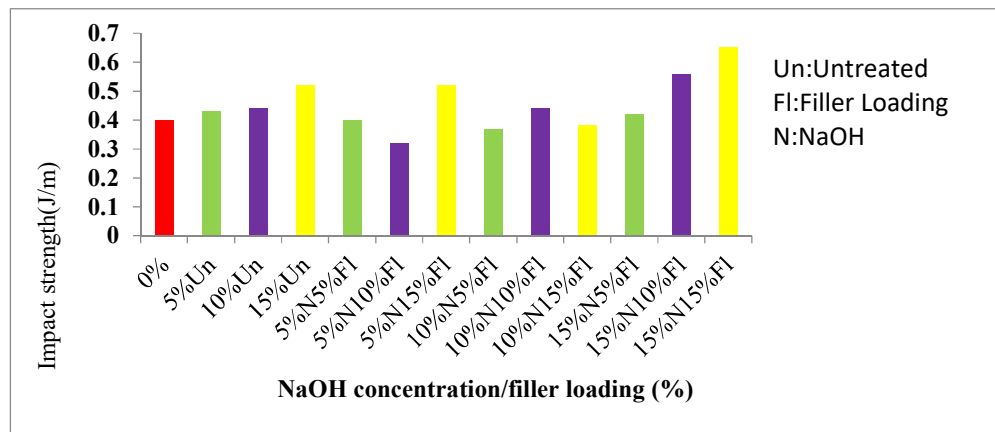


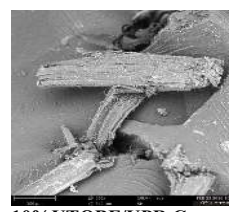
Figure 3: Impact strength versus filler loading of untreated and treated OBF/UPR Composites.



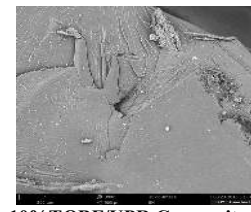
5% UTOBF/UPR Composites



5% TOBF/UPR Composites



10% UTOBF/UPR Composites



10% TOBF/UPR Composites

3.2 Percentage elongation

Figure 2 shows the effect of alkali treatment and filler loading on elongation of Okro bast fibre/UPR composites. The composite resulting from the 15% NaOH treated fibre exhibited the highest elongation at break and high ductility, corresponding to 17% which was higher than that of the control, untreated and some of the treated, Okro bast fibre composites. The values obtained for 5% NaOH were 12.5%, 6% to 6% and 9.25%, 7.5% to 3.35% for 10% alkali treatment. The untreated OBF/UPR composites have its highest elongation at 15% and later dropped to 6.5%. The increase of filler loading in the matrix (UPR) resulted in stiffening and hardening of the composites which reduced its ductility and led to lower elongation property, so also the reduction in elongation at break indicates the incapability of the filler to support the stress transfer from the matrix to the fibre. The enhanced elongation on treatment was due to the fact that more hemicelluloses are removed from the fibre as a result of treatment, which provided more surface roughness, hence giving rise to better interlocking with the matrix (Isa *et al.*, 2014)

3.3 Impact strength

Figure 3 above shows that there is significant increase in impact strength at 15% NaOH treatment with increase in filler loading and sodium hydroxide concentration. The observed values (0.42 (J/m), 0.56 (J/m) and 0.65 (J/m)). The increase in impact strength is due to reinforcement effect imparted by the fibres, which allowed stress distribution from continuous polymer matrix to dispersed fibre phase as established (Colom *et al.*, 2003). However, there was a decline in impact strength of 5% alkali treated OBF/UPR from 0.4 J/m to 0.32 J/m and further increase to 0.52 J/m and for 10% alkali treatment there was a slight improvement from 0.37 to 0.44 J/m and later decline with increase in filler loading content. The decline observed could be due to poor wetting of the fibre with the matrix, this will in turn lead to composites with weak interface (John *et al.*, 2008) for 10% alkali treatment. The untreated OBF/UPR show similar trend with the 15% alkali treated OBF/UPR with 0.43 J/m, 0.44 J/m and 0.52 J/m respectively. It has been reported that the impact strength of a composite is influenced by many factors including the matrix fracture, fibre/matrix de-bonding and fibre pull out (Obasi *et al.*, 2007). The 15% treated OBF/UPR

composites showed an improvement of the impact strength compared to the untreated OBF/UPR composites. The treatment of the OBF/UPR improves the compatibility and promotes the ability to dissipate energy during fracture of the composites

Scanning electron microscope

Morphology studies of okro bast fibre reinforced unsaturated polyester resin revealed that the use of alkali treated fibre has lead to better adhesion between the matrix and the fibre in Fig 4.b, and d above indicating good wetting and strong interface. The evidence for the same is provided from the matrix traces seen on the surface of the fibre. Very little fibre pull out suggests that the matrix has been efficient in holding on to the fibres. This indicates that the composites have higher degree of fibre orientation under the stress, which results in higher fibre efficiency factor and hence improved mechanical strength. The okro fibres protruding from the composite indicate the degree of fibre pull out and crack deflection. The fibre surfaces that protrude are not clean with some adhering matrix material on it further indicating that the fibres are well adhered to the matrix. For the untreated fibre loaded with 5% wt okro fibre composites shows fibre breakage, fibre pull out and voids or air entrapments which, is as a result of poor interfacial bonding between the fibre and matrix. (Tran Huu *et al.*, 2011).

Conclusions

Alkaline treated Okro bast fibre/unsaturated polyester resin composites were produce and analyzed. The result shows that useful materials could be produced from OBF. The tensile strength and impact strength have their highest value at 15%NaOH treatment while 5%and 10% NaOH have moderate values. The use of Okro bast fibre in composites material can be used to produce material that can find applications in areas where strength is not required. Applications like ceiling board, partition board/ walls, can be the areas where OBF/UPR composites can find useful applications, hence adding value to okro bast fibre.

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SMART MATERIAL FOR DSSC USING THE EXTRACTS OF COLA NITIDA (GBANJA) AND COLA ACUMINATA (ABATA)

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ABSTRACT

Dye sensitized solar cell (DSSC) have unique properties of organic and inorganic compound, it is technically and economically different alternative of photovoltaic devices. In DSSCs the two functions are separated i.e. light absorption and charge carrier transport. This paper reports the fabrication, saponification and characterization of cola nitida extract (Gbanja) and cola acuminata (Abata) dye sensitized solar cells and goes further to investigate its ability to change color depending on external lighting conditions showing the smart material ability of the DSSC. The Phytochemical compositions analysis reveals the presence of phytoconstituents such as flavonoids, volatile oil, tannins, saponins, thus suggesting presence of compounds that could be useful as dye for smart windows.

Key words: DSSC, Smart material, cola nitida, cola acuminata

Introduction

Solar power is the largest renewable energy resource, and the demand for higher solar power capacity is increasing every year. In urban areas, considerable surface areas of the sides and windows of buildings are not utilized for light absorption. These surface areas can be covered with solar cells that are completely transparent and colorless at night and function similar to photo chromic sunglasses, to provide for the best view, with the continuing progress of dye-sensitized solar cells (DSSC) and the appearance of different configurations and new components, [1] it has become very important to establish the properties of the prepared DSSC using a range of characterization methods, with a refined level of detail.

In urban areas, considerable surface areas of the sides and windows of buildings are not utilized for light absorption. These surface areas can be covered with solar cells that are completely transparent and colorless at night and function similar to photochromic sunglasses, to provide for the best view. The cells act as window shades during the day by tinting the glass and absorbing a section of the visible range of sunlight to generate electric power.

There are a few classes of organic compounds that exhibit this photochromic property—diarylethenes [2–5], azas [6], spiropyrans [7,8,9] and its derivatives with the spirooxazines are among the most studied organic compounds in this group, with high stability and broad visible light absorption and spirooxazines [10].

In this work, we report the fabrication and characterization of DSSCs, with the sensitizing unit being composed of a spiropyran moiety. This cell exhibits the ability to change color depending on ambient light conditions, and therefore it has the potential to be used as a solar cell to be installed on windows. The samples were also sent to the laboratory for morphology analysis using the scanning electron microscope SEM. This technique visualises the surface morphology of thin film i.e. it can intuitively distinguish the change between different films also the difference between the neat and composite film can be determined.

Method:

1. Sample collection and extraction

Different samples of the plants seed and pod were collected; the leaves were dried at 40°C in a thermostatically controlled oven until they attained a constant weight. The samples were then crushed to powder, using a manual grinding machine, so

as to enhance effective contact of solvent with sites on the plant materials and soaked in 500ml acidified methanol.

The extracting solvent and the mixture were placed in an orbital shaker (SLAUART SSL1 ORBITAL SHAKER at 25rpm) for 12 hours .The extract of each of the samples were decanted to remove the residual part of the samples.

2. Preparation and construction of cells

We used conductive FTO glass ordered from Hartford Glass Company USA with dimension of 2.5 X 7.6cm (1"X3") and 2mm in thickness. The photo anode was prepared using two slides of the conductive FTO glass. A digital multimeter was used to check the conductive side of the FTO glass and the value is 32 Ω. Adhesive –tape are applied to the face of the conductive glass plate in order to create an opening of dimension 1.5 x 1.5cm² at the centre of the glass The cells were assembled and tested using the method reported by [12].

3. Photochemical screening

Chemical tests were carried out on the aqueous extracts to identify the constituents using standard procedures as described by [12, 13,14]

Test for tannins: About 2 ml of the aqueous extract was stirred with 2 ml of distilled water and few drops of FeCl₃ solution were added. The formation of a green precipitate was an indication for the presence of tannins.

Test for saponins: 5 ml of aqueous extract was shaken vigorously with 5 ml of distilled water in a test tube and warmed. The formation of stable foam was taken as an indication for the presence of saponins.

Test for phlobatannins: About 2 ml of aqueous extract was added to 2 ml of 1% HCl and the mixture was boiled. Deposition of a red precipitate was taken as an evidence for the presence of phlobatannins.

Test for flavonoids: To 1 ml of aqueous extract was added 1 ml of 10% lead acetate solution. The formation of a yellow precipitate was taken as a positive test for flavonoids.

Tests for anthraquinones: *Borntrager's test:* 3 ml of aqueous extract was shaken with 3 ml of benzene, filtered and 5 ml of 10% ammonia solution was added to the filtrate. The mixture was shaken and the presence of a pink, red or violet colour in the ammonical (lower) phase indicates the presence of free anthraquinones.

Test for terpenoids: 2 ml of the organic extract was dissolved in 2 ml of chloroform and evaporated to dryness. 2 ml of concentrated sulphuric acid was then added and heated for about 2 min. A greyish colour indicates the presence of terpenoids.

Tests for steroids: A red colour produced in the lower chloroform layer when 2 ml of organic extract was dissolved in 2 ml of chloroform and 2 ml concentrated sulphuric acid added indicates the presence of steroids.

Test for alkaloids: 3 ml of aqueous extract was stirred with 3 ml of 1% HCl on a steam bath. Mayer's and Wagner's reagents were then added to the mixture. Turbidity of the resulting precipitate was taken as evidence for the presence of alkaloids.

Tests for carbohydrates: Molisch's test: 3 ml of the aqueous extract was added to 2 ml of Molisch's reagent and the resulting mixture shaken properly. 2 ml of concentrated H₂SO₄ was then poured carefully down the side of the test tube. A violet ring at the interphase indicates the presence of carbohydrate.

Tests for glycosides: Liebermann's test: 2 ml of the organic extract was dissolved in 2 ml of chloroform and 2 ml of acetic acid was added and the solution cooled well in ice. Sulphuric acid was then added carefully. A colour change from violet to blue to green indicates the presence of a steroidal nucleus (that is, a glycone portion of glycoside).

4. Confirmation of smart material

2ml of the aqueous extract were dropped in the FTO and their colours were taken into consideration and then place on a platform, these were then exposed to direct sunlight for about 15minutes. The colour changes were then noted to identify those with smart materials ability.



Fig (1a) and (b) Exposure of extract to sunlight before and after showing some changes in colour

Results and analysis:

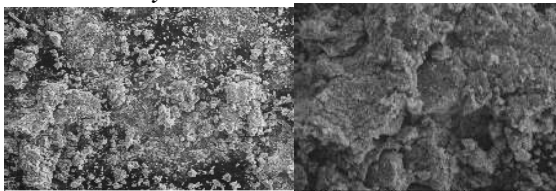


Fig.2 (a) and (b) SEM for cola nitida and cola acuminata

These results from the I-V curves were used to calculate the fill factor as well as the efficiency defined thus:

$$FF = \frac{I_{max} + V_{max}}{I_{sc} + V_{oc}} \dots \dots \dots 1$$

Where I_{max} and V_{max} denote the maximum output power current and voltage respectively, and I_{sc} and V_{oc} denote the short circuit current and open-circuit voltage respectively. The overall energy conversion efficiency (η) is defined as:

$$\eta = \frac{I_{sc} + V_{oc} + FF}{P_{in}} \dots \dots \dots 2$$

Where, P_{in} is the power of incident light

Table1 voltage and current of cola nitida

RESISTANCE Ω	VOLTAGE(V)	CURRENT(A)
100	0	14.91
200	0.32	13.67
300	0.48	12.43
400	0.5	10.67
500	0.5	6.18
600	0.5	6.09
700	0.5	4.32
800	0.5	3.92
900	0.51	2.34
1000	0.52	0

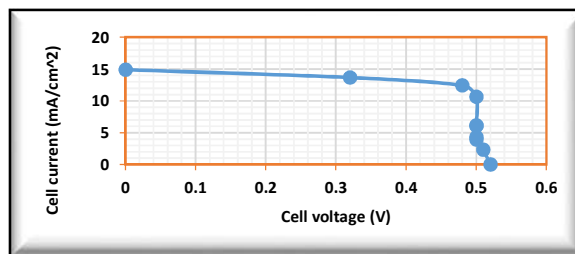


Fig.3 The graph of current against voltage for cola nitida

Fig. 2 the voltage and current of cola acuminata

RESISTANCE Ω	VOLTAGE(V)	CURRENT(A)
100	0	4.74
200	0.18	3.14
300	0.2	2.89
400	0.21	2.67
500	0.22	2.5
600	0.22	2.48
700	0.24	1.92
800	0.24	1.88
900	0.25	1.63
1000	0.28	0.00

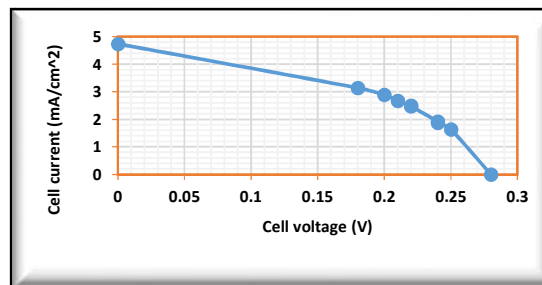


Fig.4 The graph of current against voltage for cola acuminata

Table4The value of wavelength and absorbance of cola nitida

WAVELENGTH(λ)	ABSORBANCE
350	2.032
400	1.52
500	1.101
600	0.637
700	0.545
800	0.108
900	0.151
1000	0.289

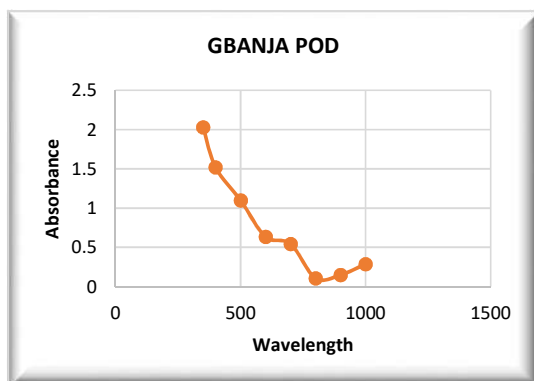


Fig.5 The graph of absorbance against wavelength of cola nitida

Table5 The value of wavelength and absorbance of cola acuminata

WAVELENGTH(λ)	ABSORBANCE
350	1.944
400	1.286
500	1.048
600	0.593
700	0.466
800	0.068
900	0.115
1000	0.245

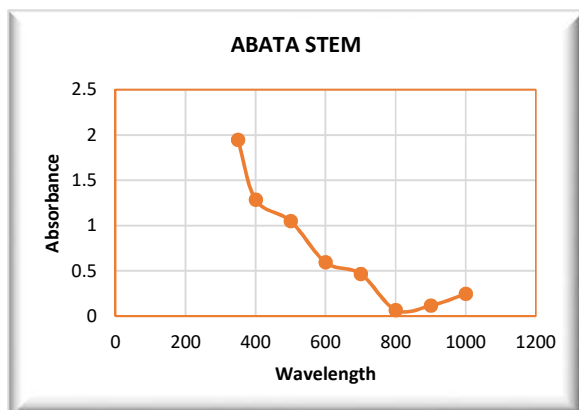


Fig.6 The graph of absorbance against wavelength of cola acuminata

Table. 6The phytochemical analysis of cola nitida and cola acuminata

Test	Gbanja pod	Abata seed	Gbanja seed	Gbanja leaf	Abata bark
Tannins	Nil	+++	++	+	+
Cardiac glycoside	Nil	+	Nil		
Flavonoid	Nil	+++	Nil	+	+
Phenol	+++	+++	+	++	+
Carbonhydrate	Nil	++	Nil	Nil	Nil
Volatile oil	+++	++	Nil	+	+

Table 7 Colour changes of the extract before and after exposure to sunlight

Extract	Pod	Before exposure	After exposure
Gbanja white		Navajo white	Nil
Abata seed		Saddle brown	Light golden yellow
Gbanja leaf		Olive	Nil
Abata leaf		Orange	Nil
gbanja pod		Dark olive green	Olive drab
Abata pod		Golden rod	Honey dew
Abata stem		Lemon chiffon	Nil

The dye of the leaf, pod, stem, and leaf of the cola nitida and cola acuminata were compared to see where dye has the highest frequency which enables the dye to absorb well. The result shows that:

Gbanja pod at a wavelength of 330nm, the absorbance level was 2.023, at 400nm it drops 1.52 and continues to drop till it get to 0.108 at 800nm, and at 1000nm, it increased to 0.289.

Gbanja seed at a wavelength of 330nm, the absorbance level was 1.963, at 400nm, it increased to 2.01, at 600nm it drops back to 0.444 and later -0.007 at 800nm and then increased to 0.178 at 1000nm

Gbanja stem at a wavelength of 330nm, it's absorbance level was 1.429, at 500nm, it decreased to 0.657 and then increased to 1.869 at 700nm before it begins to drop till it gets to -0.246 at 900nm and later increased -0.126 at 1000nm and,

Abata pod at a wavelength of 330nm, absorbance was 2.032, at 400nm it decreased to 1.52, and also at 800nm to 0.108 and rise to 0.289 at 1000nm.

Abata leaf at a wavelength of 330nm, absorbance was 1.429, at 500nm decreased to 0.657 and increased to 1.869 at 700nm and reduces to -0.286 at 800nm and later rise to -0.128 at 100nm.

Abata seed at a wavelength of 330nm, absorbance was 1.963, at 400nm increased to 2.01, at 800nm reduces to -0.007 and increased to 0.178 at 1000nm.

Table8 summary of the current, voltage, fill factor and efficiency of cola nitida and cola acuminata

S/N	DYE	$I_{sc}(mA/cm^2)$	$V_{oc}(V)$	$I_m(mA/cm^2)$	$V_m(V)$	FF	η %
1	GBANJA POD	19.8	0.08	17.1	0.05	0.5395	0.00035
2	ABATA SEED	4.24	0.32	3.47	0.3	0.7673	0.00041
3	GBANJA LEAF	3.26	0.67	2.6	0.51	0.6071	0.00052
4	GBANJA POD	14.9	0.52	12.4	0.48	0.7701	0.00232
5	ABATA POD	3.84	0.45	2.45	0.39	0.5529	0.00038
6	ABATA STEM	4.74	0.28	3.14	0.18	0.4259	0.00022

Conclusion

Desired dye-sensitized solar cell system based on TiO_2 (cola nitida & cola acuminata) using Iodine solution and Magnesium chloride as electrolyte was fabricated characterized, the phytochemical analysis and its colour changes due exposure to sunlight were noticed. Gbanja Pod has the highest efficiency of 0.00232% because the natural dyes has a wide band-gap

semiconductor and sensitizers in dye-sensitized solar cells, the absorbance of each of the extract falls within the spectrum of white light which makes the change in colour a possibility.

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PHYSICAL AND MECHANICAL PROPERTIES OF MAIZE STALK PARTICLES FILLED-RECYCLED LOW DENSITY POLYETHYLENE COMPOSITES

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ABSTRACT

The properties of composites of recycled sachet water bags (LDPE) and maize stalk were studied. Recycled LDPE/maize stalk composites with different filler loadings (10, 20, 30, 40 and 50 weight percent) with and without the alkali-treatment were prepared using a compression moulding machine. An initial investigation revealed that the mechanical properties of the virgin LDPE/waste sachet water bags were optimum at 40/60 ratios. The 40/60% LDPE blend was taken as optimum blend ratio for producing the composites and it is termed "LDPE Blend". As percentage filler loading increase, tensile strength decreases for LDPE blend/maize stalk composites. As percentage filler loading increase, elongation at break decreases for LDPE blend/maize stalk composites. The treated LDPE blend/maize stalk composites had higher value at 10.53MPa tensile strength and 18% elongation at break. However, as filler loading increase, tensile modulus increases for the maize stalk composites. The 50% treated maize stalk composites had higher tensile modulus value at 235MPa. Hardness was determined using Shore-A with the highest hardness value at 10% filler loading treated LDPE blend/maize stalk composites. These composites could be considered as a potential source of utilizing agricultural waste materials and better way of disposing sachet water bags waste without burning them. The maize stalk composites can be used as a suitable substitute for polyethylene where low strength is required e.g. packaging, bags and liners.

Keywords: Low density polyethylene (LDPE), composites, mechanical properties, recycling.

1. INTRODUCTION

Composite materials are those that are formed by the combination of two or more materials to achieve properties that are superior to those of their constituents (Wang *et al.*, 2003). Polymer composites consist of a polymer resin as the matrix, with fibres as the reinforcement medium (Callister, 2007). Considerable interest has been generated in the manufacture of thermoplastic composites due to their unique properties, including their good mechanical properties, their thermal stability, and a reduced product cost (Luyt, 2006; Kwan, *et al.*, 2002). Due to the combination of more than one material, the properties of composites are influenced by many factors such as filler characteristics, filler content, and interfacial adhesion (Liang, 2006; Osman *et al.*, 2004). This can cause the behaviour of filled polymers to be more complex than their unfilled counterpart (Suwanprateeb, 2000).

This work is aimed at effective utilization of maize stalk wastes as filler in the modification of recycled virgin LDPE/sachet water bags waste to improve their tensile strength, moisture absorption characteristics, surface morphology using SEM and provide an alternative and better way of utilizing the maize stalk and sachet water bags waste. Polyethylene is a hydrophobic polymer, while maize stalk is hydrophilic filler (Nowaczyk *et al.*, 2004). The chemical modification acts as a "bridge" between the inorganic filler and the organic polymer matrix. The "bridge" must adhere or bond to the filler and in turn must strongly interact with the polymer (Barone and Semidh, 2005).

2. EXPERIMENTAL

2.1 Materials

The maize stalk and cob were obtained from a harvested agricultural farm in Samaru, Zaria-Kaduna State, Nigeria. The low density polyethylene was obtained from Steve-Moore Laboratory Shop while the waste sachet water bags were collected from Life-span pure water company, Zaria.

2.2 Sample Preparation

The maize stalks were dried in the sun and oven at a temperature of 40°C and ground to a fine powder using electrical milling machine. The maize stalk powder was then sieved to a particle size of 600µm. The powder collected was kept in an air tight container for further use.

2.3 Treatment of the Maize Stalk Powder

Treatment with sodium hydroxide was carried out by soaking and stirring the maize stalk filler in 1% wt/v sodium hydroxide aqueous solution for about 1 hour at room temperature. 10 % wt/v of acetic acid was used to neutralized the base. Then the maize stalk filler was filtered out and washed several times with distilled water until all the sodium hydroxide was eliminated as indicated by a neutral pH of 7 before being dried up in an oven at 60°C for 48 hours.

2.4 Compounding the Composites

The preparation of the composites samples was divided into two phases. The first phase involved the determination of optimum blend between the virgin LDPE and sachet water bags waste (waste) using the compression moulding machine. The blend composition with the best mechanical properties (tensile strength, tensile modulus, elongation at break) would be selected as the optimum recycled PE/virgin ratio. The formulation is presented in Table 1. The second phase involved the use of the optimum recycled PE/virgin ratio as the matrix and the maize stalk as the filler to produce the composites. Melt mixing was carried out on a two roll mill in accordance with ASTM D3184-80 as shown in Table 2. LDPE mixing was done at 150°C for 20 minutes.

2.5 Compression Moulding

The composites were cut into dimensions slightly smaller than those of cavities. A sample of the composite was moulded in the compression moulding machine. Hot press procedures involved preheating at 150°C for 5 minutes, followed by compression for 5 minutes at the same temperature and subsequent cooling under pressure for 4 minutes.

2.6 Tensile Properties

Tensile properties were determined according to ASTM D638 using Computerize Mechanical Universal Testing Machine (Model: Series 3369; Capacity: 50KN). The test specimens were cut into a dumb-bell shape of dimension of 35mm by 5mm by 3mm (gauge length x width x thickness).

2.7 Hardness

The hardness of the different composite specimens was determined using a MUVEX Durometer hardness tester (Shore A) according to ASTM D2240 (Model number 5019 and Serial

number 01554). The composite specimens were cut into a rectangular shape i.e. 50mm x 20mm x 3mm dimension.

Table 1: Percentage composition of virgin/waste LDPE blend

VIRGIN LDPE (wt %)	WASTE (wt %)
100	0
90	10
80	20
70	30
60	40
50	50
40	60
30	70
20	80
10	90
0	100

Table 2: Percentage compositions of LDPE blend with maize stalk filler

S/N	LDPE Blend (wt %)	Maize Stalk Filler (wt %)	
		Untreated	Treated
1	100	0	0
2	90	10	10
3	80	20	20
4	70	30	30
5	60	40	40
6	50	50	50

2.8 Scanning Electron Microscopy

Studies on the morphology of the tensile fracture surface of the composites were carried out using Phenon Pro-X scanning electron microscope (SEM).

2.9 Water Absorption Test

Water absorption test was carried out in accordance with the ASTM D570 method. It involved the total immersion of three samples in distilled water at room temperature. The water absorption was determined by weighing the sample at regular intervals. It was done for a period of 30 days.

Percentage water absorption = $\frac{Y-X}{X} \times 100\%$. Where Y is the weight of test sample after swelling, X is the dry weight of test sample. The average reading of the three samples was taken.

3.0 RESULTS AND discussion

3.1 Determination of optimum blend ratio

3.1.1 Tensile properties of the virgin/waste LDPE blend

Figure 1 shows tensile modulus for the virgin/waste LDPE blend. There is no clear trend but some blend ratios i.e. 40, 60, 80 and 90 wt% show higher values i.e. 61, 44.3, 41.7 and 45.8MPa respectively. The variations here could be attributed to experimental inconsistency because modulus is an indication of rigidity that is not expected to change much in this series of blends.

Figure 2 shows tensile strength for the virgin/waste LDPE blend. It can be observed also here that 60 wt% waste content gives the highest tensile strength (19.86MPa) than the other blend composition. Based on this observation, it could be inferred that this is the optimum blend composition. Beyond this value a significant decrease in strength can be seen. This is due to improved dispersion in the polymer blends and good interaction between the blend compositions

For elongation at break, 60wt%waste content gave the highest elongation at break (692%) than the other blend compositions whereas 70wt% waste content gave the lowest elongation at break (119%) this can be due to poor mixing and interaction between the polymer blend due to the blending technique. Two roll mill has some disadvantages as compared to other mixing techniques such as internal mixing, single screw or twin screw extruder. The mixing is not as efficient, moreover operator skill play a significant role.

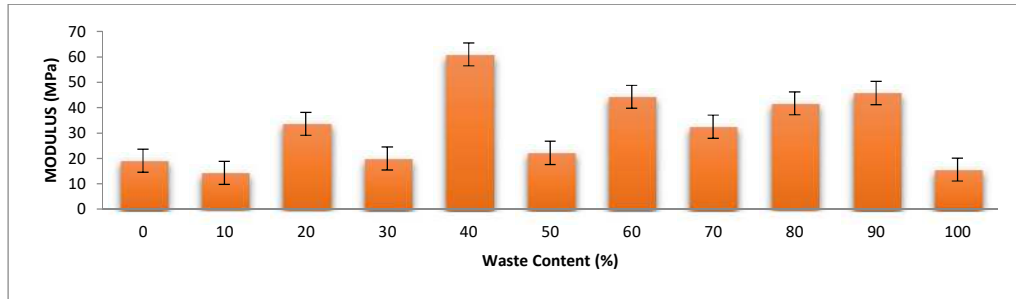


Figure 1: Modulus of virgin/waste LDPE blends of different compositions

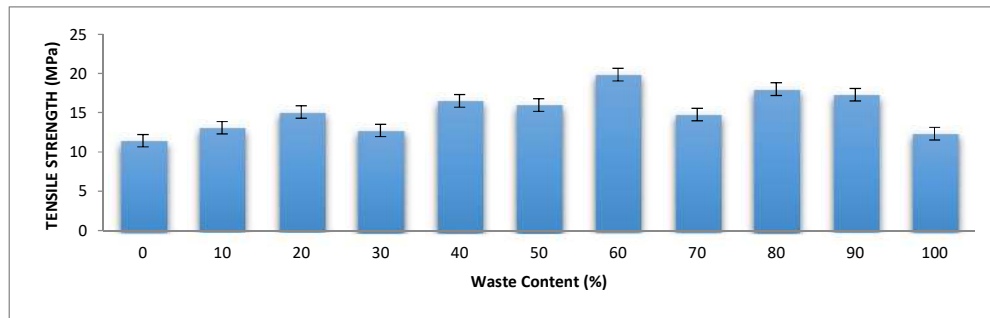


Figure 2: Tensile strength of virgin/waste LDPE blends of different compositions

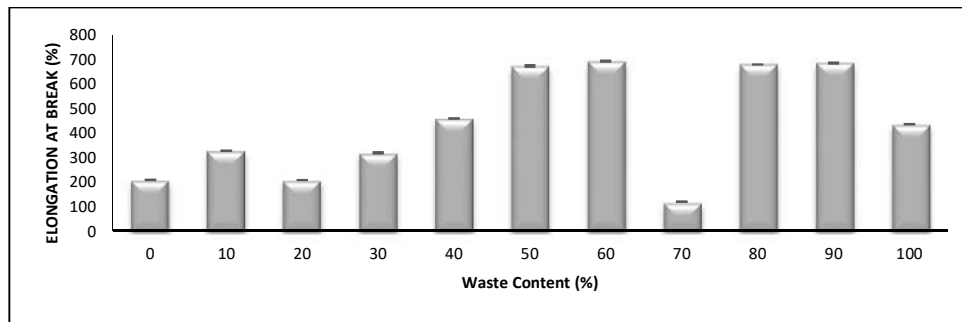


Figure 3: Elongation at break of virgin/waste LDPE blends of different compositions

3.1.2 Hardness of virgin/waste LDPE blend

The hardness test was done using Muver Hardness Tester (Shore A) according to ASTM D2240 and the result is presented Figure 4.



Figure 4: Hardness of Virgin/Waste LDPE blends different compositions

It can be seen from Figure 4 that there is no significant difference in the hardness of the blends, which ranges from 87 – 93 Shore A. This is expected since the waste LDPE is not much degraded. It shows that the difference between the virgin and waste is not much.

From the results obtained, 60wt% waste content (that is, 40/60 wt % virgin/waste LDPE blend) showed better

tensile properties than other blend composition in terms of tensile strength of 19.86MPa, tensile modulus of 44.3MPa and elongation at break of 692%. This can be attributed to better dispersion and greater interaction in the polymer blends. The 60% waste content was taken as the optimum blend ratio. This is an indication that up to 60% of the waste could be used without adversely affecting these properties.

3.2 Tensile properties of the composites

3.2.1 Tensile modulus

Figure 5 shows the effect of filler loading on the tensile modulus of maize stalk composites for the treated and untreated fillers.

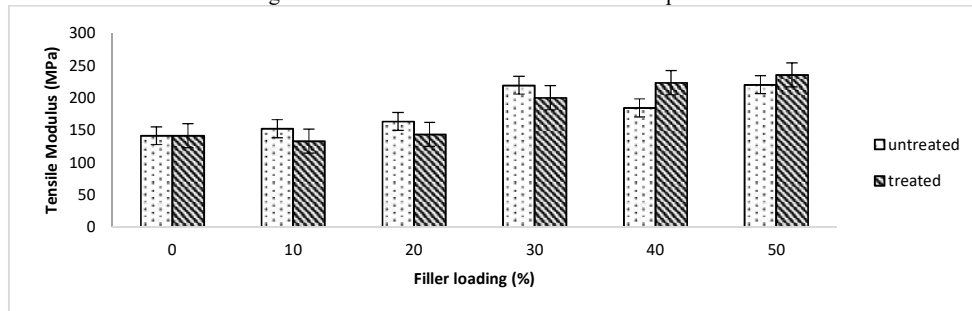


Figure 5: Effect of filler loading on tensile modulus of maize stalk composites

The tensile modulus for the untreated maize stalk composites increased with increasing filler loading. It was verified that stiffness increased from 141MPa to 220MPa. This is a common phenomenon when rigid fillers are incorporated into softer polymer matrices. Similarly, the tensile modulus of the treated maize stalk composites increased with increasing filler loading. The increase in tensile modulus in the treated and untreated maize stalk composites as filler loading increases also improves the stiffness and the tensile modulus corresponds to the intrinsic

properties of the filler where the filler may exhibit its high stiffness (Supri *et al.*, 2011).

The highest tensile modulus value obtains for both treated and untreated maize stalk composites was obtained at 50% filler loading as 235MPa and 220MPa respectively. From the results obtained, it was observed that the treated maize stalk composites showed higher modulus than the untreated fillers, this effect on tensile modulus is attributed to the improvement of the filler surface adhesive characteristics due to the removal of natural and artificial impurities.

3.2.2 Tensile strength

Figure 6 shows the effect of filler loading on the tensile strength of maize stalk composites for treated and untreated fillers.

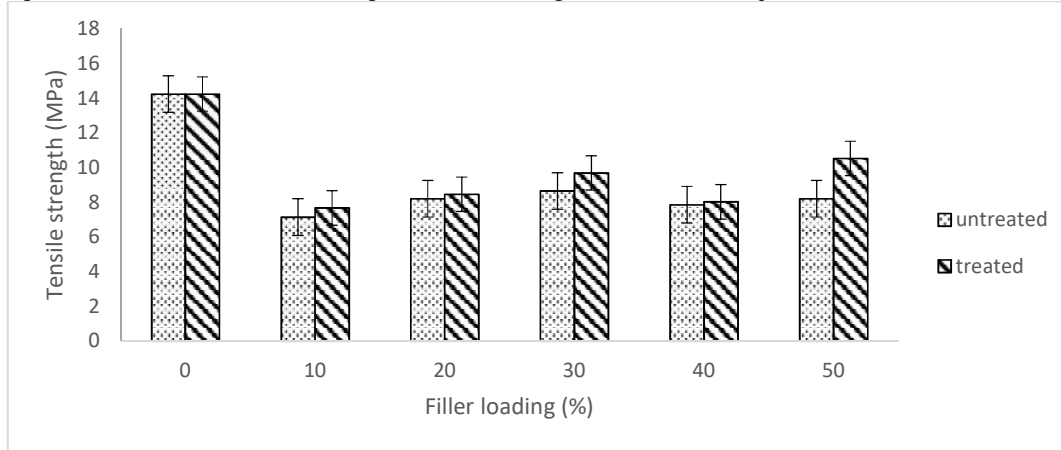


Figure 6: Effect of filler loading on tensile strength of with maize stalk composites

The tensile strength of the composites is lower than the matrix although it increases with increase in filler loading. The untreated maize stalk composites increased with increase in filler loading until it dropped at 40% and later rise at 50% filler loading, the decreased in tensile strength at 40% filler loading can be due to poor interfacial bonding between the filler and the matrix. This result is similar to reports by Jacquemin *et al.*, (2009). Similarly, the tensile strength increased with increase in filler loading for the treated maize stalk composites except for 40% filler loading. The alkali treatment helped to improved tensile strength of treated maize stalk compared to the untreated maize stalk composites. The results showed that surface modifications could remove surface impurities, increased surface roughness, better dispersion and greater interaction between the filler and the matrix which subsequently increased the tensile strength. It can be seen that treated maize stalk composites showed higher tensile strength than the untreated fillers. It was found that the alkali treatment improved the

compatibility between LDPE blend filled maize stalk composites and similar result was reported by Ray *et al.*, 2001.

3.2.3 Elongation at break

Figure 7 shows the effect of filler loading on the elongation at break of maize stalk composites for the treated and untreated fillers. Elongation at break for the untreated maize stalk composites decreased with increase in filler loading. The increase of the filler loading in the LDPE blend resulted in the stiffening and hardening of the composites which reduced its ductility, and led to lower elongation at break with increasing filler loading indicates the incapability of the filler to support the stress transfer from filler to polymer matrix. Such a reduction in elongation at break of a polymer composites with increase in filler loading, irrespective of filler particle size has been reported by Shuhadah and Supri, 2009.

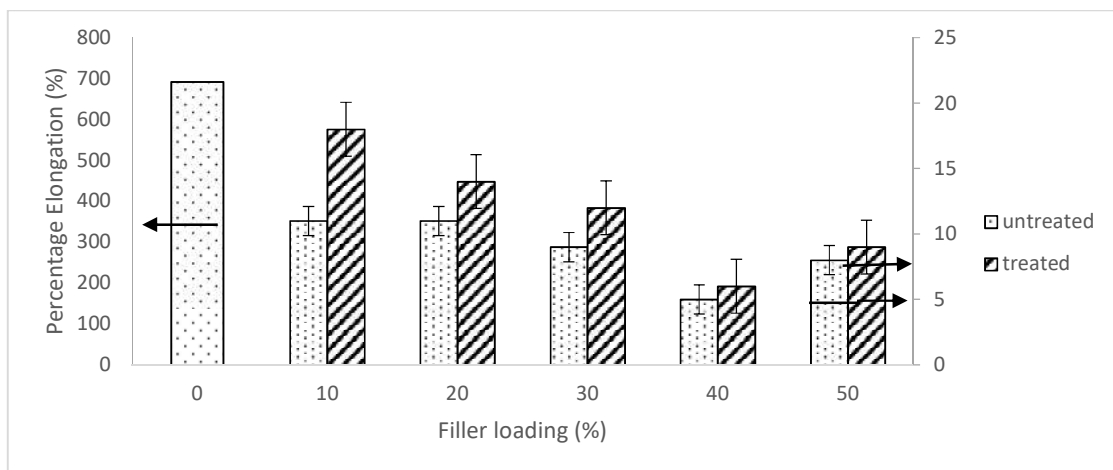


Figure 7: Effect of filler loading on percentage elongation of with maize stalk composites

It can be seen from Figure 7 that the elongation at break of the control is higher than the corresponding values for the treated or untreated maize stalk composites at any percentage of filler loading, the control LDPE blend exhibited high ductility before the break. The ductility of the maize stalk composites was greatly decreased. This demonstrated that the fillers had hardened the composites and reduced their ductility. The elongation at break of the treated maize stalk

composites is higher than for untreated maize stalk composites.

3.3 HARDNESS

Figure 8 shows the effect of filler loading on the hardness of maize stalk composites for the treated and untreated fillers. All the composites show higher values than the matrix while hardness generally increases with increasing filler content.

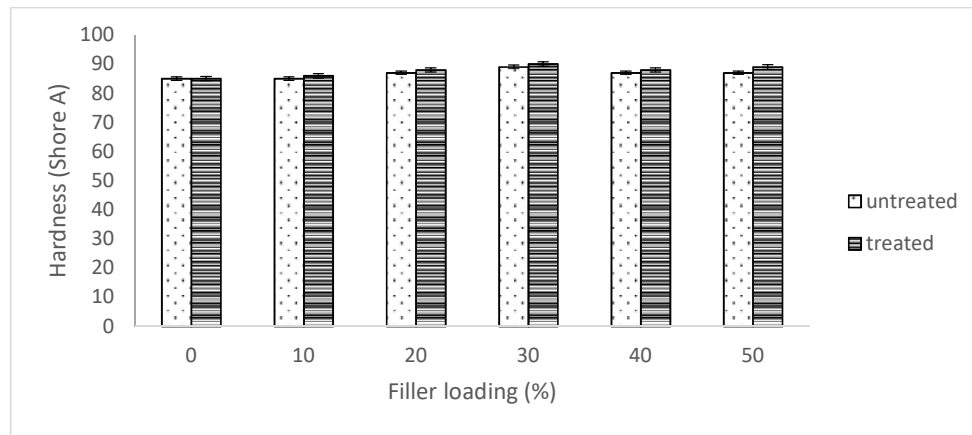


Figure 8: Hardness against filler loading of untreated and treated maize stalk composites

As depicted in figure 8, it can be seen that there is no much significant difference between the treated and untreated maize stalk composites.

3.4 Water absorption test

Figures 5 and 6 show the percentage of water absorption versus time for the untreated and treated maize stalk composites respectively. Composites with higher maize stalk fillers loading show more water absorption. This is due to the higher contents of filler loading in the composites that can absorb more water. As the filler loading increase, the formation of agglomerations increases due to the difficulties

of achieving a homogeneous dispersion of filler at high filler loading. The agglomeration of the filler in composites increases the water absorption of the composites. Scanning Electron Microscopy (SEM) showed that the surface modifications improved fibre-matrix adhesion. The superior strength of alkali treated maize stalk and cob fillers may be attributed to the fact that alkali treatment improves the adhesive characteristics of maize stalk and cob surface by removing natural and artificial impurities thereby producing a rough surface topography (Bisanda and Ansell 1991). The rate of water absorption for the thirty days can be represented as 50% > 40% > 30% > 20% > 10% filler loading.

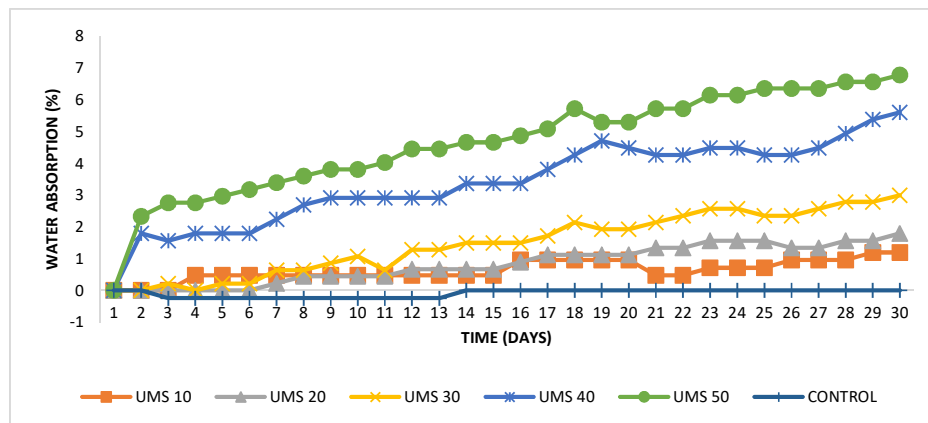


Figure 9: Water Absorption versus time of untreated maize stalk composites

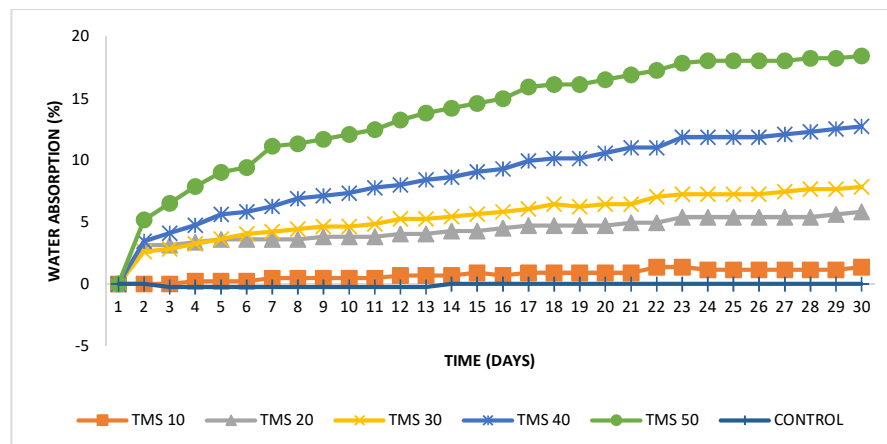


Figure 10: Water Absorption versus time of treated maize stalk composites

3.5 Morphological study

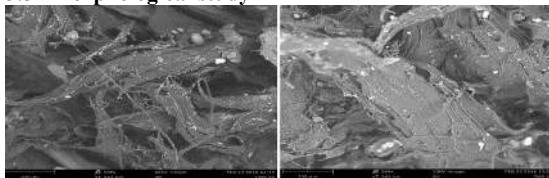


Plate 1: SEM micrograph of the 50wt% untreated maize stalk composites (500x)

Plate 2: SEM micrograph of the 50wt% treated maize stalk composites (500x)

Plate 1 shows the tensile fracture micrograph of the 50wt% untreated maize stalk (UMS) composites and Plate 2 shows the micrograph of the 50wt% treated maize stalk (TMS) composites.

It can be seen from Plate 1 that the micrograph of the untreated maize cob fracture surface has fibrillation indicating ductile failure. Plate 2 shows the fracture surface is ductile failure with cold drawing and has rough surface with multiple failure mode (matrix debonding and filler pull out). However indication of ductile failure is more in Plate 2, signifying better fibre-matrix bonding. It also shows a rougher surface than the untreated sample. The micrograph shows that the treated composites are more compatible than the untreated composites. The modification improves the compatibility by more finely dispersing the filler in the polymer matrix. This finding suggests that the adhesion between the matrix and the filler is very good. Accordingly, the interfacial strength is improved (Kuan *et al.*, 2006).

4. CONCLUSION

This study shows the successful fabrication and characterization of maize stalk filled recycled low density polyethylene composites creating a better means of disposing maize stalk and pure water bags wastes posing challenges to our environment. From the results obtained, 60% waste content showed better mechanical properties than the other blend composition in terms of tensile strength of 19.86MPa, tensile modulus of 44.3MPa and elongation at break of 692%. This can be attributed to better dispersion and greater interaction in the polymer blends. Henceforth, 40/60% virgin/waste LDPE was taken as optimum blend ratio for producing the composites.

The incorporation of maize stalk into the LDPE blend enhances the stiffness of the composites system. Hardness shows gradual improvement. In the maize stalk composites, it was found that the treated samples have better tensile properties than the untreated maize stalk composites that is, tensile modulus (235MPa), tensile strength (10.53MPa) and elongation at break (18%). Water absorption results suggested that the highest water absorption rate was observed at 50% filler loading treated maize stalk composites. The maize stalk composites can be used as a suitable substitute for polyethylene where low strength is required e.g. packaging, bags and liners.

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ASSESSMENT OF PHYSICAL PROPERTIES OF CHROME- TANNED GOAT SKINS IN RELATION TO THEIR SIZES

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ABSTRACT

The leather industry depends largely on the availability of good quality raw skins for the production of leather and their resultant articles through value chain addition with respect to grading and selection. This paper x-rays the various sizes of goat skins (shoe upper leather) with their physical properties after tanning.

Key Words: Raw skins, value addition, industry, grading, selection

Introduction

Leather processing tailors the unique fibrous architecture of animal skins into materials that possess those qualities for which they are prized such as: texture, size, thickness and visual appearance, as well as physical and chemical properties, which are often specified only as corroboration of the buyer; visual and tactile judgment. These form the basis for good quality control/standard on which leather are sold [1 and 2]. These quality standards based on physical tests and chemical analyses have been formulated by various authorities. There is no universal agreement on acceptable standards; every country has its national standard institute, working together with the International organization for standardization (ISO) [3]. With regards to the type of leather made from skins, a thorough knowledge concerning their physical and chemical characteristics will be required to judge their performance [1]. Though in this paper, only physical properties of leathers were assessed in relation to the skins sizes.

Physical Properties of Leather

Physical properties of leathers are those qualities/characteristics required of well-tanned leather, that enable it to resist various physical forces that it might encounter during usage; some general properties for leather are given by international Union of Leather Technologists and Chemists Society (IULTCS) which includes, uniform colour, light and rub fastness, thickness/firmness, handle/feel, water absorption and vapour permeability, heat insulation and heat resistance, according to their uses and values [2; 1; 4]. These properties depend on the physical structure, chemical composition and mechanical operation during the manufacture of the leather [5]. In considering the best technique for measuring the physical properties which form the basis of leather quality, there is need for knowledge of fundamental structure, since the properties of any given leather is dependent partly on the qualities of the raw skin and partly on the process of manufacturing. Therefore recognizing the nature and significance of the properties of raw stocks is great importance in the control of tanning procedure.

Selection of Raw Skins

There are clear advantages in being able to understand how the characteristic of an animal raw skin relate to the physical properties of leather produced from it, such knowledge assist in the selection of those breeds which will yield the best leather for a given application [11 and 6]. Each species of animal has a distinctive skin structure, the skin vary in total thickness, dimensions of constituents, fibres bundles, weaves pattern, and proportion of the total thickness depending on the breed, age, sex, and locality where the animal is reared [2 and 7]. The basis of good quality control is the sorting and selection of skins at this point before processing [2], since the quality of skins are usually judge by the methods of grading

and selection, which is usually influence by factors such as age, sex, breeds, origin of the animal, weight and thickness [10].

Classification of Goat Skin According to Size

Goat skins are classified according to their length as measured per square foot or in inches from the root of the tail to the neck (back of the neck). Goat skins are classified into: kid-kid, kid, light, medium and heavy. Goat skin ranges between 1 to 2mm in thickness and 6 to 8ft square. Each skin is graded individually into its size category as sampling, packing and labeling [8;9;10]. They are packed in form of bundles or bales, each bundle or bale of goat skins is clearly labeled with the following information:

- i. State of skin- fresh, air dried, salted or dry salted.
- ii. Type and grade of the skin.
- iii. Size of the skin such as kid, light, medium and heavy

Experimental Procedure

Collection of Raw Materials

Four salted goat skins of various sizes (kid, small, medium and large) were obtained from Samaru market - Zaria, Kaduna State. The sizes of the skins were taken using square foot measurement (Table 1) and were processed into shoe upper leather using conventional recipe for Chrome Retanned. The chemicals used were all obtained from the Institute tannery (NILEST).

Physical tests on samples

Samples were taken from the official sampling area (IUP2) and kept in a standard atmosphere (temperature $20 \pm 2^\circ\text{C}$, humidity $65 \pm 2\%$ RH) for 48 hours prior to testing. The following physical tests were carried out on the leather samples [12]

- i. Measurement of Thickness: It was determined in accordance with official procedure (IUP/4) – [12].
- ii. Determination of Tensile Strength and Elongation: Official procedure (IUP/6) – [12] was used and four samples were tested perpendicular and parallel to the back bone.
- iii. Determination of Grain Crack/Burst using Lastometer: These parameters were assessed via ball burst test in accordance with (IUP/9) – [12].
- iv. Measurement of water vapour Absorption: In accordance with (IUP/30) – [12].

Results and Discussion

The results for the physical properties of the goatskin leathers assessed in relation to their sizes are shown in Tables 1 to 6. In Table 1. The presentation of the sizes with respect to age may not be applicable to the large size of ages 4-5. At this point size is not a function of age.

Table 2 shows the thickness of the leather samples in three different locations with reference to Official Methods of Sampling [12] i.e. shoulder, butt and belly. The thickness taken ranges from 0.9mm – 1.3mm. This indicates that the leather thickness of each samples were within the standard thickness for light shoe upper leather between 0.75mm – 1.3mm. This variation in thickness may be due to the age, health, feeding habit and the gender of the animal before slaughtering. Although all the samples can be used for shoe upper leather depending on the customer's desire or request [3].

Tensile strength test, values were observed as follows for the butt: Large 16.66, medium 13.20, small 14.39 and kid 14.23N/mm² respectively which were closely related as presented in Table 4. The result shows that the large size gave the highest value compared to others. This might be due to the interconnectivity of the fibre network with respect to age of the animal, gender etc. The values were in agreement with the standard specifications except for the large animal that exceeded the said value of 15N/mm² [3] from literature. Percentage elongation at break as presented in Table 4 shows that the butt area for large 78.1, medium 70.1, small 68.8, and kid 37.1 % respectively. This is evident from the decrease of values from large to kid values obtained in percentage. The result for Lastometer test was presented in Table 5 were the force at burst (N/mm) and distension at break (mm) gave the following values: large 26.60, 10.93; medium 20.13, 11.05; small 16.64, 10.65 and kid 14.90, 10.19 respectively. This could be as a result of the gender, or the geographical area of the animal. Result shows that the large size has capacity to expand and contract. Therefore this must have affected the strength of the resultant leather which is applicable in lasting operation of shoe upper [3]. The result of the ball burst test as shown in Table 5 indicates the distension at which the leather burst, was above the minimum required standard (7mm).

Water Vapour Absorption test was carried out at room temperature during the prescribed time interval of 24 hours. From the result in Table 6, the Large size has the highest value (2.409x10³mg/cm²) followed by small (1.928x10³mg/cm²), medium (1.515x10³mg/cm²) then the kid has the least value (1.377x10³mg/cm²). From the result the higher the value the higher the ability of the shoe upper to behave to Water Vapour by preventing the foot from being wet i.e. the leather removes perspiration from the foot by absorption and evaporate it through the leather grain surface.

Conclusion

The physical tests carried out were aimed at assessing the quality of the various sizes of the leathers made from the goat skins in order to establish their behavior on the leathers when subjected to certain conditions during use. From the results presented, it was observed that the large size has most of its

values as the highest in each of the test carried out. Therefore from this observation it could be concluded that the large size of goat skin is highly recommended, for production of shoe uppers when the nitrogen content of the resultant leather is not considered otherwise the kid be used.

The need for quality leathers for shoe uppers is unavoidable and necessary in order to overcome the effect of poor quality shoe uppers which can be as a result of poor selection and grading of skins particularly the ones made from goat skins when considering the age, the gender, their nutrition and their geographical area.

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Table of Results

Table1. Basic Selection of the Goatskins

S/N	Sizes	Sex	Ages	Breed	Sq. Footage
I	Kid	Male	2-3 months	Sokoto Red	2.3
II	Small	✓	4-5 months	✓	3.0
III	Medium	✓	8-9 months	✓	4.2
IV	Large	✓	4-5 years	✓	6.4

Table2. Measurement of Average Thickness (mm)

S/N	Leather sizes	Shoulder		Butt		Belly	
		Before Shaving	After	Before Shaving	After	Before Shaving	After
1	Large	1.85	1.3	1.80	1.2	1.71	1.0
2	Medium	1.78	1.2	1.67	1.1	1.69	0.9
3	Small	1.70	1.1	1.40	1.1	1.55	1.1
4	Kid	1.67	0.9	1.36	0.9	1.51	0.9

Table3. Tensile Strength Test

S/N	Sample	Thickness(mm)	Width(mm)	Force at break (N)	Area mm ²	Tensile strength (N/mm ²)
Large	Shoulder	1.3	5	123.70	8.35	14.81
	Belly	1.0	5	60.26	7.55	7.98
	Butt	1.2	5	116.60	7.00	16.66
Medium	Shoulder	1.2	5	45.67	8.90	8.13
	Belly	0.9	5	123.10	8.55	14.39
	Butt	1.1	5	118.80	9.00	13.20
Small	Shoulder	1.1	5	35.27	9.25	3.81
	Belly	1.1	5	41.23	8.45	4.88
	Butt	1.1	5	97.82	6.80	14.39
Kid	Shoulder	1.2	5	60.30	8.50	7.09
	Belly	1.1	5	48.33	7.75	6.24
	Butt	1.1	5	118.8	8.35	14.23

Table4. Percentage Elongation at Break (%)

S/N	Skin Sizes	Shoulder	Butt	Belly
1	Large	79.5	78.1	50.0
2	Medium	78.8	70.0	53.1
3	Small	59.4	68.8	87.5
4	Kid	51.4	37.1	90.0

Table5. Lastometer Test

S/N	Sample	Thickness (mm)	Distention at burst (mm)	Distension at break (mm)	Force at break (N)	Force at Burst (N/mm)
1	Large	1.3	11.07	11.05	40.31	26.60
2	Medium	1.1	10.49	10.93	32.06	20.13
3	Small	0.9	9.92	10.65	29.39	16.64
4	Kid	1.2	10.03	10.19	24.57	14.90

Table 6. Water Vapor Absorption Test

S/N	Sample Sizes	Value(g/cm ²)
1	Large	2.41
2	Medium	1.93
3	Small	1.52
4	Kid	1.33

DETERMINATION OF LEVEL OF HEAVY METALS IN SELECTED BOREHOLE AND WELL WATERS IN ZARIA, NIGERIA USING DYE SENSITIZED POLYMERIC FILMS

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ABSTRACT

The importance of water supply to human health cannot be over emphasized. However, potable water supply to most Nigeria cities is still inadequate. This research work was designed to determine the concentration of heavy metals in water with a dye sensitized polymeric film. The polymeric films were made from 90% polyvinyl chloride and 10% polyvinyl alcohol using blending technique. The polymeric films were characterized by Scanning Electron Microscope (SEM). The polymeric film when submerged in water, it changes colours due to the present of heavy metals. The Acid monoazo- dye (1 - (2 - pyridylazo) - 2 - naphthol (PAN) was injected into the tested water, resulting in formation of particles of insoluble complexes. Borehole and well water samples were collected from different locations within Samaru- Zaria, Nigeria to determine their absorbance using UV –Vis spectroscopy technique. The concentrations of heavy metals (Cd, Pb, As and Cr) were determined by extrapolation from the standard calibration curve. The results showed that the concentrations of heavy metals in all the water samples were within the specification of WHO (2004) limits (for Pb is 0.001-0.01ppm, Cd 0.005-0.03, Cr 0.001-0.005ppm and As 0.001-0.01ppm), with the exception of chromium metal which was found to be higher in new extension well water (0.0051ppm) than WHO (2004) recommended limit for drinking water.

Keywords: Heavy metals, Polymeric film, Dye and Water

1.0 Introduction

The extent to which water resources development contributes to economic productivity and social well being is not usually appreciated, although all social and economic activities rely heavily on adequate quality or quantity of freshwater supply. Safe drinking water and basic sanitation are crucial to the preservation of human health, especially children [1]. Water-related diseases are the most common cause of illness and death among the poor in developing countries.

The World Bank while commenting on the world water challenge stated that access to water supply services and sanitation are major factors in reducing child mortality. It revealed that of about 1.7 million deaths that occur every year worldwide (90 per cent of which are children) are attributed to unsafe water, poor sanitation and hygiene, mainly through infectious diarrhea [2]. According to the WHO/UNICEF Joint Monitoring Programme, meeting the Millennium Development Goal (MDG), (having the proportion of people without sustainable access to safe drinking water and basic sanitation by 2015) would avert 470,000 deaths per year [3].

In spite of the importance of adequate water supply to humans, access to potable water supply in Nigerian cities lag behind demand. For instance, the joint report on water and sanitation by the WHO/UNICEF reveals that Nigeria and many other Sub-Sahara African countries are lagging behind in achieving the millennium development goals and targets set for water and sanitation, as drinking water coverage in Nigeria decreased from 49% in 1990 to 48% in 2004, as against the expected 65% coverage [4]. Such shortages can lead to serious economic disruptions and human suffering. Although Nigeria is blessed with abundant water resources, governments at all levels (federal, state and local) have not been able to successfully harness these resources to ensure a sustainable and equitable access to safe, adequate, improved and affordable water supply and sanitation to population [5].

The lack of access to safe drinking water and sanitation is probably directly related to poverty and in many cases to corruption and the inability of governments to develop the political will to provide water and sanitation systems for their citizens. Hence, the public sector has not been successful in meeting more than a small portion of the demand for water for residential and commercial uses. For example, out of the 85

million people living in urban and semi-urban areas, less than half have reasonable access to reliable water supply [6]. This situation has compelled many households, often the poor, to end up buying water from water vendors at great expense. This situation has been confirmed by studies of different cities in Nigeria [7]. For instance, despite investments and reforms, Lagos still lacks adequate treatment capacity to deliver enough clean water for drinking and household use. By the end of 2008, vigorous efforts by the state water authority achieved a water delivery capacity of 200 million gallons per day against a demand of 600 million gallons, a gap of about 66% [8]. This has made households to turn to private wells or street vendors to meet drinking water needs, which has exposed consumers to bacterial and heavy metal contamination exceeding local regulatory standards [9]. Similarly, the Urban Water Board is moribund, making it incapable of supplying potable water to households. This situation has forced the inhabitants of the metropolis to depend on other sources of water supply (wells, boreholes, etc), whose quality may not be guaranteed because of their susceptibility to quality degradation by leachate from waste disposal dumps and other sources of pollution.

Research reports from other cities in Nigeria equally echoed similar situations as obtained in Lagos and Warri-Effurun metropolis. For example, in Jema'a Local Government Area of Kaduna State, people that have pipe borne water in their houses are not satisfied with the water supply because whenever the water is pumped, it does not last more than two hours in a day. As a result, the use of alternative sources of water is indispensable. It was also revealed that the low service level of water accounts for the prevalence of water borne diseases in the area, which could get to epidemic scale if not attended to promptly (Abaje, et al., 2009). In a similar vein, in Nnewi, a town, popular for its commercial and industrial activities in Anambra State, most of the households depend on borehole, well water and 'sachet water' as major potable water sources [8]. Access to potable water supply in Ibadan is not different from what is obtainable in most cities in Nigeria. Water supply shortages have been very critical in Ibadan city since the 1980s and less than 30% of her residents are served with the public water system [10].

Some of the causes of inadequate access to potable water supply in Nigerian cities are highlighted in the Water Supply and Sanitation Interim Strategy Note on Nigeria. The report

stated that the operational efficiency of the State Water Authorities (SWAs) is unacceptably low as indicated by the monitoring indicators compiled under the National Water Rehabilitation Project (NWRP).

1.1 Heavy Metals

Heavy metals are natural components of the earth's crust, which cannot be degraded or destroyed. Heavy metals are chemical elements with a specific gravity that is at least five times the specific gravity of water [11].

Examples of heavy metals include Lead (Pb) Mercury (Hg), Cadmium (Cd), Arsenic (As) and Chromium (Cr). To a small extent, they enter our bodies via food, drinking water and air. As trace element, some heavy metals such as Copper, Zinc are essential to maintain the metabolism of the human body. However, at higher concentration they can be very poisonous [12].

Since heavy metal cannot be degraded, they are deposited, assimilated or incorporated in water [13] thus causing pollution of water bodies therefore heavy metals can be bio accumulated via drinking and finally assimilated by human consumers resulting in health risks [12].

2.2 Azo Dyes

Azo dyes are characterized by the presence of one or more azo chromophoric linkage (-N=N-) in the dye molecule which forms bridges between organic residues of which at least one is usually an aromatic nucleus.

Azo compounds are well known aromatic dyes that have the ability to form coloured complexes with heavy metals and also build up the wavelength of absorption throughout the visible region thus generating colour. In particular, 1-(2-thiazolylazo)-2-nanthol (TAN) and 1-(2-pyridylazo 2-naphthol (PAN) were widely used for spectral analysis [14].

The structure of the two commercial azo dyes are shown below

in Figure 1 and 2

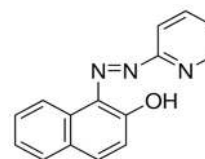


Figure 1: 1-(2-pyridylazo)-2-naphthol(PAN)

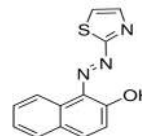


Figure 2: 1-(2-Thiazolylazo)-2-naphthol

2.0 Experimental

2.1 Materials

The studies covered commercial azo dye complexant: 1 - (2 - pyridylazo) - 2 - naphthol (PAN) which was obtained from sigma- Aldrich. Polymeric film was made from 90% polyvinyl chloride (PVC) and 10% polyvinyl alcohol (PVA). Other reagents are Bis (2-ethyl) hexylphathate (sigma- Aldrich), tetrahydrofuran (Steve Moore Chemicals), Acetone (Steve Moore Chemicals), Distilled water, Hydrochloric Acid and pure metals.

2.2 Methods

2.2.1 Water Samples Location and Collection

The water samples (borehole and well waters) were collected from different locations within Samaru Zaria, Nigeria. To avoid possibility of contamination, the empty polythene bottles were used for the collection of water samples and were labelled accurately.

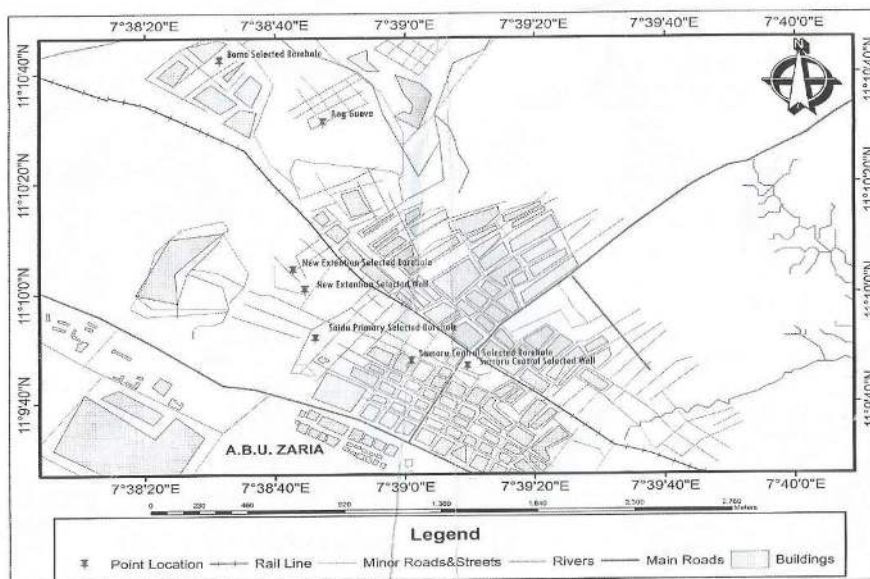


Figure 3: Map of Samaru- Zaria showing various Sample Locations

2.2.2 Preparation of the Polymeric Films

The polymeric film was made in the following ways: The film was made from 90% polyvinyl chloride (PVC), 10% polyvinyl alcohol (PVA) copolymer, plasticizer which is Bis (2-ethyl) hexylphathate was added to soften the film and tetrahydrofuran was also added as an organic solvent in the

film of a solvent to polymer ratio of 60:40. The role of this organic solvent is to change the dielectric properties of the polymeric film and the diffusivity of the cations, such that it may extract and accommodate the metal complexes. The dry polymeric film was sliced into squares and gently separated from the support.

2.2.3 Characterization

The structural analysis and physiochemical properties of the polymeric film obtained were analyzed.

2.2.3.1 Scanning Electron Microscopy (SEM)

The polymeric film made from 90% polyvinyl chloride (PVC) and 10% polyvinyl alcohol (PVA) was analyzed on a double adhesive sticker placed in a sputter coater machine for 5sec, this gives the samples a conductive property. The scanning was generated using 15kV source and proper image was produced in a NavCam mode and was transferred to an electron imaging mode, the image was then transferred to Phenom suite software where, fibre metric/pore measurements were carried out.

2.2.4 Heavy Metal Measuring Procedure

2.2.4.1 Calibration tests

A deionized water sample was spiked with heavy metals at the different concentrations (1-5 μ g/L). The pH of the solution was adjusted by addition of HCl. Azo dye was injected in acetone to make it soluble and then into the water sample of the dye concentration (0.0001g).

The polymeric films were immersed in the water sample and gently stirred at different interval of time (5-60 mins). The measurement was taken at 445 μ m at the absorbance band of the heavy metals dye complex. In all these measurements the sampling time and the concentration of the standard heavy metal varies throughout the process but dye concentration were kept constant (0.001g). Therefore same concentration was used in all the following experiments.

The instrument (UV-Vis) Spectrometer was set to zero using water blank. Each sample and standard was aspirated and its absorbance recorded. The concentration was determined by the extrapolation from the standard calibration curve.

3.0 Results and Discussion

3.1 Scanning Electron Micrograph

The scanned micrograph of the polymeric film obtained at 2200x magnification.



Plate 1: SEM images of the polymeric film at magnification

3.3 Calibration Curves for the Standard Metals

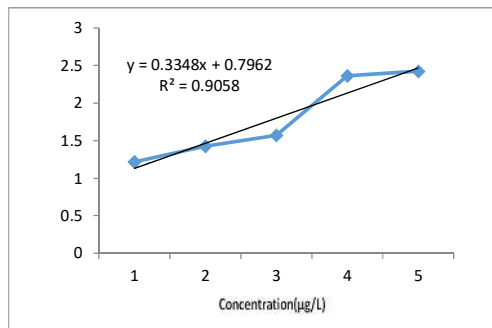


Figure 4: Calibration Curve for Standard Chromium Metal in PAN

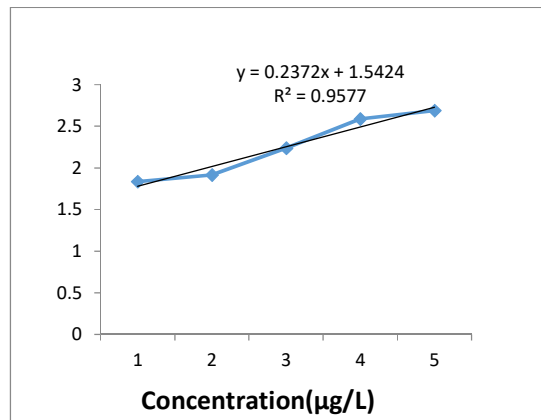


Figure 5: Calibration Curve for Standard Cadmium Metal in PAN

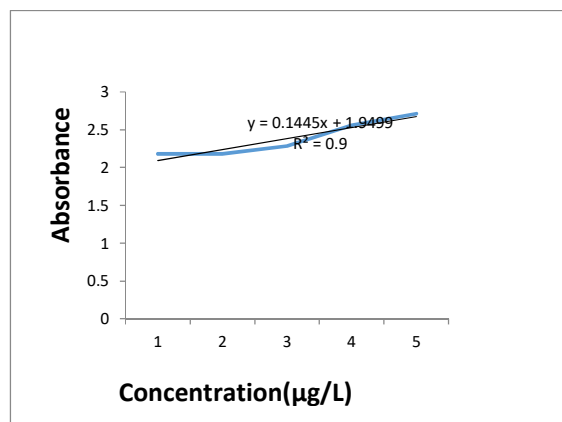


Figure 6: Calibration Curve for Standard Lead Metal in PAN

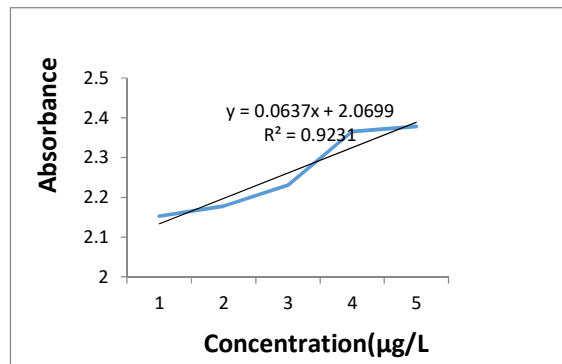


Figure 7: Calibration Curve for Standard Arsenic Metal in PAN

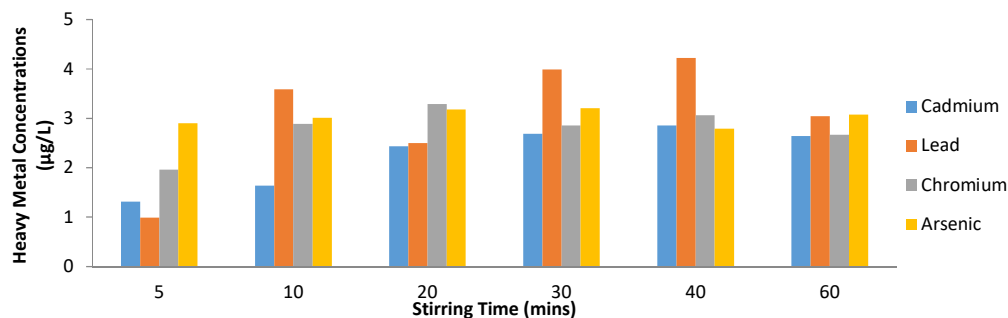


Figure 9: Concentration of heavy metals of A.B.U in selected borehole water

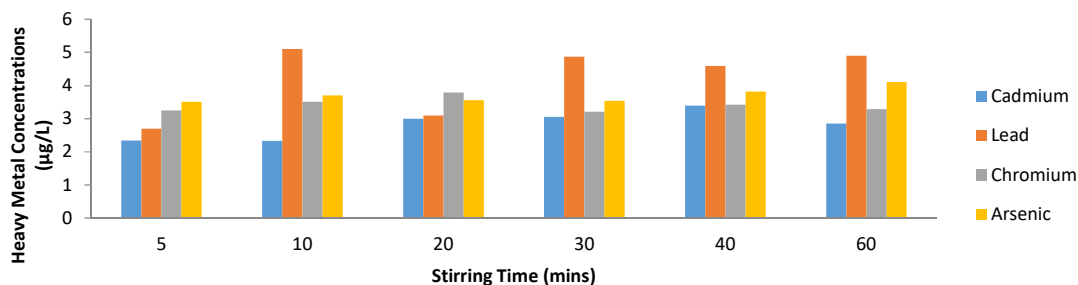


Figure 10: Concentration of heavy metals of Samaru Central in selected well water

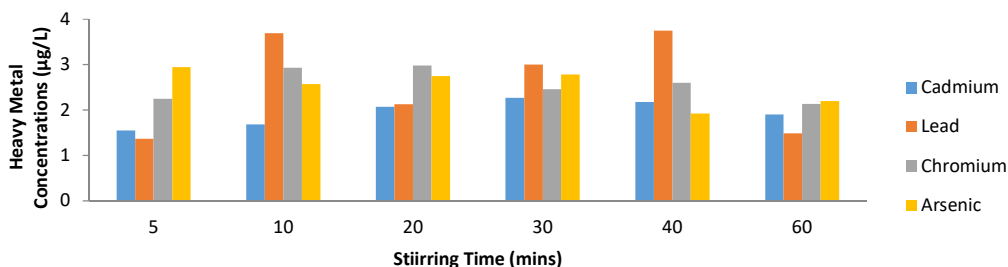


Figure 11: Concentration of heavy metals of Bomo in selected borehole water

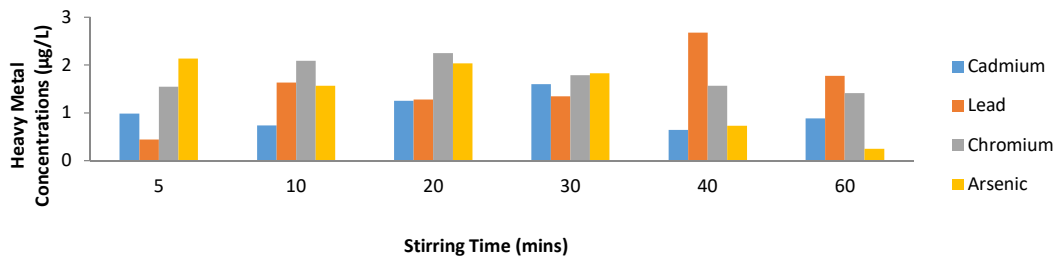


Figure 12: Concentration of heavy metals of Saidu primary school in selected borehole water

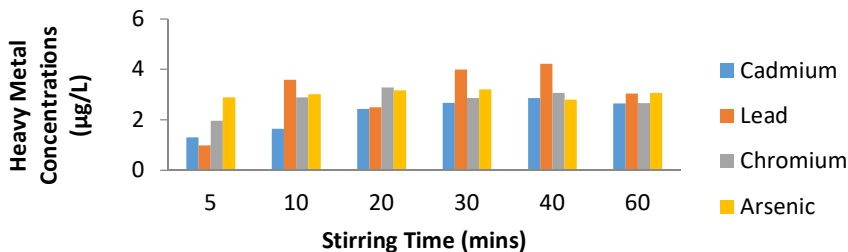


Figure 13: Concentration of heavy metals of Anguwa guava in selected borehole water

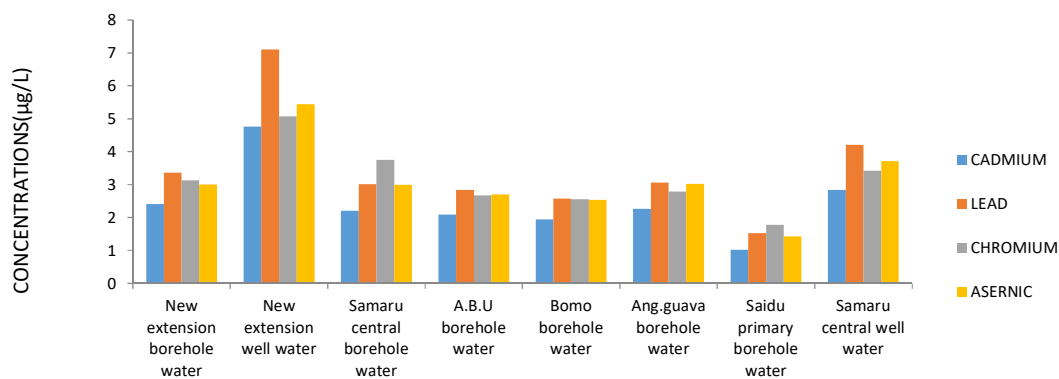


Figure 14: Mean Concentrations of the heavy metals in all the water samples (µg/L)

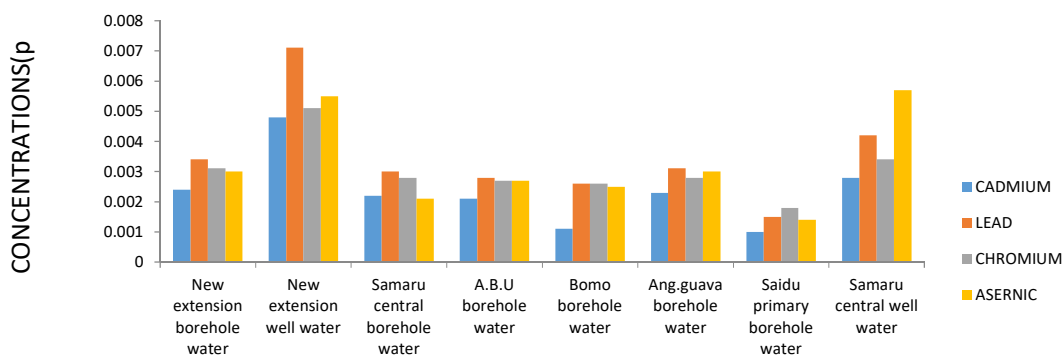


Figure 15: Mean Concentration of the heavy metals in all the water samples(ppm)

3.4 Discussion of Results

3.4.1 Scanning Electron Microscope

As seen from the image of the polymeric film at magnification shows a more open surface morphology displaying the fibrillate nature of the polymeric film. The polymeric film gives a compact and closed structure. The texture observed from the magnification might be attributed to structural transformation that has taken place during the polymeric film processing.

3.4.2 Effect of Dye Concentration and pH

The effect of dye concentration upon sensitivity showed that the major contribution to the measured absorbance is due to metal dye complexes formed in the solution and then absorbs/dissolved into the polymeric film. The absorption of the metal dye complex into the polymeric film is also affected by the pH of the solution. The pH of water determines the solubility mobility.

The effect of the dye concentration upon sensitivity shows that the major contribution to the measured absorbance is due to metal dye complexes formed in the solution and then absorbed/dissolved into the polymeric film. The absorption of the metal dye complex into the polymeric film is also affected by the pH of the solution.

The pH values fluctuated between 6.0 to 7.5. The maximum permissible limit of pH value for drinking water as specified is 6.5 to 8.5 [15, 16].

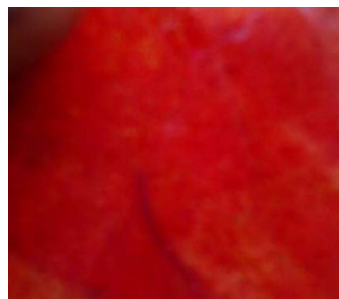


Plate 5.1: Film exposure to PAN

3.4.3 Heavy Metals Concentrations

Figure 4.10 shows the mean concentrations of heavy metals in all the water samples in ppm. From the results obtained, New Extension well water has the highest concentration of Lead metal (0.007ppm), followed by Samaru Central well water(0.0048ppm), New extension borehole water(0.0034ppm), Anguawa guava (0.0031ppm), Samaru central borehole water(0.003ppm), A.B.U. borehole

water(0.0028ppm), Bomo borehole water (0.0026ppm) and Saidu primary school (0.015ppm) which has the lowest concentration of lead metal. New Extension well water has the highest concentration of Cadmium (0.0048ppm), followed by , New extension borehole water (0.0024ppm), Anguawa guava(0.0023ppm), Samaru central borehole water(0.0022ppm), A.B.U. borehole water(0.0021ppm), Bomo borehole water (0.0011ppm)and Saidu primary school (0.010ppm) which has the lowest concentration of lead metal. New Extension well water has the highest concentration of Chromium (0.0051ppm), followed by Samaru Central well water(0.0034ppm), New extension borehole water (0.0031ppm), Anguawa guava (0.0028ppm), Samaru central borehole water (0.0028ppm), A.B.U. borehole water(0.0027ppm), Bomo borehole water (0.0026ppm) and Saidu primary school (0.018ppm) which has the lowest concentration of Chromium metal. Samaru Central well water has the highest concentration of Arsenic (0.0057ppm), followed by New Extension well water (0.0048ppm), New extension borehole water (0.0030ppm), Anguawa guava (0.0030ppm), A.B.U. borehole water (0.0027ppm), Bomo borehole water (0.0025ppm) Samaru central borehole water (0.0021ppm), and Saidu primary school (0.014ppm) which has the lowest concentration of lead metal. New Extension well water has the highest concentration of Copper (0.0042ppm), followed by Samaru Central well water (0.0040ppm), Anguawa guava (0.0040ppm), New extension borehole water (0.0035ppm), A.B.U. borehole water (0.0039ppm), Bomo borehole water (0.0039ppm) and Saidu primary school (0.0031ppm) Samaru central borehole water (0.0021ppm), which has the lowest concentration of lead metal. This is in accordance with the findings of [17] which stated that shallow wells close to sites that are contaminated will invariably be contaminated with the contaminating substances if they are less than 15m deep.

The indiscriminate dumping of all sorts of metals and the location of the boreholes and wells where the water samples were collected could be responsible for the observed lead concentrations in some of the water samples. The concentrations of heavy metals in some of the water samples are within the WHO [16], prescribed limits (for Pb is 0.001-0.01ppm, Cd 0.005-0.03, Cr 0.001-0.005ppm and as 0.001-0.01ppm) shows in table 2.1 for drinking water. Chromium concentration in new extension well water exceeded the WHO prescribed limit for drinking water. According to [18], level of chromium is high due to the presence of wastes from chromates processing facilities, when disposed improperly in land surfaces.

This implies that prolong consumption of water polluted with chromium metals will be of health risk. High concentrations of some metals (Lead, Chromium and Cadmium metals) observed in the samples could be an indications that soluble forms of the metals either present in the environment.

4.0 Summary and Conclusion

This study shows that amongst the heavy metals assessed from boreholes and well waters in Zaria, Chromium was found to be higher in new extension well water than WHO [16] recommended limit for drinking water while lead metal was also higher in the water samples but still within the recommended limit drinking. High concentration of some of the metals such lead and cadmium observed in the water samples could be an indication that soluble forms of the metals are present in the environment of the borehole and well waters locations. Consequently, water provided may not be safe for human consumption. Frequent monitoring of the quality of groundwater will be necessary to know the changes in the chemistry and possibly to put remedial measures in place. Effort of government and nongovernmental organizations has

resulted in several communities to have boreholes, although a welcome development but water from some boreholes are of doubtful quality due to the presence of colour, odour and taste which are indications of pollution result from the chemical composition of the ground water which influences health function. According to [19], the importance of ground water for human consumption and changes in quality with subsequence contamination affect human health. The pH of water body is very important in that it may affect the solubility and toxicity of metal in water [19].

5.0 Recommendations

- The results from this study could serve as guideline for water supply developers who often drill boreholes for use without any information on the chemistry of the ground water
- This study suggested using a specially designed polymeric film, which can absorb and dissolve the particulate complexes and thus allow for more accurate spectral measurements.
- Accessing the public health risks, which could arise from the intake of groundwater? It is therefore recommended that the dumpsite condition be improved to minimize the effects on the environment

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THE EFFECT OF ELECTROLYTE ON DYE SENSITIZED SOLAR CELLS USING NATURAL DYE FROM PAWPAP AND DOGOYARO LEAFS AS SENSITIZER

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ABSTRACT

The dye-sensitized solar cell (DSSC) technology, taken as a new generation of photovoltaics, is an efficient and economical way to directly convert solar energy into electricity. The significant recent development of the DSSC technology has demonstrated its promise for future renewable solar electricity generation. The effect of different electrolytes (Ferric Chloride (FeCl₃), Nickel chloride (NiCl₂) & Potassium Iodide (KI)) on the extract of pawpaw and dogoyaro leaf has help to note that potassium Iodide (KI) has a great effect on these dyes used which give an efficiency values of 0.030%, 0.027%, 0.009%, 0.025%, 0.021%, 0.019%, 0.018%, 0.017%, 0.001%, 0.024%, 0.003%, 0.006%, 0.008%, 0.027%, 0.002% & 0.003% using the dye of dogoyaro unheated potash, pawpaw leaf heated nacl, dogoyaro alum methanol, pawpaw leaf nacl unheated, pawpaw leaf potash heated, dogoyaro potash heated, pawpaw leaf methanol, dogoyaro potash unheated, dogoyaro alum heated, dogoyaro alum unheated, dogotaro nacl heated, pawpaw leaf only, pawpaw leaf alum heated, pawpaw leaf potash unheated, pawpaw leaf alum unheated, dogoyaro unheated only.

Key word: electrolyte, dogoyaro, pawpaw DSSC

INTRODUCTION

Electricity has become an integral part of modern society; it has propelled the technological revolution and allowed for the ongoing informational revolution. As our society progresses, our dependence on electricity continues to grow. The constant development of technology and the growth of second and third-world countries add to the increasing demand for electricity. In the not-so-long-term we will outstrip our ability to keep up with this demand using current energy-producing technologies. Additionally, and perhaps more urgently, current electrical production relies on fossil fuels that produce gaseous waste detrimental to global health. A number of alternatives are available to combat these problems, one such technology, solar energy, is the topic of this discussion intertwining ethics and nanotechnology. Grätzel was the first who investigated dye-sensitized solar cells (DSSCs) as a new type of solar cells in 1991[1]. Since that time, DSSCs have received an increasing interest due to many advantageous over other types. A DSSC is formed of a nanocrystalline metal oxide semiconducting layer deposited on transparent fluorine doped tin oxide (FTO) conductive glass, adsorbed dye on the semiconducting material, counter electrode, and an electrolyte containing iodide and trioxide ions[2]. In DSSCs, the adsorbed dye behaves as a sensitizer for absorbing sunlight. The conversion of solar energy into electricity in solar cells is based on charge separation. In silicon cells, an absorbed photon makes free an electron-hole pair, and the charge separation is calculated by an electric potential difference[3]. Silicon solar cell is expensive and its efficiency is highly affected when the illumination is low. DSSCs have many advantages over silicon solar cells. They are cheaper, there is no need for clean room technology, and the efficiency in low light conditions is not highly affected. The technology of DSSCs is not yet mature and a lot of research is still needed.

The use of natural dyes extracted from trees, fruits, and vegetables as sensitizers for the conversion of solar energy into electricity is very interesting because it improves the economical aspect and makes important profit from the environmental.

METHODOLOGY

Two different techniques were used in the extraction of dye from the plants viz ;

1. **EXTRACTION OF DYE USING METHANOL:**
Pawpaw, Dogoyaro leaves was air dry for twenty-four (24) hours, and then 50g of each leaf was soaked in methanol of 250ml for 24 hours, a filter paper was used to decant the dye extracted into a bottle.
2. **EXTRACTION OF DYE USING DISTILLED WATER:** This extraction is based on two methods
 - **HEATED**
Pawpaw, dogoyaro leaves was soaked in distilled water of 600ml, after 24 hours, each of the soaked leaf was sub-divided into three beakers, another 50ml of distilled water was added making 250ml for each leaf. Alum, sodium chloride (NaCl) and potash of 4g was added to each of the sub-divided leaves. It was later heated to 100°C, after these has been done, a filter paper was used to decant the dye extracted into a bottle.
 - **UNHEATED**
The same procedure was taken but it was not heated.

ABSORBANCE LEVEL

An ultraviolet spectrum machine was use to carry out these experiments taken readings of their absorbance, transmittance and concentration with a wavelength ranging from 330nm-1000nm and since they were soaked in distilled water and methanol, distilled water and methanol was used as the references during the usage of the machine.

CELL PREPARATION & FABRICATION

The followings are the step taken, in preparation the Paste, 15g of TiO₂ was mixed with 20ml of Nitric acid and stored in a test tube. A boarder of 0.2cm was formed at both edge of the conducting glass paper tape is then put on the conducting side of ITO glass, TiO₂ paste then flattened on the glass rod on the same side of the ITO glass. It is then air dried for 10minute and the boarders removed. A funnel machine is set at 450°C and the glass is placed in for 20minutes. A counter electrode is produced by using the carbon of a candle. Combining the counter electrode with the TiO₂ layer ITO glass (where the TiO₂ is the negative and the canter electrode is the positive layer).

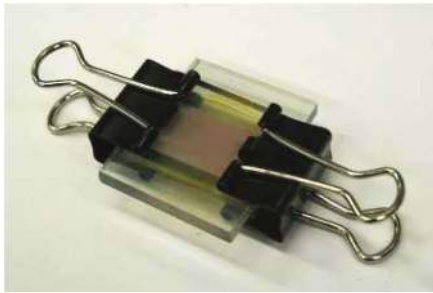


Fig 1 the counter electrode with the TiO₂ layer ITO glass

The fill factor was then calculated as shown below

$$ff = \frac{I_m \times V_m}{I_{sc} \times V_{oc}} = \frac{P_m}{I_{sc} \times V_{oc}} \dots \dots \dots 1$$

Calculate power conversion efficiency (η).

$$\text{power conversion efficiency } (\eta) = \frac{\text{Output power}}{\text{Input power}} \times 100 (\%) \dots \dots \dots 2$$

$$= \frac{P_m \text{ (mW/cm}^2\text{)}}{\text{Light intensity (mW/cm}^2\text{)}} \times 100 (\%) \dots \dots \dots 3$$

$$= \frac{I_{sc} \text{ (mA/cm}^2\text{)} \times V_{oc} \text{ (V)} \times ff}{I_{sc} \text{ (mA/cm}^2\text{)} \times V_{oc} \text{ (V)} \times ff} \times 100 (\%) \dots \dots \dots 4$$

V_{oc} ; open circuit voltage, I_{sc} ; short circuit current. I_m and V_m are the maximum cell current and voltage respectively at the maximum power point,

Result and discussion

• ABSORBANCE GRAPHS

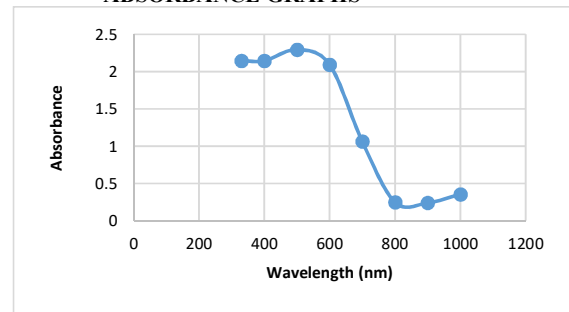


Fig2: the graph of absorbance against wavelength for pawpaw leaf with methanol

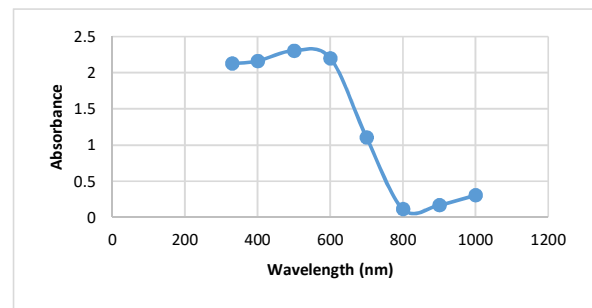


Fig3: the graph of absorbance against wavelength for dogoyaro leaf with methanol

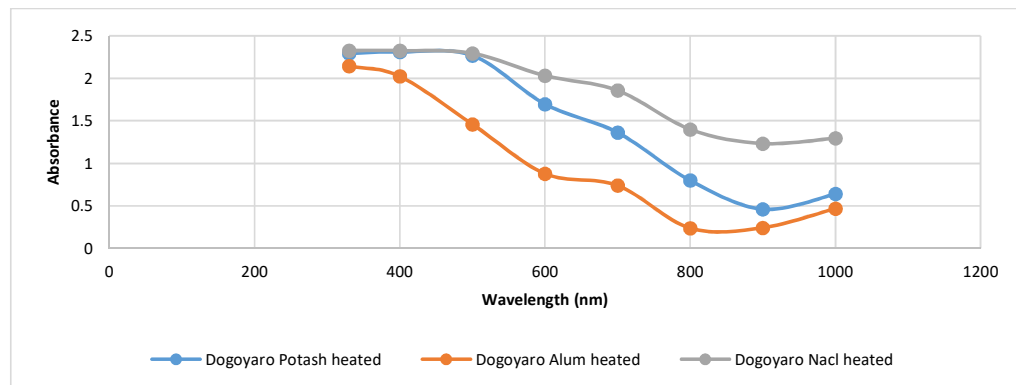


Fig4: the graph of absorbance against wavelength for dogoyaro leaf heated comparing potash, Alum and NaCl

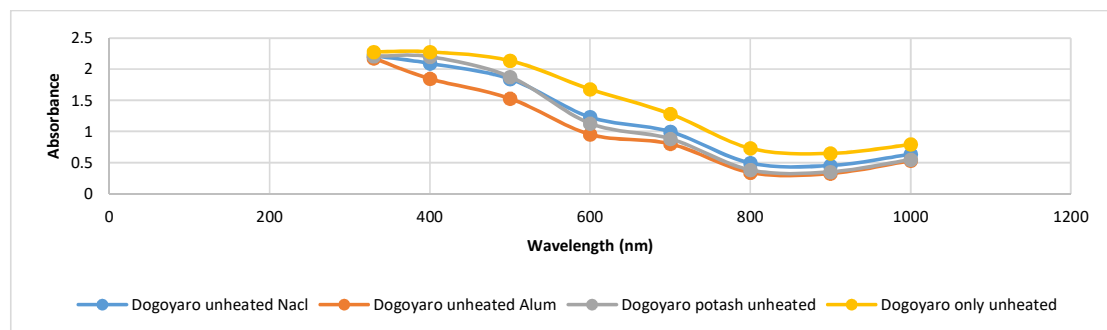


Fig5: the graph of absorbance against wavelength for dogoyaro leaf unheated comparing potash,Alum,NaCl and with dogoyaro unheated only

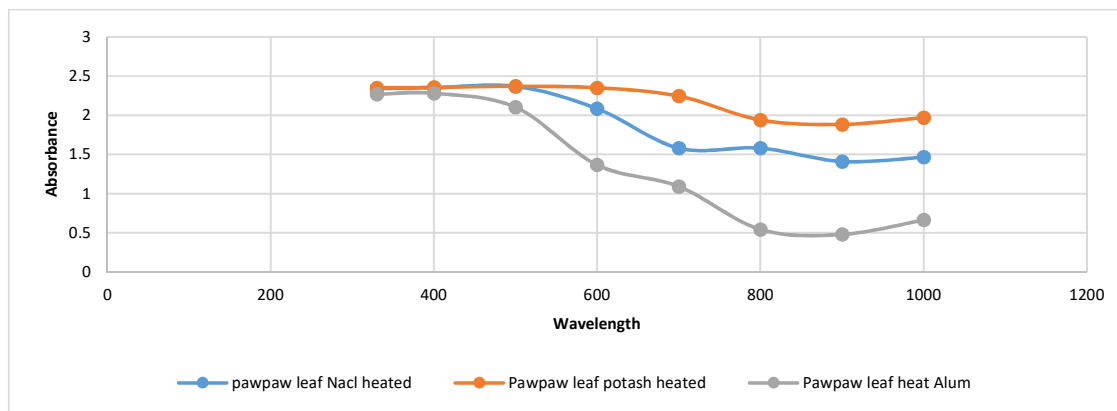


Fig6: the graph of absorbance against wavelength for pawpaw leaf heated comparing potash, Alum and NaCl

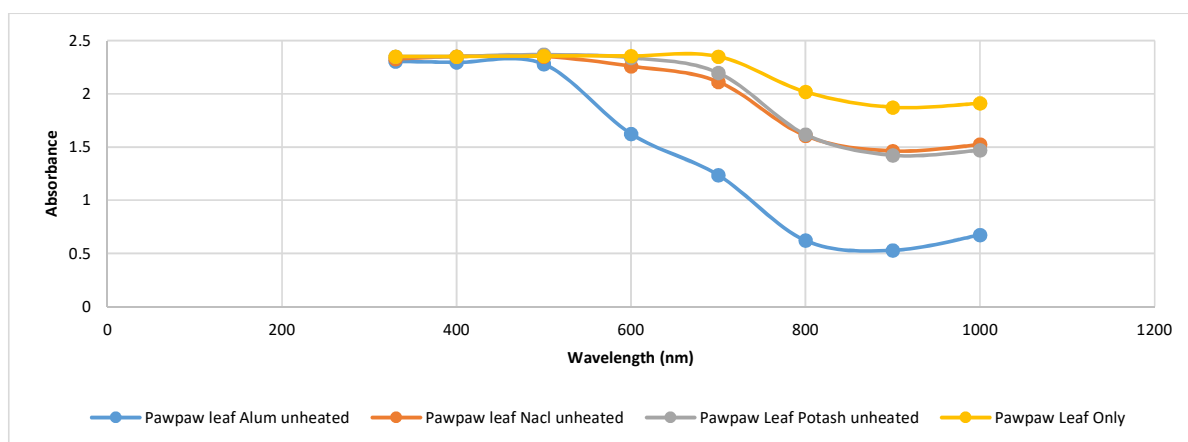


Fig4: the graph of absorbance against wavelength for pawpaw leaf unheated comparing potash, Alum, NaCl with pawpaw leaf only

Table 1 Photo currents (I_{sc} , I_m), photo voltages (V_{oc} , V_m), fill factor, and overall energy conversion efficiency for seventeen DSSCs sensitized by dyes extracted from Dogoyaro & pawpaw leaf Ferric Chloride ($FeCl_3$)

S/N	DYE	I_{sc} (mA/cm ²)	V_{oc} (V)	I_m (mA/cm ²)	V_m (V)	FF	η %
1.	DOGOYARO POTASH HEATED	0.302	33.3	0.157	31.4	0.490	0.002
2.	DOGOYARO POTASH UNHEATED	0.451	52.6	0.231	46.2	0.450	0.003
3.	PAWPAW LEAF NACL HEATED	0.437	52.6	0.223	44.5	0.438	0.004
4.	DOGOYARO ALUM METHANOL	0.296	33.3	0.15	30	0.457	0.001
5.	PAWPAW LEAF NACL UNHEATED	0.521	114.8	0.12	108.2	0.217	0.012
6.	PAWPAW LEAF POTASH HEATED	0.344	41.4	0.133	39.8	0.372	0.003
7.	DOGOYARO NACL UNHEATED	0.786	126.3	0.419	83.7	0.353	0.014
8.	PAWPAW LEAF METHANOL	0.01	179.7	0.167	150	13.940	0.009
9.	DOGOYARO ALUM HEATED	0.274	80.7	0.087	78.4	0.309	0.002
10.	DOGOYARO ALUM UNHEATED	0.04	20.6	0.019	17.1	0.394	0.0001
11.	DOGOYARO NACL HEATED	0.549	197.3	0.202	181.4	0.338	0.015
12.	PAWPAW LEAF ONLY	0.023	199.7	0.611	122.1	16.242	0.043
13.	PAWPAW LEAF ALUM HEATED	0.008	13.2	0.013	11.8	0.345	0.00001
14.	PAWPAW LEAF POTASH UNHEATED	0.296	98.9	0.106	95.2	0.345	0.007
15.	PAWPAW LEAF ALUM UNHEATED	0.595	199.1	0.218	196.3	0.361	0.029
16.	DOGOYARO UNHEATED ONLY	0.285	179.2	0.184	165.2	0.595	0.023

Table 2 Photo currents (Isc, Im), photo voltages (Voc, Vm), fill factor, and overall energy conversion efficiency for seventeen DSSCs sensitized by dyes extracted from Dogoyaro & pawpaw leaf Nickel chloride (NiCl₂)

S/N	DYE	Isc (mA/cm ²)	Voc (V)	Im (mA/cm ²)	Vm (V)	FF	η %
1.	DOGOYARO UNHEATED POTASH	0.001	3.7	0.0026	2.3	1.661	0.000001
2.	PAWPAW LEAF NACL HEATED	0.003	1.2	0.0018	0.9	0.001	0.000000001
3.	DOGOYARO METHANOL	0.0165	81.4	0.086	77.8	4.982	0.0021
4.	PAWPAW LEAF NACL UNHEATED	-0.6	-14.5	-0.2775	-55.2	1.761	0.0047
5.	PAWPAW LEAF HEATED POTASH	0.135	109.2	0.1113	100.2	0.767	0.0034
6.	DOGOYARO UNHEATED ALUM	-0.53	-7.2	-0.143	-42.9	1.608	0.0019
7.	DOGOYARO HEATED POTASH	-15.4	-1.281	-0.573	-114.6	3.329	0.6196
8.	DOGOYARO UNHEATED POTASH	0.173	5.7	0.077	15.4	1.203	0.0005
9.	PAWPAW LEAF METHANOL	0.009	0.01	0.0004	0.07	0.311	0.000000002
10.	DOGOYARO HEATED ALUM	0.014	44.2	0.045	40.4	2.938	0.0011
11.	DOGOYARO HEATED NACL	0.137	61.2	0.065	58.9	0.457	0.0028
12.	PAWPAW LEAF ONLY	0.3	181.4	0.198	178.6	0.650	0.026
13.	PAWPAW LEAF HEATED ALUM	0.341	39.2	0.173	34.6	0.448	0.0057
14.	PAWPAW LEAF HEATED POTASH	0.706	91.7	0.362	72.4	0.405	0.0266
15.	PAWPAW LEAF UNHEATED ALUM	0.504	62.2	0.26	52	0.431	0.0145
16.	DOGOYARO UNHEATED ONLY	1.058	115.1	0.531	106.1	1.837	0.069

Table 3 Photo currents (Isc, Im), photo voltages (Voc, Vm), fill factor, and overall energy conversion efficiency for seventeen DSSCs sensitized by dyes extracted from Dogoyaro & pawpaw leaf Potassium Iodide (KI)

S/N	DYE	Isc (mA/cm ²)	Voc (V)	Im (mA/cm ²)	Vm (V)	FF	η %
1.	DOGOYARO UNHEATED POTASH	1.164	117.9	0.583	116.6	0.495	0.030
2.	PAWPAW LEAF HEATED NACL	1.107	112.8	0.554	110.7	0.491	0.027
3.	DOGOYARO ALUM METHANOL	0.774	97.9	0.391	78.1	0.253	0.009
4.	PAWPAW LEAF NACL UNHEATED	1.094	110.4	0.548	109.5	0.497	0.025
5.	PAWPAW LEAF POTASH HEATED	1.113	119.1	0.559	111.8	0.446	0.021
6.	DOGOYARO POTASH HEATED	1.045	115.3	0.529	105.8	0.465	0.019
7.	PAWPAW LEAF METHANOL	0.994	109.3	0.503	100.5	0.492	0.018
8.	DOGOYARO POTASH UNHEATED	1.001	102.3	0.501	100.2	0.490	0.017
9.	DOGOYARO ALUM HEATED	0.006	37.5	0.04	36.3	6.453	0.001
10.	DOGOYARO ALUM UNHEATED	0.943	188.3	0.495	148.5	0.414	0.024
11.	DOGOYARO NACL HEATED	0.738	164.6	0.187	149.3	0.230	0.003
12.	PAWPAW LEAF ONLY	0.559	83.7	0.303	60.5	0.392	0.006
13.	PAWPAW LEAF ALUM HEATED	0.63	98.8	0.352	70.3	0.398	0.008
14.	PAWPAW LEAF POTASH UNHEATED	0.51	82	0.268	53.6	0.343	0.027
15.	PAWPAW LEAF ALUM UNHEATED	0.478	81.1	0.09	80.9	0.188	0.002
16.	DOGOYARO UNHEATED ONLY	0.436	48.8	0.22	43.9	0.454	0.003

The result from the above tables shows that Potassium iodide (KI) has the greatest effect on these dyes used in this research. According to its values of efficiency, it was observed that the level of efficiency is high compare to the others. Ferric Chloride (FeCl₃) also has a good effect on these dyes, and its efficiency value was also high, but not as Potassium Iodide (KI). Nickel chloride (NiCl₂) has a low or poor effect on the dyes of DSSC used in this research which result to poor efficiency values.

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BUILDINGS COLLAPSE: EVALUATION OF THE COMPRESSIVE STRENGTH OF SANDCRETE BLOCK IN ZARIA, NIGERIA

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ABSTRACT

The rampant cases of buildings collapse, loss of life and properties is a global issue, and Nigeria is no exception. Structural failure in housing construction has been attributed to several factors, but the larger percentage of such defects are due to poor quality of building materials. The high cost of building materials and coupled with the current economic recession in Nigeria is contributing to the production, use of substandard building materials, mainly, sands create blocks that are commonly used for housing construction. Structural failures and cracks are physical characteristics of most newly constructed houses in Zaria, Nigeria. The demand to investigate the quality determinants of sands create blocks is inevitable. Therefore, the aim of this research is to evaluate the quality determinants of the commercial sandcrete blocks produced in Zaria through the use of compressive strength analysis. The study employed experimental procedure and random sample technique used to select eleven commercial block industries in Zaria. The result of the laboratory experiment showed that the tested blocks provided a mean value of 0.75 N/mm² compressive strength which is quite below the Nigerian Industrial Standard's recommendation of 1.8 N/mm². Realisation of housing for all Nigerians is a collective responsibility of all the stakeholders in the construction industry. Certainly, there is an urgent need for the Nigeria Industrial Standards, Standard Organisation of Nigeria and other government's building regulatory agencies to control the production of commercial blocks in Nigeria. The architects and builders should endeavour to design and incorporate structural columns as well as avoidance of short lintels in the housing construction.

Keywords: Building collapse, Housing, Sandcrete block, Materials, Compressive strength

1.0 INTRODUCTION

Housing is one of the fundamental need of life. Globally, cost and quality of housing development have been the major challenge in the developing countries (Olagunju, Aremu, & Ogundele, 2013). Researchers in housing development have shown that over sixty percent of the construction's cost goes into building materials (Adedeji, 2010; Ogunsemi, 2010). The high cost of building materials and coupled with the current economic recession in Nigeria is contributing to the production and use of substandard building materials, particularly, sands create blocks that are commonly used for housing construction (Afolayan et al., 2008).

Predominately, sandcrete block is an acceptable building material for housing construction in Nigeria and other West Africa countries due to their ease of manufacture and the availability of materials required for production locally. It is the commonest building material for walling (load or non-load bearing). Persistent use of sandcrete blocks for housing construction is due to ease of workmanship and affordability, particularly, the current reality of the high cost of building materials is also a substantial contributing factor. The general public's preference for sandcrete blocks produced by the local industries over the one produced privately on-site is simply because of continuous increase in the cost of cement and labour.

Currently, over ninety percent of Nigerian urban residential and institutional buildings were built with sandcrete blocks (Sholanke et al., 2015). The trend is creating the spread of small-scale block industries in every Nigerian neighbourhood. Government promulgation of entrepreneurship development in the Nigerian economic ecosystem, low cost of establishment and absent of production control agency are all possible reasons for the proliferation of blocks industries in Nigeria, and Zaria is no exception (Anosike & Oyeade, 2012; Baiden & Tuuli, 2004). Also, Olotuah (2002) noted that the usage of sandcrete blocks in the Nigerian rural areas is increasing. The local and sustainable building materials such as earth soil fired brick, wood and stone are less use for housing construction despite the ever rising cost of cement. John (2014) stated that majority of the sandcrete blocks in the commercial block moulding industries are not up to the standardised specification of strength by and durability. Regardless of the

fact that most of the sandcrete blocks were produced in the small scale industries, the quality of those blocks differs considerably. Major factors responsible for poor quality of sandcrete blocks are methods of production, properties of the constituent materials and proportion of cement, sand and or fine granite mixture used (Ayodeji, 2011; Baiden & Tuuli, 2004).

Most of the construction failures can be directly or indirectly connected building materials. Specifically, Ayodeji (2011) stated that substandard building materials are one of the major factor attributed to the buildings' collapse. Usman (2013) posit that it is, therefore, vital to make sure that the production of sandcrete blocks are not only homogeneous in standard but regulated and efficiently monitor and control by the government agency to certify production quality. The greatest challenge is that majority of the sandcrete blocks' manufacturers in Nigeria are not registered and inadequately skilled (Usman, 2013; Anosike & Oyeade, 2012; Oyekean & Kamiyo, 2011). The fact is that production of qualitative sandcrete blocks emanate it is own challenges and prospects.

Presently, there is a need to identify gap(s) in the manufacturing process and provide appropriate recommendations that will facilitate sustainable development in the construction industry (Awolusi et al., 2015; Olagunju et al., 2013; Usman, 2013). On this account, it is imperative to investigate the quality determinants of the commercial sandcrete blocks, in an anticipation to improve the block industry's standard for sustainable development in Nigeria. Therefore, the primary aim of this research is to evaluate the quality determinants of the commercial sandcrete blocks of the randomly selected blocks industries in Zaria through experimental compressive strength analysis. The outcome of this research will contribute additional knowledge in the production of qualitative sandcrete blocks require for the construction of qualitative buildings and the sustainable development of Nigeria.

2.0 REVIEW OF LITERATURE

Globally, sandcrete blocks are extensively used for housing construction, in fact, it is a major building material in the construction industry (John, 2015). It is produced from a mixture of cement, sand and water, predominately, it is used in the building construction is for load and non-load bearing

walling component. Sholanke et al. (2015) and Usman (2013) stated that composition of the materials and production process and the technical know-how of the manufacturers determine the strength and quality of the sandcrete blocks.

Some of the merits of sandcrete blocks for housing construction are the strength, durability and stability, in fact, it withstands harsh climatic condition and prevents ground moisture if correctly used (Anosike & Oyeade, 2012). Also, the cost of maintenance is relatively low compared to the traditional building material such as earth soil. Hence, it has fire and sound insulation properties. However, Danquah (2009) stated that the compressive strength of sandcrete block is not up to that of burnt brick, but comparatively, it is more economical, available and relatively affordable to most Nigerians (Zami & Lee, 2010).

Several researchers have made a considerable effort on the application of agricultural waste as additive agents (rice husk, rice husk ash and sawdust) into the mixture of sandcrete block production but little progress is made so far. The research findings showed that compressive strength of the blocks produced with rice husk, rice husk ash and sawdust additive agent reduced after subjected to a considerable increase of this additive, hydration and temperature (Oyekan & Kamiyo, 2011; Oyetola & Abdullahi, 2006). Availability of these agricultural waste for sandcrete block production is another challenge. On the contrary, the compressive strength of blocks produced with a pure mixture of sand, cement and water increased with the intensification of hydration and established to have a significant resistance to temperature.

According to Anosike and Oyebande (2012), the configuration of a sandcrete block's production mixture is typically in the ratio one to six of cement and sand dipped with water. Then, mould into most common sizes (six and nine inches). The moulded block is allowed to set and dry naturally with two to three times curing/hydration per day for a considerable number of days as stipulated in the Nigerian Industrial Standard (NIS 87, 2000). The compressive strength of 2.5N/mm² to 3.45N/mm² are recommended for sandcrete blocks by the NIS. The primary responsibility of this agency is to ensure block industries' compliance with the stipulated standard (NIS 87:2007).

On the contrast, Ewa and Ukpata (2013) stated that the situation in most of the Nigerian cities is different because blocks manufacturers do not adhere to the stipulated standard. More so, the agency is not playing her supervisory roles that are monitoring and controlling the activities of the sandcrete block manufacturers in Nigeria. The issue is that majority of the manufacturers are illiterates who do not have engineering know-how and appreciate the value of the stipulated compressive strength (Afolayan et al., 2008; Abdullahi, 2005). As a matter of fact, few commercial sandcrete block industries in the Nigeria cities produced blocks within the endorsed standard by Nigerian Industrial Standard (Anosike & Oyeade, 2012; Awolusi et al., 2015) while the majority of the blocks' compressive strength are below 1.8N/mm².

Despite the rampant cases of buildings collapse that have been attributed to cheap building materials, patronage of low-quality blocks is still flourishing among the Nigerian public (Olagunju et al., 2013; Afolayan et al., 2008). Joan et al. (2014) reaffirmed that the patronage of these substandard sandcrete blocks by users is due to Nigerians' low purchasing power and coupled with the current economic downturns. The perception of the users is that sandcrete block's low price could automatically reduce the cost of housing construction. This case could be regarded as penny wise pound foolish because the merit of initial cost saving is nothing compare to the loss of live and property later. In a nutshell, this could lead to economic collapse for a country that is currently in a recession like Nigeria. Still, the government regulatory body NIS and Standard Organisation of Nigeria (SON) that are supposed to

ascertain the quality of the sandcrete blocks produced in Nigeria are practically inactive.

2.1 Quality Determinants and Production Process of Sandcrete block

The strength of building materials has been accorded as one of the core determinants of buildings safety and durability which translate to clients having value for their money. In addition, poor quality materials and detailed death-defying housing construction are a reason for concern as it leads to psychological and socioeconomic loss to the citizen and Nigeria as a nation. It is therefore, important that Nigerians deserve quality housing that is well designed, constructed with quality materials and maintained with minimum cost. In this regard, a safety of building could be contained by entry into the building materials' market to evaluate and assess such materials that do not certify the require standards as stipulated by the NIS.

There have been several cases of building collapse in Nigeria (Tyagher et al., 2007; Ayodeji, 2011). The majority are during construction while some existing ones are demolished due to major cracks that caused structural problems. The problem of poor construction is predominately begun with low-quality building materials and lack of technical competency on the side of the builders. In 2015, some cases of building collapse were reported in Zaria (Usman, 2013) while several other with severe cracks/structural problem are commonly observed in both Kabama and Gaskiya residential layouts.

Notable researchers have shown that compressive strength of a sandcrete block practically depends on the mixture proportion of the constituent's materials (sand, cement and water), method of production; curing/wetting's duration and temperature at the point of production (Usman, 2013; Sholanke et al., 2015). It has also been established that the strength of the walls resultantly determines the quality of building in term of durability/strength, thermal and fire resistance properties (Awolusi et al., 2015; Ewa & Ukpata, 2013). Therefore, it can be concluded that the quality of blocks is an unavoidable component accountable for structural disappointment in buildings. The implication is that walls built with substandard blocks are condition to fail and probably collapse in the future.

Demand for sandcrete blocks for housing construction is increasing among the Nigerian urban populace has created an entrepreneurial opportunity which is creating unprecedented growth in the number of block making local manufacturers. However, corruption, inexperience and other different modes of sharp practices in the production process emerged to maximised profit. Sholanke et al., (2015) stated that majority of Nigerian block industries do not meet the standard requirements specified by the Standard Organization of Nigeria (SON). The Nigeria Industrial Standard (NIS 87:2000) stipulated that only qualitative and quantitative blocks with required internal crushing strengths, dimensional tolerances with an appealing outward appearance in shape, size and devoid of defects shall be acceptable for building construction in Nigeria, but it is flaxy than reality. Sandcrete blocks should have the required internal crushing strengths, dimensional tolerances with appealing outward appearance and only qualitative and quantitative blocks in shape, size and devoid of defects shall be acceptable for building construction.

The production process and standard stipulated by the National Building Code and NIS for the hollow sandcrete block in Nigeria were discussed in this section. Several scholars reported that hollow sandcrete blocks are the predominate type of block use for construction in Nigeria (Anosike & Oyeade, 2012; Goncalves & Bergmann, 2007; Baiden & Tuuli. 2004). The vibrating machine used for large scale production. The standard mix proportion of 1:6 cement to sand ratios implies one part by volume of cement to six parts by volume of sharp sand. The sizes of blocks produced are usually 225 x 225 x

450mm (9") and 150 x 225 x 450mm (6") with one-third of their volume hollow. As reported by Sholanke et al. (2015), the production process of blocks is through the mixture of sand and cement together with hand shovel continuously until a standardised mix with uniform colour was achieved. Water is usually added through a fire hose, and it is further turned over to secure adhesion. It is then rammed into the machine moulds, compacted and smoothed off with a steel face tool. After removal from the machine moulds, the blocks are left on pallets under cover in separate rows, one block high and with a space between 2 blocks for the curing period. They are kept wet during this period by watering daily. After curing, the blocks are stacked and stored ready for transportation to project sites for use (Okoli et al., 2008).

In addition, the National Building Code stipulated that sandcrete blocks are a composite material made up of cement, sharp sand and water. Standard vibrating machine recommended for compaction and moulding of sandcrete blocks in the various sizes of 450mm x 225mm x 150mm; 450mm x 225mm x 225mm and 450mm x 225mm x 100mm. The aggregate includes both coarse and fine, from natural

sources. The sand shall be of approved clean, sharp, fresh water or pit sand, free from clay, loam, dirt, organic or saline water of any description and shall mainly pass 4.70mm test sieve. The mix proportion used for blocks shall not be less than one part by volume of cement to six parts of fine aggregate (sand) except that the ratio of cement to mix aggregate may be reduced to 1:4 $\frac{1}{2}$ and the thickness of the internal skeleton of the block shall not be less than 25mm). The stipulated strength requirements: for the sandcrete blocks shall possess resistance to crushing as stated below and the 28day compressive strength for a load bearing wall of two or three story building shall not be less than 1.75N/mm². In addition, the 28days compressive strength of a sandcrete block shall not be less than the above value and in compliance with the NIS specification. Proper and sufficient curing recommended for sandcrete blocks after moulding for at least seven days before use for construction. Therefore, Figure 1 provided the assessment framework for the quality determinants and the production process for the hollow sandcrete block.

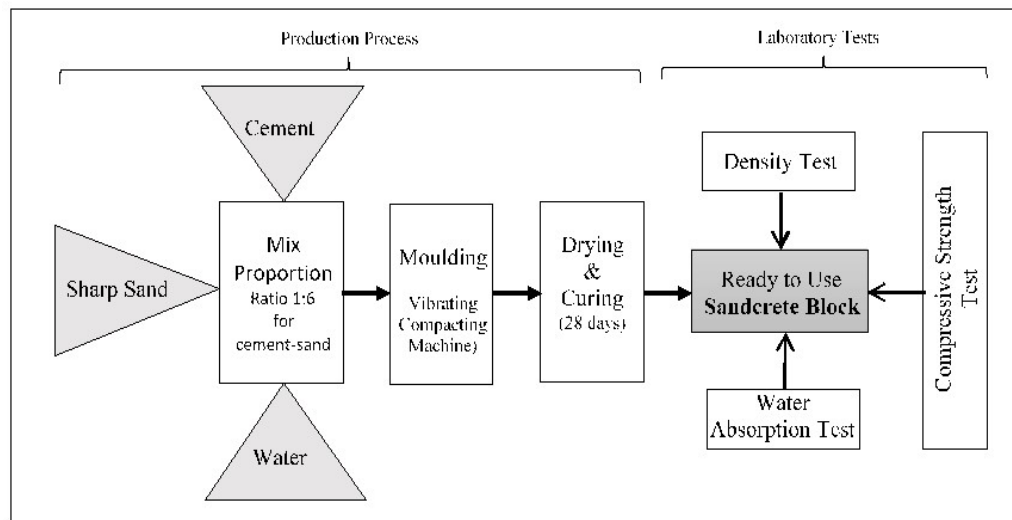


Figure 1.0: Assessment Framework for Sandcrete Block's Quality Determinants and Production Process

3.0 Research's Materials and Methods

The research employed experimental procedure through the use of density, water absorption and compressive strength tests analysis (Usman, 2013). Ten commercial block industries in Zaria were randomly selected in the Samara environ. Five hollow sandcrete blocks (450mm x 225mm x 225mm and 450mm x 225mm x 150mm) were also randomly selected from each production site for the laboratory test been the most used block sizes in Zaria, Nigeria. The tests mentioned above were performed in the laboratory to establish the quality or structural strength of the blocks. Primarily, the method was used to determine the load bearing capacity of the block (Awolusi et al., 2015; Afolayan et al., 2008).

The selected blocks from the manufacturers' stacking were certified to have been adequately and more efficiently cured for at least twenty-eight days before used for laboratory test. The reason was to confirm that the blocks used have attained the stipulated days required for compressive strength test (NIS, 2007). In the laboratory, each block was weighed (BW) and recorded before density, and water absorption of each block was established. After weighing, water was poured into a graduated cylinder container and the initial water volume (WV1) noted. The block was then immersed in the cylinder tank, and the final water volume (WV2) was taken. Block's density was established by dividing the block's weight (BW) with the difference between the initial water volume (WV1)

and final water volume (WV2). The process was replicated for all the selected blocks respectively. Afterwards, the blocks were cured for 28 days in agreement with NIS recommendation. Then, each block was subjected to compression test in the compressive strength machine. As the block were crushed their respective failure load were recorded one after the other and their compressive strength determined. The crushing force was divided by the sectional area of the block to give the compressive strength. The strength value was the average of ten specimens.

4.0 Research's Results and Discussion

A simple descriptive analysis was used to analysis the data collected from the laboratory tests. The outcomes of density and absorption tests for both 450mm x 225mm x 225mm (9") and 450mm x 225mm x 150mm (6") Hollow sandcrete blocks were presented in Table 1.

Table 1.0: Density Test Scores for 225mm (9") and 150mm (6") Hollow Sandcrete Blocks

Block Industry (BI)	Density Test (9" Blocks)		Density Test (6" blocks)	
	Mean Density	Mean Density	Mean Density	Mean Density
	Weight Dry	Weight Wet	Weight Dry	Weight Wet
	Blocks (Kg/m ³)	Blocks (Kg/m ³)	Blocks (Kg/m ³)	Blocks (Kg/m ³)
BI1	7316	6722	1208	1143
BI2	7482	6771	1286	1213
BI3	7517	6812	1209	1172
BI4	7382	6378	1256	1197
BI5	7318	6365	1178	1108
BI6	7454	7001	1173	1117
BI7	7815	7207	1254	1194
BI8	7732	7152	1167	1002
BI9	7744	7218	1173	1112
BI10	7823	7311	1177	1104

As presented in Table 1, the laboratory findings for the nine and six inches hollow sandcrete blocks showed that the densities score for dry nine and six inches' blocks were within the range of 7316 Kg/m³ to 7823 Kg/m³ and 1167 Kg/m³ to 1286 Kg/m³. Also, the densities score for wet nine and six inches' blocks were within the range of 6365 Kg/m³ to 7311Kg/m³ and 1002 Kg/m³ to 1213 Kg/m³ respectively. The densities value for both the nine and six inches' blocks were slightly different, and higher compare to the research conducted by Ogah and Igbe (2016) and Raheem (2006). Possibly, this could be due to mixing proportion of the materials and nature of the sand used. In fact, most of the manufacturers stated that they do get their sand supply from Geri town in Katsina state because of it peculiar coarseness and present of fine stones aggregate composite. As shown in Table 1, the blocks from block industry 10 produced the highest mean density score of 7823kg/m³ while block industry number 1 provided the smallest mean density score of 7316kg/m³. Subsequently, the block with the highest mean density score came from block industry two while block industry 8 produced block with the lowest score.

In Table 2, the compressive test for both 450mm x 225mm x 225mm (9") and 450mm x 225mm x 150mm (6") Hollow sandcrete blocks sampled from the ten block industries were presented. As shown in Table 2, the laboratory findings

for the nine and six inches hollow sandcrete blocks showed that the compressive strength score for both the nine and six inches' blocks was within the range of 0.74 N/mm² to 1.29 N/mm² and 0.72 N/mm² to 1.25 N/mm². The result presented a relative similarity in the compressive strength of both nine and six inches blocks from the ten block industries surveyed. At the same time, Block industry 10 possessed the blocks with the highest compressive strength in the category of nine inches' block. Conversely, Block industry 4 produced the block with the least compressive strength score as indicated in Table 2 and Figure 2.

In the case of six inches' block, the highest compressive strength score was realised among the blocks produced in the block industry ten while block with the lowest compressive strength score was identified in the block industry 4. As showed in Figure 2, matched compressive strength of nine and six inches blocks produced in Zaria are comparatively similar in the structural strength and quality. The product of tenth block industry was comparatively stronger than the products from other tested factories (see Figure 2). Likely, the reason could be due to the introduction of fine stone dust in the composition of the blocks' production mixture. This a possible area of future research.

Table 2.0: Compressive Strength Test for 225mm (9") and 150mm (6") Hollow Sandcrete Blocks

Block Industry (BI)	Compressive Strength Test (9" Blocks)	Compressive Strength Test (6" blocks)
	Mean	Mean
	Compressive Strength (N/mm ²)	Compressive Strength (N/mm ²)
BI1	0.84	0.95
BI2	0.81	1.16
BI3	0.93	0.83
BI4	0.74	0.72
BI5	0.78	0.86
BI6	0.87	0.97
BI7	1.17	0.84
BI8	0.75	0.77
BI9	0.92	0.99
BI10	1.29	1.25

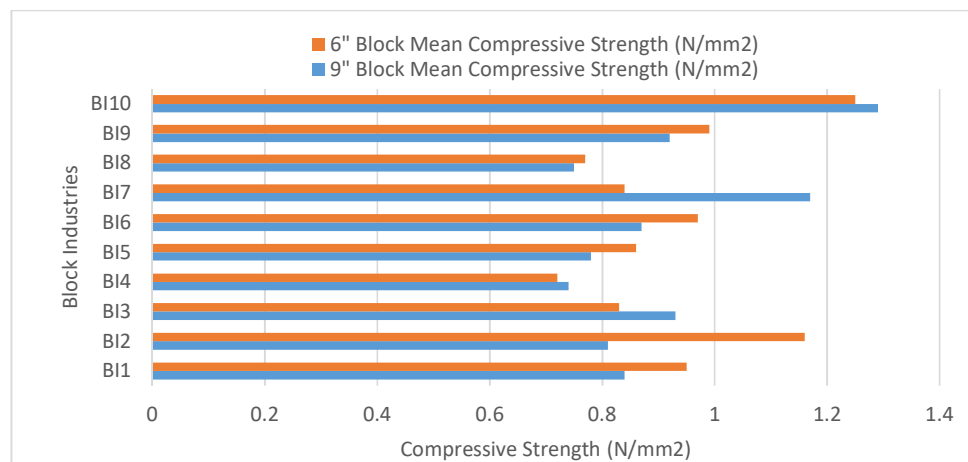


Figure 2: Matched Compressive Strength Test for 225mm (9") and 150mm (6") Hollow Sandcrete Blocks

Comparing the outcome of this research with other past studies, the result obtained are slightly the same with Ogah and Igbe (2016) findings and quite higher than results obtained by Ewa & Ukpata (2013) in Calabar, Nigeria. On the contrary, Raheem (2006) findings were quite higher, and the scores ranged from 1.01 to 1.68 N/mm² and 0.53 to 1.59 N/mm² for nine inches and six inches' block sandcrete hollow blocks after 28 days cured.

Currently, cement is quite expensive compared to the period when Raheem (2006) conducted his investigation. The interpretation is that maybe local block industries have developed sharp practices in the production process to maximised profit. Hence, this will reduce the quality and strength of the blocks they are producing now. More so, the higher compressive strength recorded in the Raheem (2006) study were probably due to the stronger mix ratio of 1:6 (cement: sand) while most of the tested blocks were produced with weaker mix ratio above 1:6. More so, Raheem's blocks were purposely produced for the experimentation, and the aim was not for profitability which is the primary goal of the commercial block industries in most Nigerian cities. This factor probably explains why this research finding is closely related to result obtained by Ewa and Ukpata (2013) since both studies focused on local commercial block industries in Nigeria. As a matter of fact, the findings of this research showed that commercial blocks produced in Zaria fall short of the required specifications stipulated by Nigeria Industrial Standard. Therefore, the strength and quality of these blocks are not satisfactory and not appropriate for building construction of any type.

5.0 Conclusions

The dream and actualisation of housing for all Nigerians by year 2020 is a collective responsibility of all the stakeholders in the construction industry, even though achieving it within the space of remaining four years is a myth far from reality. Obviously, Nigerian housing need and demand for quality and affordable housing will intensification in the future. This is due to continuous growth in population and couple with the current economic recession that is reducing the economic strength of most Nigerian in building their own house.

Building materials, particularly, blocks are one of the vital component of housing construction. Notable scholars have shown that buildings' structural failure, cracks on the load bearing walls and rampant collapse of building in most Nigerian cities are caused by the use of substandard materials, particularly, sandcrete block that is mostly used for walling component of housing construction. Physical characteristics of most high density residential housing in Zaria, Nigeria are cracks and structural defects which was ascribed to the use of low quality sandcrete blocks. On this account, laboratory tests were carried out on some of the commercial hollow sandcrete blocks in Zaria in order to establish their structural strength. The research's results have made known that the compressive strengths of sandcrete blocks produced in Zaria by local commercial block industries fall short of the required specifications stipulated by Nigeria Industrial Standards.

As recommended by other past researchers, there is urgent need for all the stakeholders in the construction industry, particularly, Nigeria Industrial Standards, Standard Organisation of Nigeria and other government's building regulatory agencies to control the production of commercial blocks in Nigeria. This should not just be a white paper policy but with full enforcement and heavy punishments for the fraudulent manufacturers. For the general Nigerian public, they should endeavour to report deceitful block producers and avoid patronising their product. In addition, every developer should incorporate structural columns and avoidance of short lintels,

particularly in the housing construction whether bungalow or storey buildings

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ELECTRICAL CONDUCTIVITY OF POLYETHYLENE TEREPHTHALATE (PET) FABRIC FUNCTIONALIZED WITH MULTI-WALLED CARBON NANOTUBES

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ABSTRACT

Low aspect ratio pristine Multi-walled carbon nanotubes prepared by carbon vapour deposition (CVD) were dispersed in Miranol, Cetyl pyridinium chloride and a 50:50 ratio mixture of them. They were each applied on 100% PET fabric using classical polyester dyeing techniques (exhaust dyeing) as well as cold padding by 3, 5-minute dip-dry techniques under controlled conditions. Exhaust dyeing yielded poor, uneven uptake; cold padding gave good, level uptake. The chroma characteristics of the dyed fabrics conformed to the Kubelka-Munk equation for determining additive reflectance functions. The polyester fabric became electrically conductive at a percolation threshold between 1-2.5% shade (owf). The electrical conductivity increased with the concentration of carbon nanotubes, up to 5.0×10^{-3} S/m at 5 % shade concentration. From the percolation threshold onwards, the conductivity was able to power light-emitting diodes (LEDs).

Key words: Carbon nanotubes; sonication; dispersion; cold-padding; exhaustion; electrical conductivity.

1. Introduction

In the last two decades, there has been increasing interest in new materials with unique characteristics. One of the most interesting is the demands placed on intelligent and multifunctional fibrous materials which have active functions in addition to traditional textile properties. The novel functions were imagined to be obtained by modifying the textile material or integrating the active component(s) into the textile structure. Textile structures on their part, are particularly suitable for this purpose because they possess the requisite structure, porosity, flexibility in addition to cheap and easy processability.

In particular, the demand for electrically conductive textiles is growing rapidly not only in relation to industrial needs such as sensing, electromagnetic interference (EMI) shielding, electrostatic discharge, data transfer in clothing, dust and germ-free clothing, corrosion protection, but also for military applications such as camouflage and stealth technology (Kim *et al.*, 2006).

As usual, it started with making a conductive polymer composite which will either be used as-constructed, or subsequently be fabricated into other preferred forms or articles. During this period, carbon nanotubes (CNTs) have established itself as a novel material with exceptionally unique collection of properties. Its nanometer dimensions (1 billionth or 10^{-9} m diameter) and high aspect ratio (up to 132,000,000:1) in addition to its high strength, modulus, flexibility, electrical and thermal conductivity as well as optical characteristics make them particularly suitable for reinforcement of metals, polymers and ceramics. Multi-walled carbon nanotubes (MWNTs) produced by catalytic carbon vapour deposition (CVD) grow in wavy, entangled assemblies which hold them together mechanically (Battisti, 2009). Although they do not possess reactive groups such as $-OH$, $-NH_2$, $-COOH$ on their surfaces or ends, strong electrostatic forces keep CNTs together: van der Waals forces acting on a high surface area, e.g. $300 \text{ m}^2/\text{g}$ (Sahoo *et al.*, 2010; Choudhary and Gupta, 2011). In addition, the absence of reactive groups makes them relatively inert in much the same way as graphene. Consequently, in the pristine form, they do not classically dissolve, but form poor dispersions in solvents - a distribution of particles which lack the capacity to form a homogenous mixture composed of only one continuous phase.

Achievement of a good dispersion is a prerequisite for improving the performance of any composite, but this has yet to be satisfactorily achieved in CNTs (Fiedler *et al.*, 2005; Sahoo *et al.*, 2010; Chaudhary and Gupta, 2011). This challenge is partly responsible for the inability to obtain optimum materials' property enhancement.

On its part, Polyethylene terephthalate (polyester, PET) is the most common and popular member of the thermoplastic-polyester family, and is the third most-produced polymer, after polyethylene and polypropylene.

In its natural form and even after fibre extrusion and processing to yarns and fabrics, the polymer is saturated. This explains its relative inertness, hydrophobicity and therefore its low moisture regain, as well as resistance to chemicals. The issue of reinforcing this inert material with an equally inert carbon nanotubes has proved challenging over the past decade or so.

Recently, however, there have been reports of PET fibres prepared by electrospinning (Ahn *et al.*, 2008) and melt-spinning PET incorporating acid-functionalized MWNTs (Yoo *et al.*, 2012). In both cases, the fibres had improved electrical, thermal and mechanical properties.

2. Experimental

2.1 Materials and Reagents

Plain woven 100 % Polyester (Dacron, 171 g/m^2) was obtained from the Laboratory stores of TECS, College of Textiles, NCSU, USA. Its details are shown in Table 3.1. Long-length MWNTs prepared by catalytic carbon vapour deposition using Fe/Co catalysts (average length – 500 nm) was obtained from TECS, College of Textiles, NCSU, USA. The short-length MWNTs was obtained from US Research Nanomaterials Inc., Houston, Texas (US 4353): (average length : 0.5 - 2.0 nm; Cetyl Pyridinium Chloride (CPC) was obtained from Sigma-Aldrich, U.S.A. and Sodium Lauroamphoacetate (Miranol) from Rhodia, U.S.A.

3. Methods

3.1 Preparatory experimental procedures

3.1.1 Fabric Scouring

The polyester fabric was scoured at 100°C for 30 mins in a bath containing 2g/l non-ionic surfactant (Primasol NMB) and 2g/l soda ash at a LR 50:1; It was rinsed copiously with water and dried.

3.1.2 Dispersion of CNTs

(a) 0.025g of the pristine *long-length* CNTs was placed in a 100mls stoppered flat-bottomed flask containing 50mls of 1% surfactant in de-ionised water (CPC, Miranol or their 50:50 ratio mixtures). This was then stirred for 30 mins using a probe sonicator (Misonix model XL 2020) operating at 550 watts at a frequency of 20 kHz at room temperature.

(b) The same procedure as in (a) was repeated with pristine *short-length* CNTs.

3.2 Application of CNTs on the fabric

3.2.1 High temperature (exhaust) dyeing method

On its part, polyester is relatively inert, and in fabric form, in most cases, disperse dyes are used to dye them, popularly by high temperature (exhaust) dyeing or carrier dyeing. In order not to tamper with the inherent qualities of the CNTs by chemicals normally employed in carrier dyeing, exhaust dyeing was selected as a suitable method by which they could be applied onto the polyester fabric.

(a) Baths with normal pH

The Ahiba Nuance top speed dyeing machine was used to dye the samples using standard high temperature (exhaust) dyeing techniques normally employed for 100% Polyester fabrics. It has 16 detachable, tight-lidded sample containers, uses infrared (IR) heating with programmable dyeing temperature and rate of heating/cooling.

Baths were prepared containing 1 (v/v) % of surfactant and 0.05 (w/v) % CNTs. Using a liquid-to-goods ratio (LR) of 50:1; 1 g of fabric was entered into individual sample containers at room temperature, and the machine was programmed to increase at 20 °C/min up to a maximum of 130 °C. The agitation rate was 15 rpm. Dyeing was carried out at this temperature for 1 hr and then cooled to room temperature at 3°C/min.

The same procedure was used to dye fabric pieces in the surfactant only (henceforth referred to as 'blank' or control).

(b) Baths with adjusted pH

The procedure in 3.2.1(a) was repeated, but with the pH of the baths adjusted first to 5, and then to 4 using 10 % acetic acid (to decrease the pH) and 10 % sodium carbonate (to increase it).

(c) Baths with adjusted pH and electrolyte (sodium chloride, NaCl)

The procedure in 3.2.1(b) was repeated in the presence of NaCl (1 w/v) %.

3.2.2 Cold-padding

A bath was prepared containing 1 (v/v) % surfactant and 0.05 (w/v) % CNTs at a LR 20:1.

Fabric samples (1 g) were impregnated in this bath for 5 mins with occasional stirring, removed and squeezed. This was repeated 3 times. On the third time, the excess was squeezed out at 20 % expression using a mini pad mangle.

This was repeated (i) with bath pH adjusted and (ii) with bath pH adjusted in the presence of the electrolyte. The results are as shown in Fig. 4.

4. Analytical techniques

Unless otherwise stated, all analyses were carried out under standard conditions of testing textile materials (ASTM International D 1776 - conditioning at 21±1°C, 65±2% relative humidity for 4 hours)

4.1. Reflectance spectroscopy

The equipment used is a digital spectrophotometer, Spectralite III-i7 model, supplied by x-rite, USA. Essentially, it measures chromatic information based on the CIE L* a* b* colour scales.

The equipment was calibrated using a 6 mm aperture and the standard white and black discs under standard laboratory conditions. One after the other, the samples were mounted in front of the reflectance aperture and closed. The sample identification data was entered, the type of test and number of replications were selected in the CPU software to remove the effects of the the control from the other dependent variables, and the test run. The results are shown in Fig.

4.2. Field-emission scanning electron microscopy (FE-SEM)

The FE-SEM equipment used was obtained from Phenom Nanoscience Instruments Inc.. It was used to examine the surface morphology of the fabric samples at various magnifications. The ultra-high resolution equipment required that samples should be conductive, otherwise they needed to be coated with a conducting material. The control sample (non-conductive) was first gold-sputtered in an accessory chamber for 10 mins before mounting in the analyzer. In the analyzer, the sample surface was scanned through various magnifications until the right resolution was obtained; the images were then captured.

4.3. Electrical Conductivity Measurements

Three types of equipment were used:

- The 2-point probe, Metex auto/manual range dual display digital multimeter with PC interface (M-3860D) by Metex, USA, was used to measure the resistance between two probes separated by selected distances apart.
- The 4-point probe, consisting of Keithley 6221 DC and AC current source and a Keithley 2182A Nanovoltmeter using a current range ± 20 E-6 ($\pm 20 \times 10^{-6}$ A) and a voltage range of 10 V that automatically takes and averages 250 readings. It was used to measure surface and bulk resistivity in high-resistance substrates over each square unit centimeter or volume.

4. Results and Discussion

4.1 Dispersion of CNTs

In this report, only the effects of surfactants are considered, being the only solvents that do not classically react chemically with carbon nanotubes. At first, long nanotubes were used. Their nanoscale dimensions and high aspect ratio made them more difficult to disperse, since as the surface area increases, so does the attractive forces between aggregates. In addition, each flexible tube associates with its neighbours over a longer length, and is more likely to get entangled and aggregate in a liquid medium when left undisturbed, compared to shorter tubes. It is logical to assume that media that can appreciably disperse long tubes will invariably perform better with shorter tubes which was confirmed in this work. When shorter tubes were used, a reasonably better dispersion was achieved which could remain stable for at least one week.

In this case the surfactants were ranked Miranol (Zwitterionic) > CPC (cationic) > CPC/Miranol mixture.

The adsorption of surfactants into inorganic and organic surfaces usually depends on the chemical characteristics of the particles, surfactant molecules, the solvent, concentration of the surfactant, electrolyte, pH, temperature, etc. (Vaisman *et al.*, 2006; Zhang and Somasundaran, 2006).

The driving force for the adsorption of ionic (cationic and anionic) on charged surfaces is the coulombic or electrostatic interactions e.g. between the surfactant's positively- or negatively-charged head group and the negatively- or positively-charged surface (CPC is a cationic quarternary ammonium compound); the mechanism by which non-ionic surfactants adsorb onto a hydrophobic surface is based on a strong attraction between the solid surface and the surfactant's hydrophobic tail, including hydrogen bonding or non-polar interactions. Miranol is zwitterionic (has two

quarternary amino groups, $-\text{COO}^- \text{Na}^+$ and $-\text{OH}$). Zwitterionics are amphoteric, and therefore, behave basically like non-ionics, but can also behave like the cationics or anionics, depending on the pH of the solution. Hydrogen bonding between surfactant species and the solid surface species could occur in systems containing hydroxyl, phenolic, carboxylic and amine groups on the surfactant. Other forces include lateral associative interaction, solvation, and desolvation (Zhang and Somasundaran, 2006).

4.2 Application of CNTs on the fabric

When CNTs were adequately dispersed, a black ink-like solution was obtained. This appearance suggests it can be used in dyeing, printing, painting or any such-like activities. Since the corresponding substrate is a fabric and making it electrically conductive is the goal, dyeing it with CNTs appears to be one of the best application methods of choice.

5.2.1 High temperature (exhaust) dyeing

From available reports (Battisti, 2009; Sahoo *et al.*, 2010; Chaudhary and Gupta, 2011) and experience during dispersion, the length of the nanotubes is a major contributor to poor dispersibility, and could therefore be to uniform application and distribution on the fabric. This is responsible for the patchy and unlevel dyeing obtained and, therefore the need to opt for shorter nanotubes.

Shorter nanotubes gave better dispersions, and were applied first in acidic conditions of different severities (pH 4 and 5). It was observed that some surfactants create a better dyeing environment in more acidic conditions (e.g. Miranol and CPC; pH 4). This condition also proved better than application in the surfactant's natural pH (unadjusted). Deeper shades were obtained in acidic conditions, but addition of NaCl in the acidic bath further improved both shade and levelness.

Cold padding, however, gave better and more level dyeing under the same bath conditions. With shorter dip-dry times, it eliminates the application of high temperature and its associated equipment and other controls.

This explains why this technique was subsequently adopted as the application method of choice for all the fabric samples.

Acidic dyebath conditions tend to improve absorption of the CNTs. Dyeing of polyester had always preferred acidic conditions, but our peculiar case corroborates the work of Gonçalves (Gonçalves *et al.*, 2012) who functionalized MWNTs with oxygen-containing surface groups and incorporated them into cotton and polyester fabrics by a process similar to traditional industrial dyeing. He concluded that the incorporation efficiency was higher in acidic conditions. The presence of an electrolyte actually improves levelness. This is consistent with the traditional role of electrolytes in textile dyeing operations, and is particularly important because the more niform the application, the better and more consistent the fabric properties-enhancement.

4.2.3 Application at different shades

From the results obtained in section 4.2.2, one of the surfactants (Miranol) was selected, mainly due to its lower cost and availability, and was used to dye 1 g pieces of fabric to 0.1 %, 0.5 %, 1 %, 2.5 %, 3.5 % and 5 % shades (owf). The results, along with their corresponding chroma characteristics are as shown in Plate XXVIII.

4.3 Analytical techniques

4.3.1 Reflectance spectroscopy

The transmittance/absorbance of the dispersions before and after dyeing could not be measured because black solutions usually absorb all the uv-visible radiation passed through them

and transmit none for detection and measurement. The chromatic information obtained using the digital spectrophotometer are shown in Figs.5 and 6.

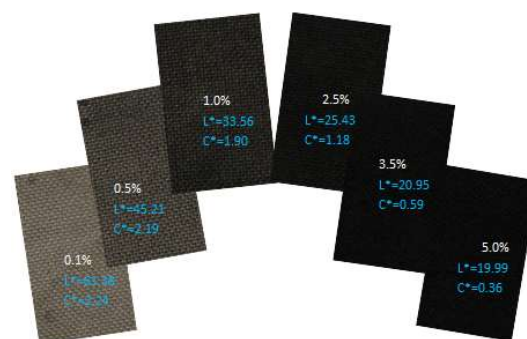


Fig. 5: CNT concentrations and their chroma characteristics.

For all the fabric samples, the higher the concentration of CNTs (owf), the lower the values of L^* and C^* , and the darker the shade, and vice-versa (Plate XXVIII). It also gave the Kubelka-Munk (K/S) values for determining additive reflectance for coloured objects. For all our samples, the K/S values increased with increase in concentration of CNTs (Figs. 4.1 and 4.2).

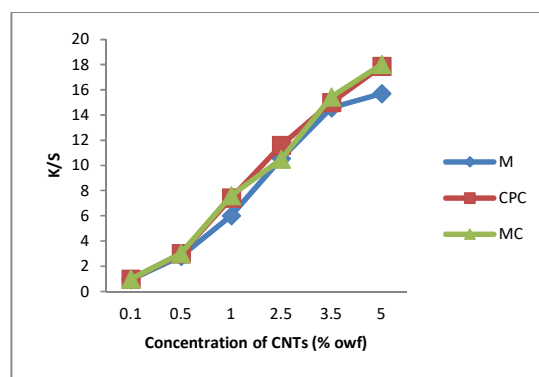
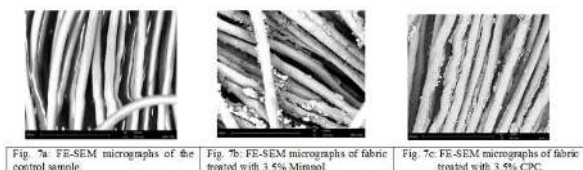


Fig. 6: K/S versus concentration for Miranol (M), CPC and their mixtures (MC).

4.3.2 Field emission scanning electron microscopy (FE-SEM)

Plate XXIX shows a micrograph of the control sample magnified 1000 times. Figs 7b and 7c present the fabrics processed in 3.5 % Miranol and CPC respectively, at the same magnification. The FE-SEM images of the plain and the dyed polyester samples are shown in Fig. 7. The control fabric shows long, lustrous, even shiny filaments running along the yarns without any discontinuity along their lengths. There is also no sign of broken fibre heads or ends within the micrograph (Fig. 7a); this is an indication that the fabric was made from continuous filament yarns, not staple. The micrograph of the dyed fabric (Fig. 7a and 7b) showed that all the lustre had been eliminated from the fibres. This suggests that some of the CNTs actually penetrated into the filaments, and of course, a larger percentage can be seen coating the filaments and also lodged between their interstices. This corroborates the results from the work of Fugetsu *et al.*, (2009) who impregnated polyester multifilaments in MWNTs dispersed in a mixture of zwitterionic and anionic surfactants. SEM images revealed a CNT-skin, with the CNTs arranged in continuously interconnected networks over the surfaces of the filaments, which functions as the electrically conductive layer (ECL).



4.3.3 Electrical properties

Figs. 4.3 and 4.4 show the variation of resistivity with type of surfactant in the warp and weft directions respectively. Except for MC, adjusting the pH to acidic conditions and introducing NaCl into the bath significantly reduced the resistivity.

In each case, the peaks for S, SP and SPE are displayed for the warp and weft direction; all of them show evidence of the large difference between application in S only on one hand, and application in SP and SPE on the other, where S – surfactant only;

SP – surfactant in adjusted pH;

SPE – surfactant, adjusted pH + electrolyte

M – Miranol;

C – CPC (Cetyl pyridinium chloride);

MC – Mixture of M and C (50:50);

Wa or wa – warp; and

We or we – weft.

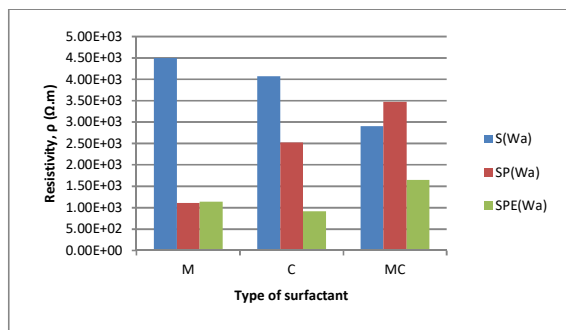


Fig. 8a: Variation of resistivity with type of surfactant (warp direction).

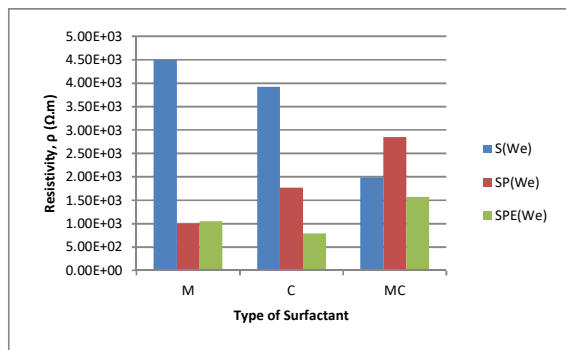


Fig. 8b: Variation of resistivity with type of surfactant (weft direction).

The electrical resistivity of the samples dyed from 0.1-5% owf were measured using the 2-point probe at a probe separation of 3 cm, and the results for both the warp and weft directions are shown in Fig. 4.11. The resistivity, ρ , decreased with increase in the concentration of the CNTs. This implies an increase in conductivity, σ , in the same manner. The bulk resistivity, ρ and conductivity, σ , are related by the equation

$$\sigma = \left(\frac{1}{\rho t} \right) \dots \dots \dots \text{eq. 1}$$

where t is the thickness of the material.

It should be noted that the actual height/peak of the histogram for 0.1 - 1.0 % owf could not be shown on this graph because they will practically dwarf or diminish those of 2.5 - 5.0 %, so that they will appear as zero.

On the same graph, it can be observed that there is a sharp drop in resistivity between 1 % and 2.5 %. This region highlighted the percolation threshold - the critical concentration above which electrical conductivity started manifesting in the fabrics. After the percolation threshold, conductivity increased with increase in the concentration of CNTs, up to a maximum of 5.5-6 % (owf), after which the fabric ceases to absorb more nanotubes.

In Fig. 8, the resistivities were highest when only surfactants were used, decreased in acidic conditions and was least when surfactants were used in acidic conditions in the presence of an electrolyte. CPC gave the least resistivity, followed by Miranol and then their mixture.

It is noteworthy that in Figs. 8, the actual peak value of the resistances for Miranol could not be adequately fitted on these graphs because they are much higher than the others in such a way that representing them together will diminish the value of the others to almost zero.

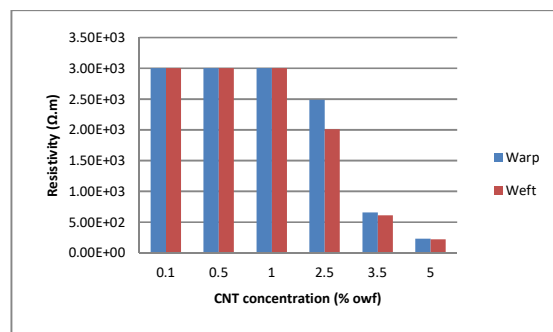


Fig. 9: Resistivity as a function of CNT concentration (Miranol).

Fig. 10a and b show the variation in the bulk resistivity from control to 5% (owf). In (a) the values for 2.5 – 5% are much smaller than the control so that they appear to be zero, but (b) shows the magnified relationship between 2.5 – 5%, while (c) shows the corresponding conductivity from the control to 5% (owf)

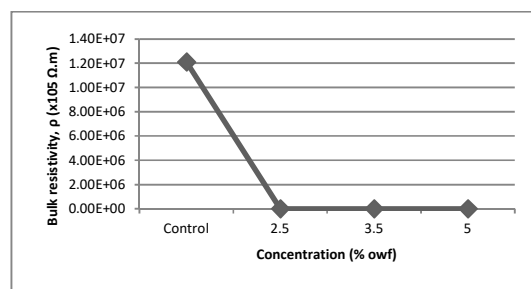


Fig. 10a: Bulk resistivity, ρ , as a function of concentration (% owf).

The conductivity achieved was through a network of conductive pathways generated by the CNTs when adjacent tubes are in contact. The statistical chances of forming these conductive pathways increases with the concentration of the CNTs. In addition, there is a considerable body of evidence suggesting the presence of an insulating layer between the nanotube particles even above the percolation threshold, just as is the case for other types of conductive fillers (Grossiord *et al.*, 2008). This implies that the percolating nanotubes may not necessarily be in actual contact with each other and that

conductivity may occur via some tunneling or hopping process through the insulating layer separating them. This can only happen if the distance between two neighbouring tubes is below a certain critical value (Grossiord *et al.*, 2008).

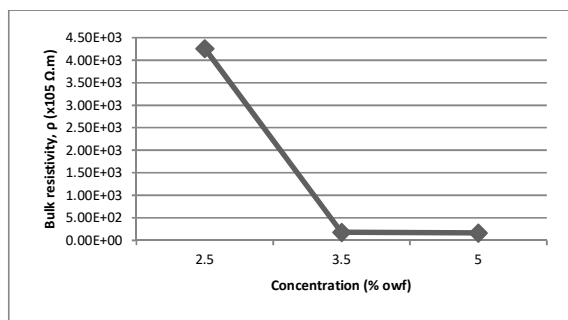


Fig. 10b: Bulk resistivity, ρ , as a function of concentration (% owf).

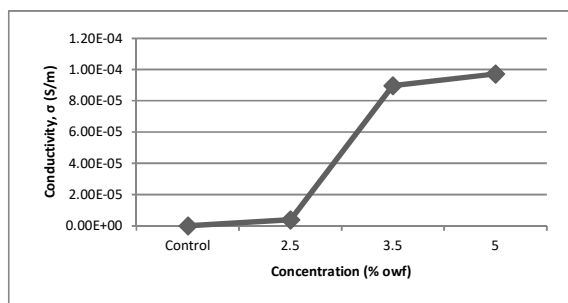


Fig. 10c: Conductivity, σ , as a function of concentration (% owf).

6.1 Conclusion

Although CNT dispersions are dye-like solutions, they are not classical dyes and, therefore, should not be applied onto polyester fabrics as such. The 'exhaust' style, a typical, almost traditional method of dyeing polyester, did not yield good results.

Miranol, CPC and their mixtures gave good dispersions for short periods of sonication. They were best applied on polyester fabrics by cold padding, especially short, drip-dry cycles in acidic dye baths in the presence of an electrolyte. After curing, washing with water has very little noticeable effect on the dyed fabric.

For all the 3 surfactants used, the polyester fabric was made electrically conductive. The electrical conductivity obtained varied with the type of surfactant: CPC > Miranol > Miranol+CPC. Miranol, the statistical median of the 3-reagent observations, had a percolation threshold of between 1-2.5% (owf). This implies that the percolation threshold of CPC was less than that of Miranol (1-2.5%), while that of a mixture of Miranol and CPC was greater than that of Miranol.

The dyed fabric exhibited good electrical conductivity in the region of 5.0×10^{-3} S/m. After the percolation threshold, conductivity increased with increase in the concentration of CNTs, just as demonstrated in other

composites involving pristine nanotubes (Sun *et al.*, 2013), up to a maximum of 5.5-6% (owf), after which the fabric ceased to absorb more nanotubes.

The electrical behaviour of the fabric was found to vary in a similar way as that of metals i.e., the resistivity or conductivity varies with the length of the conductor.

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CHARACTERISTICS STRENGTH OF REINFORCEMENT STEEL BARS (A CASE STUDY OF GUSAU METROPOLIS)

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ABSTRACT

The recent incidences of buildings collapses in various part of Nigeria have been a source of concern to Engineers and other building experts. The task of knowing the behavior and properties of the reinforcing steel bar use in Nigeria need to be understood. To achieve this reinforcement steel bars were obtained from Gusau market of which samples were taken for these research from three companies as company (A, B, and C). The test conducted and analyzed includes; bar size identification, ultimate tensile strength, percentage elongation and bend test for 10mm steel reinforcement. These samples were tested to a standard tensile test pieces and tensile test was done on it with the use of tensile testing machine. The results obtained were compared with that of the BS449 1997, reinforcement steel bars standards of 460N/mm² yield strength and 600 N/mm² of the ultimate yield strength, ASTM A706 reinforcement steel bars, standard limits of 415 N/mm² yield strength and 420 N/mm² for ultimate yield strength, Nigerian's professional's prescription of 410N/mm² yield strength and 580 N/mm² ultimate yield strength respectively. The results revealed that most of the 10mm selected steel bars are not up to standard with what is required in local and international standards, except that, in the case of elongation test all the reinforcement bars meet the required standard. The bending test was satisfactory because there was no sign of crack or residue to the physical eye after the bending.

INTRODUCTION

Concrete has been the most common building material in Nigeria and world at large and is best used in conjunction with reinforcing steel for optimal results. It is not easily corroded in the cement environment and it forms a relatively strong adhesive bond with cured concrete. This adhesion according to Arther et al., 2004 may be enhanced with the incorporation of contours unto the surface of the steel member which permits a greater degree of mechanical interlocking. The natural roughness of the mill scale of hot rolled reinforcing bars further provide bond or adhesion (Callister, 1997).

Incidence of building collapse is very frequent in Nigeria, and Anthony et al 2014 reported that over 95% of the cases of collapse affect reinforce concrete structure. This Nwakonobi and Umar, (2015) pointed out is due to these steels used in buildings without being subjected to any test to confirm the adequacy and compliance with Engineering standard.

Substitution of inferior steel to that specified in reinforcing has been reported as one of the major causes of structural failure (Jibrin, 2012).

The 10mm, steel rod is an important reinforcing bar for concrete. Information on the properties of this product from our local industries and imported ones are never available. This may be responsible for the high failure rate of construction projects in the nation. This work therefore is to assess some relevant mechanical properties of steel rods (10mm) produced by some steel industries in Nigeria and to compare same with some standards such as; Nigerian Steel Standard (Nst65-Mn, 1994), British Standard (BS4449, 1997), and American Society for Testing and Materials (ASTM,A706).

This means that adequate knowledge of materials and their properties will no doubt help the Engineers and designers to avoid mistakes that may lead to engineering failure. This is to determine the strength of reinforcement steel bars sold in Gusau area, and if known it will help to reduce the collapse or failure of structure in Gusau metropolis.

3.1 METHODOLOGY

3.2 MATERIALS

- i. Reinforcement steel bars (10mm)
- ii. Universal testing machine.
- iii. Vanier caliper.
- iv. Weighing balance.
- v. Bending machine/Compression machine.

3.3 COLLECTION OF MATERIALS

All the reinforcement steel bars samples were collected in Gusau, Zamfara state and all the samples were collected from shops in the market which are 10mm of average length of 500mm. The materials were taken to Civil Engineering Department of Federal Polytechnic Kaduna where all practical were conducted.

3.4 SAMPLES PREPARATION

The various samples specimens were arrange according to their product which where label as company A, B and C in other to achieve an accurate results. The specimens were first measured to know the actual length of each specimen which is 500mm diameter of average length the material was also weighed.

3.5 TENSILE STRENGTH TEST

The tension test specimen are measured to know the original length by using tape and the size of the steel is measure to know the original size of the steel bars by using the venire caliper before it was gage to the tension machine. When it is place in the machine the piece is grip or hold in the machine before the transmission of the load from the heads of the machine to the specimen under test then release it to allow the specimen until it break as shown with plate 1. Then all the readings or data are recorded for all the specimens. All this is done for all the samples specimens.

The load at which there is a halt or hesitation of the load indicating pointer is noted and termed the "yield point". The stress at this point is computed and termed the yield stress. The yield stress is calculated by dividing the load at the "yield point" by the nominal cross-sectional area of the test specimen.

Tensile Strength – Calculate the tensile strength of the Deformed Bar by dividing the maximum load the specimen sustains during a tension test by the original cross sectional area of the specimen.

$$\text{Yield Stress} = \frac{\text{Load at yield point}}{\text{Nominal Cross sectional Area}}$$

$$\text{Tensile Strength} = \frac{\text{Maximum load}}{\text{Nominal Cross sectional Area}}$$

3.6 ELONGATION

The percentage of elongation is determined by fitting the ends of the fractured Specimens together carefully and measure the distance between the gage marks to the nearest 1/8" (0.32 cm). The elongation is the increase in length of the gage length, expressed as a percentage of the original gage length. In reporting elongation values, give both the percentage increase and the original gage length.

$$EL = \frac{(\text{elongation at rapture}) \times 100}{(\text{initial gage length})}$$

Where EL = percentage elongation

3.7 BENDING TEST

The bend test is one method for evaluating ductility, but it cannot be considered as a quantitative means of predicting service performance in bending operations. The severity of the bend test is primarily a function of the angle of bend and inside diameter to which the specimen is bent, and of the cross-section of the specimen. These conditions are varied according to location and orientation of the test specimen and the chemical

composition, tensile properties, hardness, type, and quality of the steel specified. Bend the test specimen at room temperature to an inside diameter, as designated by the applicable product specifications, to the extent specified without major cracking on the outside of the bent portion as shown on plate 2 and 3. The speed of bending is ordinarily not an important factor.

4.0 RESULTS AND DISCUSSION

The results obtained from laboratory tests were used, to determine the percentage pass and failure rate of the materials being tested using a standard of 460N/mm² from BS 4449: 1997. But in Nigeria, structural designers are forced to adopt yield strength of 410N/mm² due to the substandard quality of reinforcement produced within the country and imported from other countries.

4.1 TENSILE STRENGTH TEST ANALYSIS

The average actual diameter of the sample, the Yield and maximum load, yield stress values, Maximum stress and percentage elongation obtained with the samples for tensile and elongation test are shown on Table 1. This shows that COMPANY A and B have values which are below the standard limit of 460N/mm² (Table 2) set by BS 4449; 1997 but also above limits of 415N/mm² and 420N/mm² set by ASTM A706. But company C are all above the standard. The ultimate or maximum tensile strength of all the steel product samples from COMPANY A, B and C tested were lower than the recommended limit of 600N/mm² by BS449, 1997 and Nst65-Mn1994 limit of 580 N/mm² by ASTM A706. The company A, B and C have low yield strength and ultimate strengths which are not good for construction companies.

TABLE 1: The average Yield Stress, Maximum Stress, and Elongation.

Identification no	Actual Diameter(mm)	Area (mm ²)	Yield Load (kN)	Maximum Load (kN)	Yield Stress (N/mm ²)	Maximum Stress (N/mm ²)	Elongation % at Max. Stress
A ₁₀ T	9.7	74.5	28.0	33.0	376	439.0	23
B ₁₀ T	9.5	71.5	28.0	31.7	390.9	442.7	25
C ₁₀ T	9.7	74.6	28	37	373	496.0	26

TABLE 2: TENSILE STRENGTH TEST

Identification no	Maximum Stress (N/mm ²)	BS449 (1997) Min. Provisions
A ₁₀ T	439.0	460
B ₁₀ T	442.7	460
C ₁₀ T	496.0	460

3. The elongation test for the entire reinforcement bar sample meet the requirement.
4. The yield stress and maximum stress for company (C) met the requirement and company A and B non meet the required standard.

5.2 RECOMMENDATIONS

- (i) It is also recommended that professional bodies and regulatory like the Council for the Regulation of Engineering in Nigeria (COREN) and Nigerian Society of Engineers (NSE) should collaborate with SON to ensure that trained technical personnel are employed to ascertain that due quality process are practiced in these industries.
- (iii) More research work should be necessary carry out from various localities to ascertain the suitability of the materials available in our local markets for use by the construction industries.

ACKNOWLEDGMENT

The technical staff of concrete and materials laboratory of the Department of Civil Engineering Technology of Federal Polytechnic Kaduna in person of Engr. Benjamin is acknowledged for his assistant during the laboratory experiments.

3.8 BENDING TEST ANALYSIS

For all the companies no cracks in the specimens

5.0 CONCLUSION AND RECOMMENDATIONS

5.1 CONCLUSION

Based on the results of the tests conducted and the analysis carried out on 30 samples collected from Gusau, the following conclusions were made.

1. The characteristic strength values for most of the 10mm diameter bar samples are low compared to the BS4449:1969, 1995& 1997 standards for high tensile steel which is 460N/mm² and 600N/mm² for maximum minimum value.
2. The characteristic strength values in respect of the bars as determined by the tensile test results. This implies the products are actually mild steel rolled and openly sold as high yield tensile steel.

Samples after Fracture and Bending Test



Plate 1: Tensile Test



Plate 2: Bending Test



Plate 3: Fractured and Bended Samples

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AUTOMATED COOLANT FLOW AND RECYCLING CONTROL DISTILLATION SYSTEMS

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ABSTRACT

Optimization of Glass Condensers by Solid Modelling was studied to determine the optimal lengths of the same designs and the optimal designs of the same lengths of Liebig, Allihn, Graham, Zigzag and their unconventional forms. 240 condensing glass solid models were designed and fabricated. Incidentally, the experiment was carried out when Ahmadu Bello University, Zaria's Dam was being dredged, so there was little or no water supplied to the laboratories for use. Therefore, an Automated Coolant Flow and Recycling Control Distillation Systems (ACFARECODS) for test running the 240 condensing models was designed and constructed. Automation can be programmable, flexible or fixed one. The latter form of automation is presented here and as opposed to open loop control system, it's a closed loop control type. Competitive materials speaking, ACFARECODS consisted of 60% polymeric, 16% metallic, 14% wooden and 10% glass materials. Four differential distillation sets ran concurrently. The models were characterized using tap water as purification liquid in distillation flasks and coolant flowed from 300litres upper GP tank to condense vapour from distillation flask and recycled back to another 300litres lower GP tank by gravitational force. The automated recycling system saved 99.54litres of coolant per hour from wastage. Consequently, the coolant lasted for a year before it was replaced with a fresh one. With four distillation sets operated concurrently and sequentially when necessary the time required for conducting four experiments was reduced from eight to two hours. ACFARECODS could be employed where distillation, refluxing and allied experiments required constant supply of tap water as coolant; in teaching science laboratories and by entrepreneurs interested in establishing small scale distilled water production businesses, especially in the rural areas or where there is scarcity of water.

Introduction

Optimization of Glass Condensers by Solid Modelling was a research conducted to determine the optimal lengths of the same designs and the optimal designs of the same lengths of common laboratory glass condensers viz; Liebig, Allihn, Graham and Zigzag condensers although the latter was a new design. 240 condensing glass solid models were designed and fabricated. Characterization of the models was by simple distillation rate and was carried out at the Department of Industrial Design, Ahmadu Bello University (ABU), Zaria. Incidentally, the experiment was carried out when ABU Dam was being dredged, so there was little or no water supply for use in the laboratory. Therefore, the need for an Automated Coolant Flow and Recycling Distillation Systems was imperative. Automation, laboratory automation, types of automation systems, control and types of control loops, design and fabrication of solid glass condensing models, distillation and Automated Coolant Flow Recycling Control Distillation Systems (ACFARECODS) are highlighted below.

Automation

Every day we come across technology and automated processes. Mankind has always tried to make work easier through mechanization and automation (Garavaglia, 2015). It is certainly difficult to make definitions in such a complex field as automation in which not only mechanisms, machines and instruments, but also reaction kinetics and measurement of physical quantities play important roles (Malissa, 2015). The term "automation" is now widely used and misunderstood in analytical chemistry, to mean either complete or partial replacement of a manual operation or sequence in or during analysis. This loose application of the term robs it of any precise meaning and results in it being in many cases a synonym for mechanization and instrumentation. Automation principles apply common sense approach which emphasizes on understanding an existing production process, simplifying the process and automating the process (O'Sullivan, 2009). Types of production process may include job shop production, batch production and mass production

Furthermore, Bissell (2009) highlighted that automatic control, particularly the application of feedback, has been fundamental to the development of automation. Chemical analyst considers

automation as a process by which analytical instruments perform many tests with the least involvement of an individual. The International Union of Pure and Applied Chemistry (IUPAC) define automation as "the replacement of human manipulative effort and facilities in the performance of a given process by mechanical and instrumental devices that are regulated by feedback of information so that an apparatus is self-monitoring or self adjusting". Presently no available instrument fully meets this definition, however, the term 'automation' is applicable to the individual steps in many analytical processes and modern instrumentation in improvising with more and more intelligence built into new generations of laboratory analyzers to soon come up to the IUPAC definition (Luthra, 2008; Corns, 1991 and Browner, 1979). This should not be confused with mechanization which is the use of mechanical devices to replace, refine, extend or supplement human effort (¹Anonymous 2015; O'Sullivan, 2009 and ²Anonymous, 2015).

Automation is a term which includes those developments which minimize human intervention in chemical analysis and thus releases the analyst for more demanding tasks, with an improvement in the efficiency of the analytical process (Stockwell, 1990). Kumar (2015) on the other hand, considered automation as a technology dealing with the application of mechatronics and computers for production of goods and services. And he broadly classified it into manufacturing automation and service automation. Manufacturing automation can be divided into fixed, programmable and flexible all with control systems (Kumar, 2015; O'Sullivan, 2009 and Gautam, 2015).

Fixed automation refers to the use of custom-engineered or special purpose equipment to automate a fixed sequence of processing or assembly operations for high production rates and inflexible product design (Kumar, 2015). This is also called hard automation. The primary drawbacks are the large initial investment in equipment and the relative inflexibility (Gautam, 2015 and O'Sullivan, 2009). ACFARECODS is a good example of fixed automation. Kumar (2015) opined that in programmable automation, the equipment is designed to accommodate a specific class of product changes and the processing or assembly operations can be changed by

modifying the control program suited to batch production. In programmable automation, reconfiguring the system for a new product is time consuming because it involves reprogramming and set up for the machines, and new fixtures and tools (O'Sullivan, 2009 and Gautam, 2015).

In flexible automation, the equipment is designed to manufacture a variety of products or parts and very little time is spent on changing from one product to another. A flexible manufacturing system can be used to manufacture various combinations of products according to any specified schedule for low production rates, varying product design and demand (Kumar, 2015; O'Sullivan, 2009 and Gautam, 2015).

Control Systems

A control system is an arrangement of physical components connected or related in such a manner as to command, direct, or regulate itself or another system. Fixed automation, programmable automation and flexible automation cannot work successfully without control systems. There are essentially two categories of control systems: open-loop and closed-loop. Both maintain a chosen variable at a selected level with different levels of success. Open- and closed-loop control systems try to maintain a variable at a predetermined value. Control systems incorporate measurement systems, but unlike a pure measurement system the output from a control system regulates a parameter whose value is not necessarily displayed to the user (Omirou, 2015).

Open Loop Control System

Open loop and closed loop control systems share most of their constituent parts. The first section of a control system is an input. This can be analog or digital, and can indeed take nearly any form imaginable. An open-loop control system is one in which the control action is independent of the output (Figure 1). Open-loop control systems are in general relatively simple in design and in-expensive. However, they can be inefficient and require frequent operator intervention. Under many

circumstances pre-set values become incorrect due to the parameter they are controlling changing in some way, and so they need resetting. The pre-set value often needs a high level of skill or judgment to set it correctly. Examples of inputs are position, velocity, heat, or intensity of light. A characteristic of the open-loop controller is that it does not use feedback to determine if its output has achieved the desired goal of the input. This means that the system does not observe the output of the processes that it is controlling. Consequently, a true open-loop system can not engage in machine learning and also cannot correct any errors that it could make. It also may not compensate for disturbances in the system (Hayden *et al*, 2014; Bishop, 2002; Bissell, 2009; Omirou, 2015 and Anonymous, 2015).

Closed Loop Control Systems

In closed loop control, the system is self adjusting. A closed-loop control system is one in which the control action is somehow dependent on the output (Figure 2). The state of the output directly affects the input condition. A closed-loop control system measures the value of the parameter being controlled at the output of the system and compares this to the desired value. Data does not flow one way; it may pass back from a specific amplifier (such as velocity or position) to the start of the control system, telling it to adjust itself accordingly. Many physical systems are closed loop control at the lowest level since the data about velocity and current position modify the output (also position) at consistent rate. Close loop control systems use the open loop systems (as forward path) and feedback from the output to decide the input level to the open loop system. And because the input is decided based on how much away the output is from the desired level, the non idealities in forward path do not degrade the system performance. The accuracy of the output thus depends on the feedback path, which in general can be made very accurate (Hayden *et al*, 2014; Bishop, 2002; Bissell, 2009; Omirou, 2015 and Anonymous, 2015).

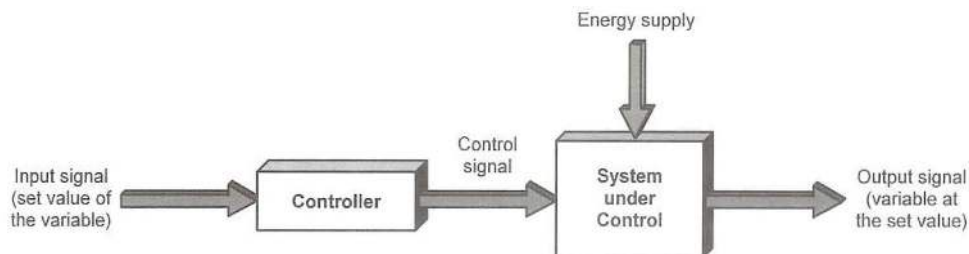


Fig. 1: Open-loop Control System (Source: Omirou, 2015)

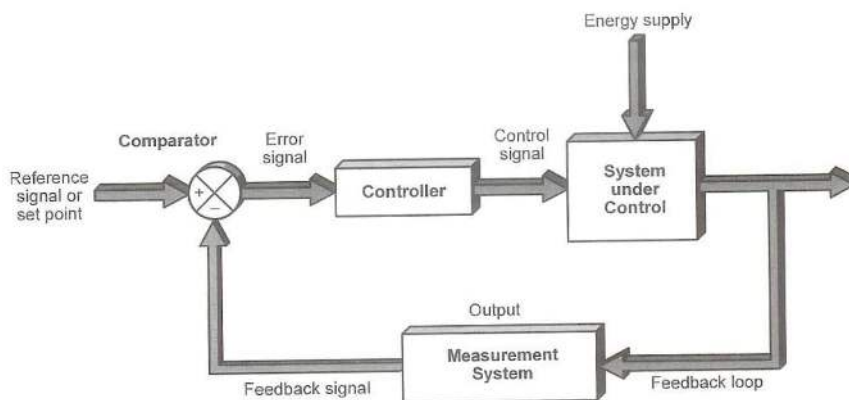


Fig. 2: Closed-loop Control Systems (Source: Omirou, 2015)

Once the input passes into the start of the system, it undergoes amplification of various kinds. The two primary types of amplifiers are transfer functions and gains. Transfer functions modify the input in some way to put it into a format desired for output, and generally take the form of output (from the transfer function) over input (into the transfer function). Gains, on the other hand, are usually flat multipliers to increase or decrease the value of the signal.

The data leaves the system through the output, which is the end point of the signal. Sufficiently complex systems can be broken down into more simple inputs and outputs, and vice versa. For example, a very complex control system with multiple gains, transfer functions, and feedback can have it all simplified to a single transfer function, though it may be harder to understand the source of each mathematical section (Hayden *et al.*, 2014; Bishop, 2002; Bissell, 2009; Omirou, 2015 and ¹Anonymous, 2015).

Fig 2 shows a closed-loop system in flow diagram form, the desired value is known as the reference signal, or set point. This is compared to the signal from the measurement device, known as the feedback signal. The difference between the feedback signal and the reference signal is known as the error signal. The error signal is then modified so that it can adjust the performance of the system. For example, if the error signal is an electrical signal, it may need amplification. The modified error signal is called the control signal. The control signal then adjusts the output of the system, to try to match the feedback signal to the reference signal. This would reduce the error signal to zero and so achieve the desired value (Hayden *et al.*, 2014; Bishop, 2002; Omirou, 2015 and ¹Anonymous, 2015).

Finally, some control systems have disturbance, which is data that modifies or corrupts the signal in an unwanted way, and affects the output as such. Good control systems seek to minimize disturbance and keep the original input signal as pure as possible (Hayden *et al.*, 2014; Bishop, 2002 and ¹Anonymous, 2015).

Automation in the Laboratory

Koch (2015) expressed that automation of analytical processes becomes a necessity both in research and industrial laboratories whenever a large number of identical tests have to be carried out as rationally and reliably as possible. This task is relatively easy to accomplish when the choice of the method is left to the investigator; it is much more difficult when, for production control, individual results must be made available within a very short period of time which is dictated by the process pursued, in which case only such a method can be selected that meets with these requirements. It is certainly not only the chemical industry which depends on the information from analytical chemistry for control and regulation of automated processes (Mallissa, 2015). By its very nature, it is a multidisciplinary subject involving chemistry, computing, design, mechatronic and economics. This concept of automation is becoming increasingly important and to ensure rapid developments in the field of laboratory automation, collection of specialists must work together as a multidisciplinary team.

The momentum behind analytical automation began in the late 1950's when air-segmented continuous flow was introduced by Technicon (Bristol, 2000). This approach dominated laboratory automation for many years. The main reason for automating an analytical process has always been and always will be related to economic considerations. The basic costs of performing both manual and automated analysis have been expressed algebraically (Corns, 1991 and Stockwell, 1990). The cost of manual analysis (C_{MAN}) is expressed as:

$$C_{MAN} = F_{MAN} (T_s A_s + T_p A_p + T_m A_m + T_c A_c) \text{ -----(1)}$$

where T_s , T_p , T_m and T_c represent the time taken for sampling, pretreatment, measurement and calculation of the result respectively. The corresponding 'A' factors represent the proportion of the operators time for each stage of the analysis. Therefore time consuming operations such as drying or ashing would have large 'A' values. 'F' is a tariff factor which converts time into money. The cost of the same analysis using fully automated procedures (C_{AUTO}) can be expressed as:

$$C_{AUTO} = F_{AUTO} (T_{AUTO} A_{AUTO} + T_{MAINT} A_{MAINT}) \text{ -----(2)}$$

where T_{AUTO} and T_{MAINT} are the times for automatic analysis and maintenance of the equipment respectively. A_{AUTO} and A_{MAINT} represent the amount of activity or involvement of the operator for analysis and maintenance respectively. By consideration of the terms within equations (1) and (2) it is also possible to represent algebraically semi-automated systems. Although these expressions are only approximate they allow one to assess whether or not the introduction of automation for a particular application is cost effective (Corns, 1991).

Christian (2004) explained that there are two basic types of automation equipment. Automatic devices perform specific operations at given points in an analysis, frequently the measurement steps. He continued, thus an automatic titrator will stop a titration at the end point, either mechanically or electrically, upon sensing a change in the property of the solution. Whereas automated devices, on the other hand, control and regulate a process without human intervention. They do so through mechanical and electronic devices that is regulated by means of feedback information from a sensor or sensors. Hence an automated titrator may maintain a sample pH at a preset level by addition of acid or base as drift from the set pH is sensed by a pH electrode (Christian, 2004).

Terminology of Automation in and with Analytical Chemistry

Mallissa (2015) numerated the following terminologies: (a) Mechanization: for production and transmitting of movements. (b) Instrumentation: for machines which are mainly producing useful signals but can also include movements. (c) Automation: a system in which a part of the human power of decision is removed by a combination of machines and/or instruments. (d) Kybermatation: is when the (final) result of the (analytical) control step is used to the regulation of the (chemical) process concerned, without further human decision (Mallissa, 2015).

Automation in and with Analytical Chemistry

Mallissa (2015) highlighted that there is a great difference in "automation in analytical chemistry" and "automation with analytical chemistry". The former is usually connected with a high degree of instrumentation plus the strong use of computers for getting analytical results; the latter—which leads doubtless to kybermatation -is using the analytical signals and/or results in order to get via transfer (feed-back or feed-forward) a self-regulation (without human decision) of the process. To achieve a real automation in and with analytical chemistry the proper use of chemical and/or physical reaction, the knowledge of kybernetics and other disciplines is necessary. It may be that a new kind of language and symbolism must be developed (a) for automation in analytical chemistry: Anachel (Analytical chemistry language); (b) for kybermatation: Chemprol (Chemistry processing language) (Mallissa, 2015).

Advantages of Automation

One of the major economic advantages offered by the introduction of totally automated systems is the capability of

equipment to be operational during non-working hours. This requires a high order of reliability and safety. Most fully automated systems possess shut down procedures, for use when major deviations in instrument performance occur. Minor deviations are more difficult to detect and often go unnoticed. Automated systems not only increase sample throughput, but also offer a more effective division of labour throughout the laboratory, reducing the need for people to do routine repetitive tasks and freeing them for more interesting work.

Slightly different views in respect of the social implications of automation and mechanization are held that intelligent machines in some instances may replace skilled workers, demoting them to do unskilled work, consequently retiring those originally doing the unskilled work. He also stressed the importance of the realization that the abilities of machines and people are different, and complementary, and that the designer of the automated system should consider these different qualities (Frey and Osborne, 2013).

Apart from the economic benefits, automation also offers scientific advantages. One of these being the improved precision obtained for the analysis of large batches of samples, from the elimination of human error and fatigue. Applications which involve accurately timed reaction sequences also become more reproducible when automated. The possibility of performing automatic analysis in closed systems, especially for materials which are toxic or unstable in air is also of considerable importance for certain applications, such as those involving radioactivity.

Limitations of Automation

Limitations of automation also exist; most automated analytical equipments are designed in most instances to process batches of samples of similar composition. Samples with varying concentration and matrix composition may affect the measurement device, thereby giving inaccurate results. This situation is more likely to occur in industry, where samples may have a variety of sources, compared to say clinical samples such as blood and urine which have similar compositions. This problem can be overcome by the skill of the analytical chemist by devising new methods of analysis. In designing an automated system the hardware available may cause restraints on the four materials used in construction, the engineer's role in the development of automated analytical equipment is therefore vital.

Further limitations arise when staffs of limited experience and qualifications operate automated equipment. This arrangement is common practice and normally very successful, however, any minor deviation in instrument performance may be unnoticed by inexperienced staff. There is also a human element that one must consider when introducing new automated analytical equipment into the laboratory, in that, the new user will often try to undermine the performance of the instrument in an attempt to prove that the analyst can perform a more efficient job. The concern over technological unemployment is hardly a recent phenomenon. Throughout history, the process of creative destruction, following technological inventions, has created enormous wealth, but also undesired disruptions (Frey and Osborne, 2013).

In addition, there are a number of situations which manual labour is usually preferred over automation: when a task is too technological difficult to be automated, for short product life cycle, customized product, coping with ups and downs in demand and to reduce risk of product failure (O'Sullivan, 2009). The above definitions, types, advantages, disadvantages and multidisciplinary nature of automation were adopted for

the design and fabrication of the "Automated Coolant Flow and Recycling Control in Multiple Distillation Systems".

Design and Fabrication

240 surface glass condensers of 240mm, 360mm, 480mm, 600mm and 720mm lengths per design were designed and fabricated. Steam flows through the inner concentric tubes in type 'As' and through the outer concentric tubes in type 'Bs'. Every design consisted of five varied lengths of 240mm, 360mm, 480mm, 600mm and 720mm which made up a total of 240 condensing models.

In conventional practice, 120mm and 600mm lengths are the shortest and longest respectively. However, in this design research 240mm was adopted as the shortest and 720mm as longest to accommodate structural designs and modifications. The new condensing models would optimally affect performance, quantities of fluids resident within the exchangers, amount of materials for fabrication, cost and safety. Borosilicate glass material was selected for fabrication on the premise of its thermal, mechanical, chemical and safety considerations.

Principle of Distillation

A simple distillation principle was adopted for the characterization. Distillation is one of the oldest and still most common methods for both the purification and the identification of liquids. It is a physical process used to separate chemicals from a mixture by the difference in how easily they vaporize. The rate of distillation largely depends on the efficiency of the heat exchanger. As the liquid is heated, the temperature rises until it reaches the temperature of the boiling substance in the Wirtz flask. The resultant hot vapour passes into a heat exchanger and is converted to the liquid, which is then collected in a receiver container.

Automated Coolant Flow and Recycling Distillation System

The experiment was carried out in Glass Technology Laboratory, Department of Industrial Design, Ahmadu Bello University, Zaria. A system of four differential distillation sets were designed, assembled and run concurrently as shown in Figure 3 and Plates I and II). A set was made up of a laboratory jack, a heating mantle, 1000mls distillation flask, a condenser, two thermometers, two rubber bungs, a delivery adaptor and two distillate collectors (two 50mls measuring cylinders). Tap water was employed as both distillation solvent and coolant in the characterization. To avoid the risks of water bumping over the flasks, the distillation flask was 2/3 filled with tap water and 50 glass beads were put in it. Water as coolant flowed through the four distillation sets. The upper and the lower water tanks served as the source and destination of the coolant respectively. From the angle of competitive materials selection approach, the Automated Coolant Flow and Recycling Control Distillation Systems consisted of about 60% polymeric, 16% metallic, 14% wooden and 10% glass materials.

The four distillation sets were arranged in parallel with two sets on each side and both operated concurrently (Figure 3 and Plates I and II). However, one or more could be in operation while other sets are not. Two distillation sets were arranged in series on each side with common coolant supply from a split main pipe coming from the upper (top) 300litres GP tank. The outlet-coolant for one set became the inlet coolant for the second set, and then the coolant returned to the lower (bottom) 300litres GP tank from the outlet of the second set through PVC tubing by gravity force. In other words, coolant flows from upper tank to condensers arranged in series; used coolant flows into lower tank, which is automatically pumped back to the upper tank (Plates I and II); the cycle continues so long as the system is connected to source of power. 750mls tap water and

50 glass balls or beads were put into each 1000mls Wurtz flasks. With the aid of rubber bungs glass condensing models were fitted to the stems of the Wurtz flasks, thermometers were inserted into the mouths of the four Wurtz flasks and adaptor deliveries to distillate collectors with the aid of rubber bungs and corks. Coolants were first turned on, followed by turning on SEARCHTECH instrument heating mantles. Distillates were read and collected in 50mls measuring cylinders into jerrycans in five minutes intervals per hour per every glass condensing model (Plates I and II).

Results, Discussion and Conclusion

Based on materials selection approach, Automated Coolant Flow and Recycling Control Distillation Systems consisted of 60% polymeric, 16% metallic, 14% wooden and 10% glass materials. The improvised ACFARECODS designed, fabricated and employed for characterizing 240 condensing solid models saved 99.54litres of coolant (water) per hour from being wasted. Consequently, the coolant lasted for a year before it was replaced with a fresh one. With the designed and fabricated improvised coolant automated recycling systems, four distillation sets operated concurrently and sequentially when necessary; thereby reducing the time of conducting four experiments from eight to two hours. The improvised coolant automated recycling system designed and fabricated as an alternative to running tap water can be adapted in teaching science laboratories and by entrepreneurs interested in establishing small scale distilled water production businesses, especially in the rural areas or where there is scarcity of water.

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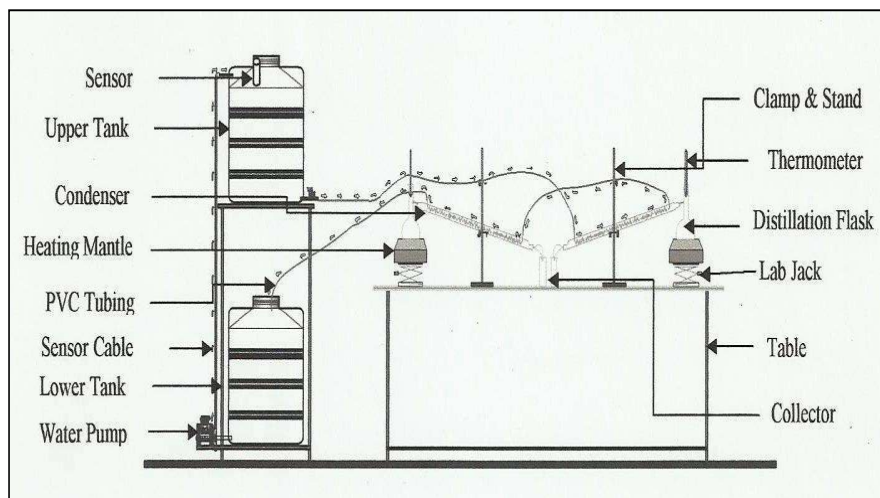


Figure 3: Automated Coolant Flow and Recycling Distillation System



Plate I: Automated Coolant Recycling Distillation System



Plate II: Arrows Showing the Directions of Coolant Flow

THE EFFECT OF CHICKEN FEATHER ON THE PRODUCTION OF BIOGAS FROM COW DUNG

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ABSTRACT

This study was carried out to evaluate the potential use of cow dung (CD) and chicken feather (CF) in producing Biogas and through anaerobic co-digestion with each other at different percentage ratios for a period of 37 days retention time. The total volumes of the gas produced were 0.171188m³, 0.094286m³, 0.059321m³, 0.030594m³, and 0.000304m³ for 100%CD, 75%CD-25%CF, 50%CD50%CF, 25%CD 75%CF, 100%CF respectively. It was observed that biogas production was optimized when cow dung and chicken feather were mixed in different ratio of (0-100%). It was observed that 100%CD produced the highest Biogas, but when the Chicken feather increases the production rate decreases, this could be as a results of inhibiting factor such as high keratin content with long fatty Acids associated with the feather, and was regarded as failed digester as it does not produce significant amount of biogas. The average temperatures of the digesters recorded in the morning, afternoon and evening were between 26⁰C-43⁰C while the average ambient temperature observed during the study was 34⁰C which were within the mesophilic range. The pH values of the media in all the substrates digested varied almost within the optimal limits for methanogenic bacteria (pH: 6.0 -7.4), except for 100% Chicken feather which shows slightly acidic. The carbon to nitrogen ratio measured was within the optimum range of **20:1 to 30:1**. The modified Gompertz equation was used to adequately describe the cumulative biogas production from these digesters. The constants were determined using the non linear regression approach with the aid the solver function of the Microsoft excel tool pack. Biogas production is found to be feasible from the wastes; the inflammability test was conducted during anaerobic digestion.

Keywords: Cow dung; Chicken feather; Anaerobic; Modified gomperzt model.

1.1 Introduction

Biogas is a clean, environmental friendly and renewable form of energy generated when micro-organisms degrade organic materials in an oxygen free environment. The formation of biogas can occur either in natural environment or controlled conditions in constructed biogas plants, so called anaerobic degradation (AD). Swamps, marshes, river beds, rumen of herbivorous animals are some of the areas where biogas is formed naturally; the same microbial activities are achieved in both natural and controlled conditions. The feedstock for biogas production in constructed plants is more or less any organic fractions from household organic waste to dedicated energy crops like maize (Lantz et al., 2007). The potential feedstock for the production of biogas include; municipal solid waste, industrial organic waste, garden waste, agricultural waste (manure and crop residue), energy crops, cellulose rich biomass, algae and seaweed (water based), by-products of ethanol and bio diesel production (Lantz et al., 2007).

Inadequate energy supply and environmental pollution are gargantuan problems confronting Nigeria. With high population growth rate, access to adequate energy and healthy environment demands for a diversification of sources of energy supply, if Nigeria is to achieve any meaningful growth and development, Biogas generation from anaerobic digestion of readily available wastes could contribute to solving these problems. From the global perspective, the over- dependence on fossil fuels as primary source of energy has resulted in climate change, many environmental destruction and related human health problems (Budiyo et al., 2010). The joint challenge of global pollution and depletion of fossil fuels is driving intense research into alternative renewable energy sources, among which is the biogas. (Alfa et al., 2012). Biogas is produced by the Anaerobic Digestion (AD) of organic waste through the synergistic metabolic activities of consortia of hydrolytic, acidogenic, acetogenic and methanogenic bacteria on organic materials (Li Yebo et al., 2011).

The purpose of this research therefore is to investigate the effects of co-digestion with chicken feather on the production of biogas from cow dung within the mesophilic temperature range. Biogas modeled kinetics were developed using modified Gompertz models with cumulative biogas production.

2.0 Materials and Methods

2.1 Collection and Preparation of Cow dung and Chicken Feather.

In order to accomplish this research, two kinds of organic waste substances were collected from Zaria city and utilized for biogas production and model study experiments. These substrates are Cow dung (CM), and Chicken feather (CF). Freshly plucked chicken feathers was collected from the poultry slaughter house of Zaria city market, and then washed with tap water to remove sand and other particles. The washed chicken feathers were placed in dryer boxes at 450C (Xia et al., 2012). After drying, the feathers was grinded using a hammer mill to a very small particle size of about 4mm. Cow dung was collected from Zaria city and divided into six (6) samples and neatly stored in six different polyethene bags labeled PM1, PM2, PM3, PM4 and PM5. Laboratory analyses and operational parameters of the chosen substrates were conducted such as Carbon nitrogen ratio, temperature and pH. Etc

2.2 Experimental Design of pilot scale anaerobic digesters

The design theory adopted for this study combines the (Alfa, 2013) comparative production and utilization of biogas for cooking, using cow dung, chicken droppings, *Cymbopogon citratus* (lemon grass) as well as the respective co-digestion of cow dung and chicken droppings with *Cymbopogon citratus* (lemon grass) and Ajoy Karki's kitchen waste Biogas model (Karki, 2002) and the separate floating gas holder system. The cylindrical shape was adopted to enhance better mixing. The separate gas holder system was incorporated into this design to allow for ease of measurement of gas volume at atmospheric pressure. The succeeding sections give details of the principles and design consideration for the digester type adopted (Alfa, 2013). The digester is a separate

component, with the gas holder (inverted drum) floating in a separate water jacket.

The theory behind the design is simply “downward delivery and upward displacement”. The slurry on fermenting in the digester produces gas. This gas is delivered to the bottom of the water jacket via a pipe; the pipe extends above the surface of the water level (water seal) in the water jacket. The gas displaces the gas holder (upward) and gets trapped between

the gas holder and the water seal. The displacement of the gas holder is dependent on the pressure and volume of the gas produced.

The main constituents of this gas, methane and CO₂ are only sparingly soluble in water, thus the gas is collected and transferred to the kitchen where it is used for cooking. Figure 1 shows a schematic view of the plant set up.

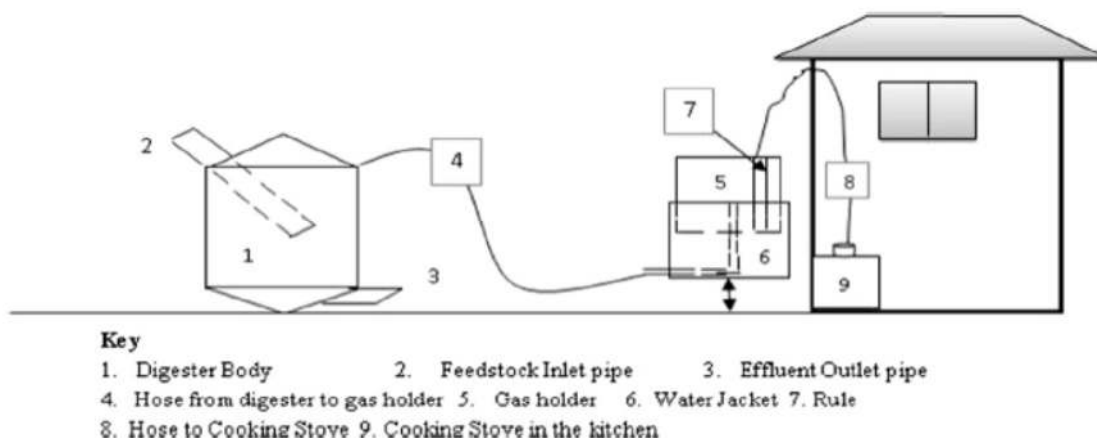


Fig. 1. Schematic View of the Project Set up (Alfa *et al.*, 2014)

2.3 Experimental design and set-up

A Set of five batch reactors fabricated were used as digesters. Each digester contained organic waste and co-digested at different percentage ratios (Ranging from 0-100%). the substrates are mixed at different ratios to obtain slurry, 6kg of the respective wastes mixed with water to form slurry in the ratio 1:1 by volume were separately introduced into each digester through an inlet pipe of 50mm at the top of the digester tank. In the case of the synergies of the cow dung and chicken feather respectively. Percentage of each substrate was varied at different ratios. Each co-substrate contributed from 25%, 50%, 75% and 100% (1.5kg 3kg, 4.5k, 6kg) each to make the 6kg of biomass which was then mixed with water to form slurry in the ratio 1:1. The slurry is allowed to occupy three quarter of the digester space leaving a clear height of about 0.0625m as space for the gas production. The inflow was directed downward to cause the solids to accumulate at the bottom of the tank where after digestion they were easily removed. Before feeding the reactors, the flexible plastic pipe connecting the gas outlet from the reactor to the gas holder was disconnected, such that the gas outlet from the reactor was left open. This was done to prevent negative pressure build up in the reactor. The gas was collected from the digester through a 15mm diameter flexible host connected from the digester to the bottom of the gas collection system. The collected gas is allowed to pass through water and slaked lime respectively as scrubbers. (Alfa *et al.*, 2013).

2.4. Method of measurement of gas production

The gas holder was calibrated with the aid of a rule to enable the reading of the daily gas production from digested. The volume of biogas produced was measured each day at 5pm by computing the volume of the gas holder floating over water level in the water jacket. The details of this method of measurement has been described in (Alfa *et al.*, 2013)

2.5 Analysis of the Cumulative Biogas Production with the Modified Gompertz Model

The scope of the model study in this research was restricted to the studying of the cumulative biogas production using the modified gompertz equation. Thus, modified gompertz equation was used to model cumulative biogas production from cow dung, horse dung and chicken feather.

The equation (2.1) shows modified gompertz equation

$$Y = A \exp \left\{ - \exp \left[\frac{\mu_m e}{A} (\lambda - T) + 1 \right] \right\} \quad 2.1$$

where:

Y (t) = cumulative biogas produced (m³) at any time (t)

A = biogas production potential (M³)

λ = Lag phase period (days), which is the min time taken to produce biogas or time taken for bacterial to acclimatize to the environment.

t = cumulative time for biogas production (days) and

e = mathematical constant (2.718282)

μ = maximum biogas production rate

(mathari *et al.*, 2015; yusuf *et al.*, 2011; Alfa *et al.*, 2016).

The constants A, μ_m and λ were determined using the non linear regression approach with the aid the solver function of the Microsoft excel tool pack.

The modified gompertz equation has been extensively used by researchers to study the cumulative/methane production as well as bacteria growth in both biogas and biogas production studies (budiyo *et al.*, 2010; lay *et al.*, 1996; mathari *et al* 2015, Alfa *et al.*, 2016).

3.0 RESULTS AND DISCUSSION

The quantity of biogas produced from cow dung and chicken feather over a period of 37 days retention time at an average ambient temperature of 34.1 ± 2 °C are as presented in Fig. 1

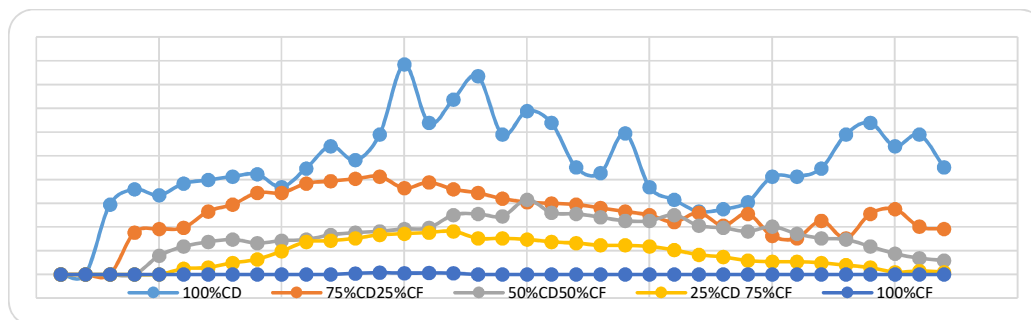


Figure 1: daily biogas production from cow dung and chicken feather at different percentage ratios.

Table 1: Substrate pH during the Retention Period

R. Time	25%CD75%CF	50%CD50%CF	75%CD 25%CF	100% CD	100%CF
1	6.24	6.36	5.78	5.74	5.7
5	6.32	6.5	6.43	6.2	6.0
10	6.7	6.6	6.61	6.4	6.3
15	6.8	6.71	6.73	6.7	6.1
20	6.8	6.61	6.74	6.97	6.0
25	6.82	6.7	6.81	7.15	5.7
30	6.81	6.71	6.1	7.2	5.4
35	6.64	6.71	6.46	6.62	5.3

Source: Ishaq (2016)

Biogas production was first observed on the second, third, fourth, fifth and fourteen day as 100%CD, 75%CD-25%CF, 50%CD-50%CF, 25%CD-75%CF and 100%CF respectively, of setting up the digester. Biogas production from the Cow dung in the digester increased gradually before reaching a maximum daily output.

All the feedstock showed a general increase in pH with minimal fluctuation. This progressive increase in pH could account for steady rate of gas production which is in agreement with the studies carried out previously by Ahmadu (2009) and Igboro (2011), except for chicken feather which shows a downward trend. The pH falls from 6.5 to 5.2. This could be associated with the low gas production, which is in agreement with the studies carried out previously by Ahmadu (2009), Golueke (2002), Igboro (2011), which suggest low pH as a limiting factor for biogas production.

Methanogenic bacteria are very sensitive to pH and do not thrive below a value of 6.0 (Karki *et al*, 2005).

Carbon to nitrogen Ratio of Cow dung and Chicken feathers is fairly in agreement with the optimum i.e. carbon to nitrogen ratio (C/N) of **20:1 to 30:1** as stated by Braun, 1982.

3.1 Results analysis of the cumulative biogas production with the modified gompertz model.

The results of the cumulative biogas production from the co-digestion of cow dung with chicken feathers are presented on figure 3. The total volume of biogas produced 0.171188m³, 0.094286m³, 0.059321m³, 0.030594m³, and 0.000304m³ for 100%CD, 75%CD-25%CF, 50%CD-50%CF, 25%CD-75%CF and 100%CF respectively. It was observed that cow dung alone produced the highest biogas yield and this could attribute to multiply of microbial organism within the methanogenesis stage, which increased the substantial production of biogas. However, there was a steady reduction in the biogas production as chicken feather increases, the biogas potential decreases and this could be inferred that, the chicken feather was either neutral in the digestion process or had inhibiting effects (keratin content) in the process. This assertion could be validated from the result of cow dung digested singly.

However, (Salminen *et al.*, 2003) shows that chicken feathers produced low methane yield, when subjected to pretreatments and enzymatic (commercial alkaline endopeptidase) there would be an increased of methane yield by 37 to 50%. Chemical such as sodium hydroxide improved methane yield by 5 to 32% by breaking down the disulfide bonds, thus, opening up the keratin structure and the sulphur content liberated as hydrogen sulphide H₂S. Therefore anaerobic digestion of chicken feather appears promising possibility because of the high methane yield and nitrogen content.

The modified Gompertz model was used to fit the cumulative biogas production which was observed to adequately describe the biogas production from these substrates as shown in Figure 3.

The total biogas volume as well as the estimated kinetics parameters evaluated using non-linear regression is shown in Table 2.

During the retention Period of 37days 100%CD had the highest biogas production potential biogas production potential (A) of 0.1711875m³ at a maximum biogas production rate (μ) 0.006326m³/day with a lag phase (λ) of 5.718365days. at 75%CD-25%CF biogas production potential (A) of 0.0942857m³ at a maximum biogas production rate (μ) 0.003849m³/day with a lag phase (λ) of 5.629287days. At 50%CD-50%CF biogas production potential (A) of 0.0724784m³ at a maximum biogas production rate (μ) 0.002537m³/day with a lag phase (λ) of 8.59421days. At 25%CD-75%CF biogas production potential (A) of 0.0305938m³ at a maximum biogas production rate (μ) 0.00176m³/day with a lag phase (λ) of 9.216072days. AT **100%CF** biogas production potential (A) of 0.0003045m³ at a maximum biogas production rate (μ) 7.04E-05m³/day with a lag phase (λ) of 12days. Digester with 100%CF failed to produce any significant amount of biogas and this could be attributed to the sub-optimum carbon to nitrogen ratio present and/or the increase in the lignin content of this mixture as percentage of chicken feather increased. The model was able to fit the data set with a goodness of fit (R^2) of 0.9608.

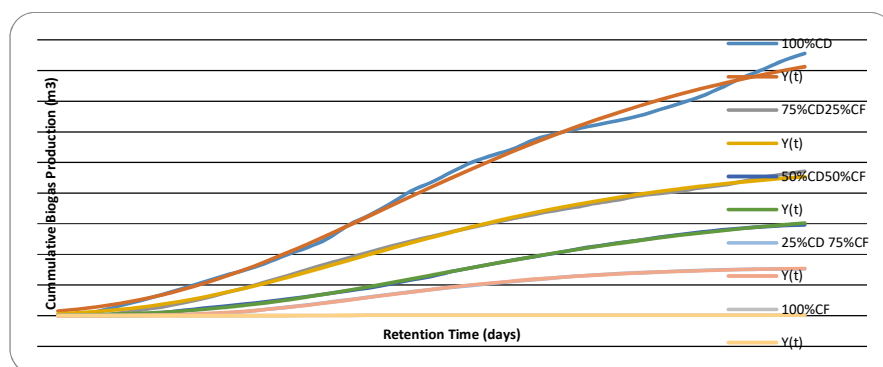


Figure 3 Gompertz cumulative biogas productions from cow dung and chicken feather.

Table 2: Model Study with Modified Gompertz Equation using excel solver function.

SUBSTRATES	TOTAL BIOGAS(m ³)	A (m ³)	μ (m ³ /day)	λ (days)	SSE	R ²
100%CD	0.1711875	0.1711875	0.006326	5.718365	4.5E-04	0.962302
75%CD25%CF	0.094285714	0.0942857	0.003849	5.629287	8.5E-05	0.992651
50%CD50%CF	0.059321429	0.0724784	0.002537	8.59421	1.03E-05	0.999335
25%CD75%CF	0.03059375	0.0305938	0.00176	9.216072	1.01E-06	0.999934
100%CF	0.000304464	0.0003045	7.04E-05	12	2.82E-09	1

CONCLUSIONS

Biogas production from cow dung was established here to be feasible at room temperature. Application of the modified Gompertz equation in studying the biogas production was able to predict the pattern of biogas production with time. It was observed that the maximum biogas production could be obtained from substrate in digester (100% cow dung) which was closely followed by substrate mixture containing (75% cowdung-25%chicken feather), (50%CD-50%CF), (25%CD-75%CF) and lastly by substrate mixture comprising (100% CF). Digester with 100% chicken feather digested alone was classified as failed digesters because of their inability to produce any measurable amount of biogas at the end of the digestion period.

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EFFECT OF REACTION VARIABLES ON ESTERIFICATION OF OLEIC ACID

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ABSTRACT

The influence of reaction variables namely oil (oleic acid) to methanol molar ratio, catalyst loading and reaction time on methyl oleate yield as well as the conversion of oleic acid was investigated. The oil/ methanol molar ratio was studied within the range of 1:3-1:15, catalyst loading was studied within the range of 3wt% to 9wt% and reaction time was studied within 1h to 9h. The experimental design was achieved using design expert 7.6.1 based on box Behnken design (BBD). The sulfated titania- silica catalyst used was prepared by reacting silica with titanium isopropoxide and then impregnated in sulfuric acid for 24 h. The analysis of variance (ANOVA) shows that oil /methanol molar ratio, reaction time as well as catalyst loading were all found to be significant and therefore influence the responses. The interaction between reaction time and catalyst loading as well as between reaction time and molar ratio revealed synergistic effect while the interaction between molar ratio and catalyst loading showed antagonistic effect and therefore has less influence. The esterification gave rise to methyl oleate yield of 81% and oleic acid conversion of 94% respectively.

Keywords: Esterification, titanium isopropoxide, sulfated titania-silica catalyst.

1. Introduction

Esterification replaces transesterification when oils and fats characterized with high FFA are used. Esterification is usually conducted in a homogeneous phase using acid catalysts such as H₂SO₄, HF, H₃PO₄, HCl and p-toluene sulfonic acid (Carmo *et al.*, 2009). However, because the aforementioned acids are hazardous and corrosive, their use is dangerous. Therefore, acid heterogeneous catalysts are employed as a better option to mitigate the environmental effects as well as the end biodiesel cost (Do Nascimento *et al.*, 2011). Several solid acid catalysts such as zirconium oxide, titanium oxide, tin oxide, sulfonic ion-exchange resin, sulfonic modified mesostructure silica, sulfonated carbon-based catalyst, heteropolyacids (HPAs) (Badday *et al.*, 2012); have been studied for the esterification of FFA. Lately, the use of aluminosilicates (mordenite, halloysite, kaolinite), zirconium oxides and cation-exchange resins as heterogeneous acid solids were also studied (Jung and Grange, 2001).

Transesterification can be classified into (a) catalytic and (b) non catalytic. However, this research focuses only on the catalytic transesterification. The use of different types of catalysts improves the reaction rate as well as the yield of the biodiesel produced. Transesterification reaction is a reversible process and it is favoured by having alcohol as the excess reactant. This is because excess alcohol shifts the equilibrium to the product side (Ma and Hanna, 1999; Talebean et al 2013). Equations 1-3 show the general transesterification reaction steps.

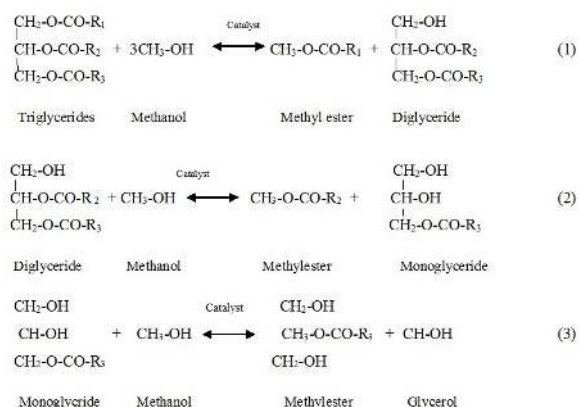


Fig.1-3: Steps for transesterification reaction

Esterification as well as transesterification is governed by certain key parameters which include molar ratio of oil to solvent, catalyst loading, reaction time, reaction temperature, stirring rate as well as other factors depending on the expected outcome of the process in question. In this study, only three variables were studied (Lee *et al.*, 2014).

Molar ratio is a very important variable that affects the yield of FAME produced during transesterification reaction. In general, transesterification is an equilibrium reaction; FAME formation can usually be increased by adding excess alcohol to shift the equilibrium to the product side (Suski and Tarniowy, 2001). The stoichiometric requirement of transesterification is 3 moles of alcohol to 1 mole of triglyceride molecules, this in turn give rise to 3 mole FAME and 1 mole glycerol.

Catalyst loading is a vital aspect in transesterification reaction as it influences the reaction and promotes its yield appropriately. Catalysts tend to reduce the activation energy of the reaction which makes the reaction to attain equilibrium faster (Wang *et al.*, 2012). Thinnakorn and Tscheikuna (2014) studied the transesterification of palm olein oil using sodium phosphate catalyst at constant molar ratio of alcohol to oil of 18:1 and constant reaction temperature of 210 °C. The effect of catalyst loading was investigated between 0 wt% to 1wt%. In the absence of the catalyst (0 wt % catalyst loading), <5% of FAME was obtained. When 0.1 wt% of the catalyst was added, a significant increase of FAME up to 20% was observed. The FAME yield continued to increase steadily with increase in catalyst loading until at catalyst loading of 1 wt % the palm olein oil was completely converted to FAME within 30 min.

Reaction time of a transesterification reaction is also observed to favor the conversion of an oil feedstock into FAME. In the transesterification of palm oil using waste obtuse horn shell derived CaO catalyst, the percentage conversion increased gradually from 34.088% to 86.75% from a period of 4 h to 6 h. The conversion however declined to 73.62% when the time was increased to 7 h. This was explained to be as a result of the formation of white emulsion and gel in the biodiesel (Leung, *et al.*, 2010; Taufiq-Yap *et al.*, 2014).

2. Experimental

2.1 Catalyst Preparation

The sulfated titania-silica catalyst was prepared by slowly adding 50 g of silica crystals to 200 ml of 0.5 M titanium isopropoxide solution. The mixture was agitated under reflux

for 4 h, it was then filtered and dried at 110°C for 2 h. The dried powder was calcined at 450°C for 4 h and TiO₂-SiO₂ particles was obtained. The resulting particles was impregnated in a 0.5 M H₂SO₄ solution for 24 h, after which it was filtered and dried. The sulfated titania-silica composite (SO₄²⁻/ TiO₂-SiO₂) was obtained by calcining the dried sample at 400 °C for 5h.

2.2 Esterification of Oleic Acid

Esterification of oleic acid was conducted in a 500 ml three-neck round bottom flask. The reaction mixture constituting oil (oleic acid), sulfated titania-silica catalyst and methanol; all in compliance with the design ratios from BBD were charged into the flask and heated. The mixture was well stirred at a constant steering speed of 200 rpm and constant temperature of 65 °C. On completion of each run, the reacted mixture was emptied into a separating funnel and allowed to settle for 1h. The mixture was found to have separated into two distinct layers; the upper layer was FAME while the lower layer consist of unreacted methanol, catalyst, and water. The FAME was separated from the other constituents by decantation, the residual catalyst was collected for reuse and the FAME was further filtered. The filtrate was then washed thoroughly with distilled water and dried in an oven at a temperature of 110 °C for 1 h.

3. Results and discussions

3.2 Effect of Experimental Variables on Esterification of Oleic Acid

The effects of molar ratio, catalyst loading and reaction time were investigated in the esterification of oleic acid. Constant stirring speed and temperature of 200 rpm and 65 °C were maintained throughout the study.

3.3 Oleic acid to Methanol Molar ratio

The effect of oleic acid to methanol molar ratios ranging from 1:3-1:15 on the conversion of oleic acid was examined. Catalyst loading of 5 wt% and 6 h reaction time were maintained.

The relationship between the conversion of oleic acid with respect to different molar ratios of methanol are as shown in fig 1a. It is observed that the conversion of oleic acid proceeds expeditiously with an increase in the molar ratio of methanol from 1:3 to 1:9. The conversion steadily increased from 58.3% to 87.5%. This implies that the conversion increases with a higher molar ratio from 1:3 to 1:9. However, as the molar ratio was increased to 1:11, a little decline in the conversion from 87.5% to 86.8% was noticed. Further increase in the molar ratio to 1:13 showed no significant change in conversion, implying that the increase at that point has no effect on the conversion. However, an increase in the methanol ratio to 1:15 led to continuous decrease in the conversion from 86.4% to 86.3%. Therefore, oleic acid to methanol molar ratio of 9:1 was chosen as the maximum value in the design of experiments.

Oleic acid is very soluble in methanol at molar ratios above 3:1, the presence of the sulfated titania-silica as a solid catalyst also makes the reacting mixture a three phase which in turn militate against the effective contact between the reactants and the catalyst arising from mass transfer limitations (Encinar *et al.*, 2012).

3.4 Catalyst loading

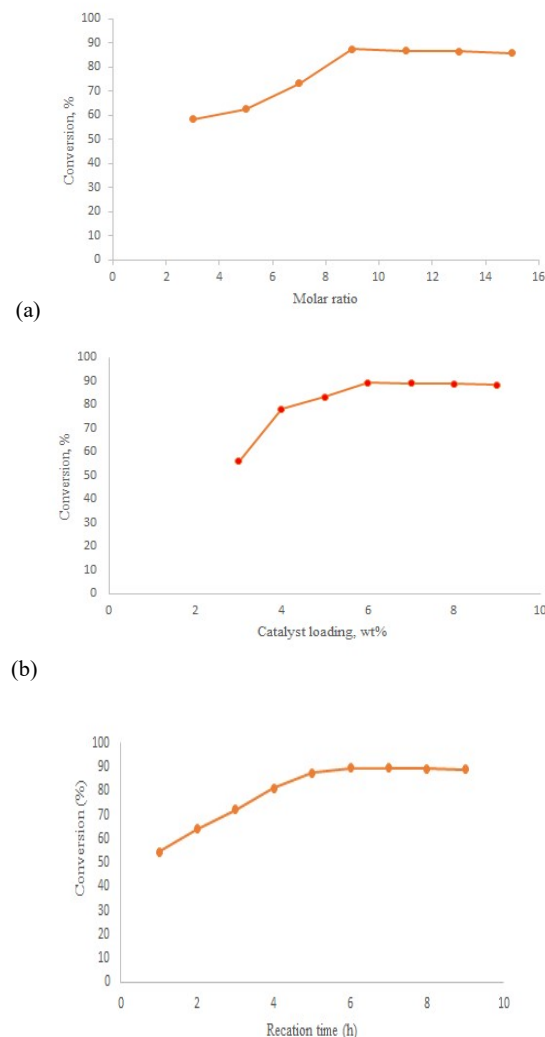
The effect of catalyst loading on the conversion of oleic acid was studied using various amounts of sulfated titania-silica catalyst ranging from 3 wt% to 9 wt%; molar ratio of 1:9 and reaction time of 6 h were maintained. As shown in fig.1b conversion of 56 % was achieved with catalyst loading of 3 wt%, the conversion increased steadily up to 89.2% with catalyst loading of 6 wt%. An increase in the catalyst loading to 7 wt% showed an infinitesimal decrease to 89.1% and

subsequently, the conversion declined to 88.8% and 88.4% with catalyst loadings of 8 wt and 9 wt% respectively. From fig.1b, it can be deduced that 6 wt% is the appropriate catalyst loading for optimal BBD experimental design for the esterification of oleic acid

It implies that the activation energy is much more lowered with catalyst loading of 6 wt% and 20 wt% respectively. This could cause the reactions to go into completion earlier and therefore at higher amounts, there will be decline or no change in the conversion.

3.5 Reaction time

The reaction time was investigated for the esterification of oleic acid from 1 h to 9 h. Catalyst loading and molar ratio of 6 wt% and 1:9 were maintained in this study. From fig. 1c, it can be visualized that at reaction time of 1 h to 6 h, the conversion increased steadily from 54.5 % to 89.7 %. From 7 h to 9 h, it reduced gradually to 89 %. The conversion was seen to increase with reaction time until the reactants were exhausted and the conversion of oleic acid seized to change and was even seen to decline.



(c) Fig.1: (a) Effect of oleic acid/methanol molar ratio on the conversion of oleic acid (b) Effect of catalyst loading on the conversion of oleic acid (c) Effect of reaction time on the conversion of oleic acid

3.6 Esterification of Oleic Acid Using Sulfated Titania-Silica Catalyst: Optimization Using Response Surface Methodology (RSM)

Optimization of the esterification of oleic acid and PFAD-oleic acid blend using sulfated titania-silica catalyst was carried out using response surface methodology (RSM) based on Box Behnken design (BBD). The responses studied from the optimization of the process parameters are methyl oleate yield (Y_1) and the conversion of oleic acid (Y_2).

To facilitate the optimization of the process variables under the esterification of oleic acid using sulfated titania-silica catalyst, a total of 17 experimental runs were conducted in accordance

with the design of experiments (DOE) using Box-Behnken design (BBD). The results obtained from these experiments were then used to analyze the responses.

$$Y_1 = 81.04 + 0.53A - 0.087B - 0.29C + 0.025AB - 0.32AC + 0.7BC - 0.75A^2 - 0.62B^2 - 0.72C^2 \quad (1)$$

$$Y_2 = 92.14 + 0.61A - 0.050B + 0.31C + 0.075AB - 0.40AC + 0.72BC - 0.87A^2 - 0.75B^2 - 0.87C^2 \quad (2)$$

where A is the molar ratio, B is the catalyst loading and C is the reaction time. The definition of these variables holds for the entire experiments. Tables 1 and 2 are the experimental design and runs respectively.

Table 1: Experimental range and levels for esterification of oleic acid

Independent Variables	Units	Range and Levels		
		Low -1	Centre 0	High +1
A: Oleic acid/ Methanol	v/v	6	9	12
B: Catalyst loading	wt%	3	6	9
C: Reaction time	h	3	6	9

Table 2: Design of experiments for the esterification of oleic acid using response surface methodology with Box Behnken design (BBD).

Run	A (v/v)	B (wt %)	C (h)	Conversion (%)		Yield (%)	
				Actual	Predicted	Actual	Predicted
1	9	6	6	92.00	92.14	81.00	81.04
2	6	9	6	89.70	89.79	79.00	79.04
3	9	6	6	92.40	92.14	81.30	81.04
4	12	6	3	91.30	91.10	80.30	80.14
5	9	9	9	91.80	91.51	80.80	80.60
6	9	6	6	92.30	92.14	81.20	81.04
7	6	3	6	90.20	90.04	79.40	79.26
8	9	6	6	92.00	92.14	81.00	81.04
9	9	9	3	89.40	89.44	78.60	78.63
10	12	9	3	91.00	91.16	80.00	80.14
11	6	6	3	89.20	89.08	78.50	78.44
12	9	3	9	90.20	90.16	79.40	79.38
13	9	6	6	91.80	92.14	80.70	81.04
14	6	6	9	90.30	90.50	79.50	79.60
15	9	3	3	90.70	90.99	80.00	80.20
16	12	3	6	91.20	91.11	80.30	80.26
17	12	6	9	90.80	90.93	80.00	80.06

Equation 1 depicts that A, B, C, AB and BC all have positive influence on methyl oleate yield while AC, A^2 , B^2 and C^2 indicates negative effects. Similarly, equation 2 showed that the same variables A, B, C, AB and BC have positive effects on the conversion of oleic acid while the variable AC, A^2 , B^2 and C^2 portray negative influences. The terms that display positive influence tend to increase the methyl oleate yield and oleic acid conversion while the negative terms does not improve any of the responses. The positive and negative signs denote synergistic and antagonistic effects respectively. The interaction of variables portraying synergistic effect improve the responses while the ones showing antagonistic effect retards the responses (Wu *et al.*, 2014).

3.7 Reaction time and Catalyst Loading

The response surface plot shown in fig.2a indicates the reaction time being studied from 3 h to 9 h and catalyst loading from 3 wt% to 9 wt%. The highest methyl oleate yield of 81% was obtained with catalyst loading of 6 wt% at reaction time of 6 h. Likewise, fig.2b show that the highest conversion of 92% was obtained at 6 h with catalyst loading of 6 wt%. This explains a low catalyst loading and a high reaction time; further increase in the catalyst amount or the reaction time did not increase the conversion. This implies that both methyl oleate yield and oleic acid conversion is favoured by low catalyst amount and moderate reaction time. The catalyst tend to reduce the activation energy and make the reaction rate faster than usual which in turn reduces the reaction time (Thinnakorn and Tscheikuna, 2014). This is in line with findings made by (Fauzi, *et al.*, 2014).

Table 3 :Analysis of variance (ANOVA) and coefficients of the model for methyl oleate yield

Source	Sum of squares	Degree of freedom	Mean square	F-value	P-value
Model	12.17	9	1.35	23.99	0.0002 Significant
A – Molar ratio	2.21	1	2.21	39.13	0.0004
B–Catalyst loading	0.061	1	0.061	1.09	0.0813
C – Reaction time	0.66	1	0.66	11.73	0.0111
AB	2.500E-003	1	2.500E-003	0.044	0.8392
AC	0.42	1	0.42	7.50	0.0290
BC	1.96	1	1.96	34.78	0.0006
A ²	2.34	1	2.34	41.47	0.0004
B ²	1.62	1	1.62	28.72	0.0011
C ²	2.18	1	2.18	38.73	0.0004
Residual	0.39	7	0.056		
Lack of Fit	0.18	3	0.061	1.15	0.4317 Not significant
Pure Error	0.21	4	0.053		
Cor Total	12.56	16			

Table 3 :Analysis of variance (ANOVA) and coefficients of the model for the conversion of oleic acid.

Source	Sum of squares	Degree of freedom	Mean square	F-value	P-value
Model	16.30	9	1.81	21.87	0.0003 Significant
A – Molar ratio	3.0	1	3.00	36.25	0.0005
B–Catalyst loading	0.02	1	0.020	0.24	0.0481
C – Reaction time	0.78	1	0.78	9.44	0.0180
AB	0.022	1	0.022	0.27	0.6182
AC	0.64	1	0.64	7.73	0.0273
BC	2.10	1	2.10	25.40	0.0015
A ²	3.19	1	3.19	38.50	0.0004
B ²	2.34	1	2.34	28.23	0.0011
C ²	3.19	1	3.19	38.50	0.0004
Residual	0.58	7	0.083		
Lack of Fit	0.35	3	0.12	2.0	0.2568 Not significant
Pure Error	0.23	4	0.058		
CorTotal	16.88	16			

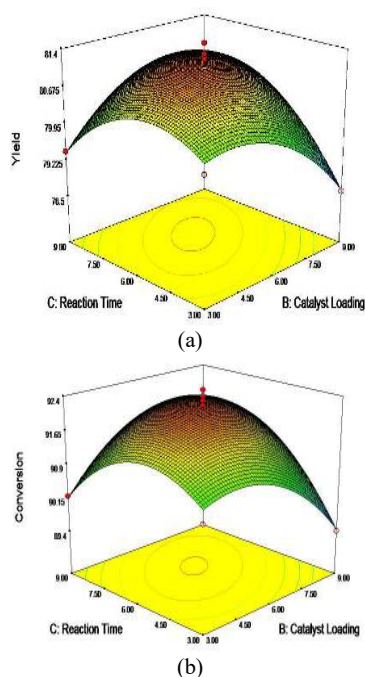


Fig.2: (a)Effect of reaction time and catalyst loading on methyl oleate yield (b) Effect of reaction time and catalyst loading on the conversion of oleic acid.

3.8 Reaction Time and oil/methanol Molar ratio

The relationship between reaction time and oleic acid to methanol molar ratio as it affects the responses namely methyl oleate yield and oleic acid conversion are shown on the 3D response surface plots in fig. 3 (a) and (b) respectively. Figure 3 (a) visualized the reaction time being investigated from 3 h to 9 h and the molar ratio from 1: 6 to 1: 12. The highest methyl oleate yield of 81% was however obtained at 6 h and molar ratio of 10. Further increase in both variables resulted to a decline in methyl oleate yield.

Similarly, fig. 3b the highest conversion of 92% was achieved at reaction time of 6 h and molar ratio of 10. Further increase in both parameters resulted to a drop in the conversion.

This implies that long reaction time and a high molar ratio of oleic acid to methanol increase the methyl oleate yield as well as the conversion of oleic acid. The elliptical nature of the contour plot also show significant interaction between the variables and methyl oleate yield as well as conversion of oleic acid (Omar and Amin, 2011). The same trend was observed by (Marchetti *et al.*, 2007) in their study of heterogeneous esterification of oils with high amount of free fatty acid. At high molar ratio and reaction time, the yield and conversion decreased. Often, much extended time in most reversible reactions tend to favour the backward reaction which in turn reduce the yield and conversion of the forward reaction (Leung and Guo, 2006). In the case of very high molar ratio, the reaction could be limited by the bulk transport of the methanol

to the oleic acid phase. High amount of methanol in the system dilutes the methyl oleate produced, thereby lowering its viscosity which facilitates better mass transfer. This boost the methyl oleate yield as well as oleic acid conversion. However, when the methanol is in excess, the tendency for catalyst leaching increases and subsequently the methyl oleate yield decreases (Dossin, *et al.*, 2006).

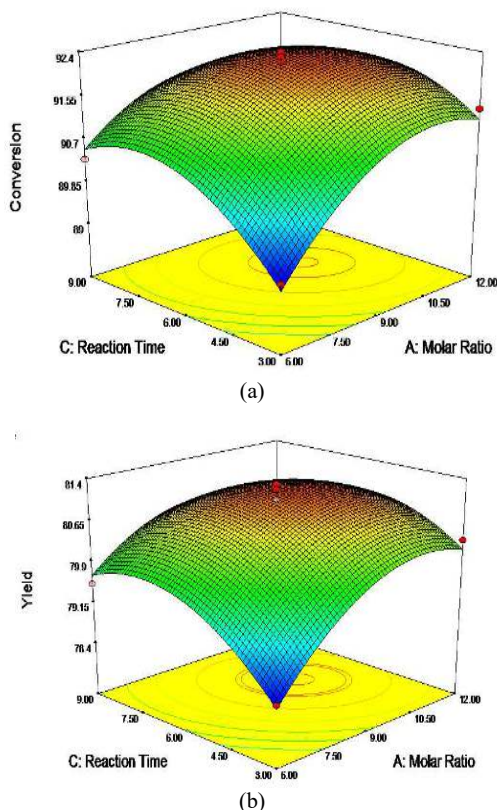


Fig. 3: (a) Effect of reaction time and methanol to oleic acid molar ratio on methyl oleate yield (b) Effect of reaction time and methanol to oleic acid molar ratio on the conversion of oleic acid

4. Conclusion

The effect of process variables namely oleic acid/ methanol molar ratio, catalyst loading and reaction time on the esterification of oleic acid using sulfated titania silica catalyst was studied and analyzed using CCD based on BBD design. The model obtained deduced that it fits the experimental values obtained and is therefore valid. The analysis of variance deduced that the molar ratio and time have more influence on the experiment while the catalyst loading was seen to have less effect. However, the interaction between the variables show that the synergy between molar ratio and reaction time improves the reaction responses. Similarly, the synergy between catalyst loading as well as reaction time also improve the responses of the reaction. The interaction between molar ratio and catalyst loading did not have any significant effect on the reaction. The highest methyl oleate yield as well as oleic acid conversion are 81% and 94% respectively.

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ABSTRACT

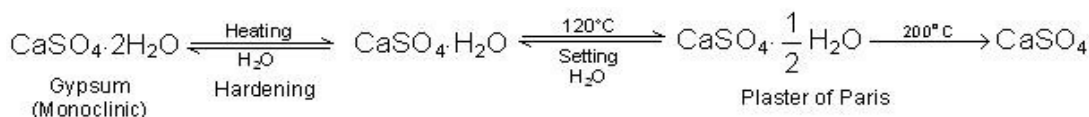
A Study on the quantitative leaching of gypsum ore in hydrochloric acid solution has been undertaken for possible development of hydrometallurgical route for the production of highly pure gypsum. The chemical composition, phase and morphology of ore with particle size $90 + 63\mu\text{m}$ were examined by X-ray Fluorescence (XRF), X-ray Diffraction (XRD), and Scanning Electron Microscope (SEM). The effects of contact time, acid concentration, temperature, particle size and solid-liquid ratio on the dissolution of the gypsum ore was investigated. The rate depends on the hydrogen ion concentration with temperature having little effect on the reaction system. The activation energy for the dissolution reaction was estimated to be 9.6 kJmol^{-1} . About 99.7% dissolution was achieved within 120 min. by 6 M HCl solution, temperature of 80°C , stirring speed of 400 rpm and using $90 + 63\mu\text{m}$ particle size.

Keywords: Gypsum ore, Hydrochloric Acid, Dissolution kinetics

1.0 INTRODUCTION

Gypsum is a sedimentary rock (Grotzinger *et al.*, 2007), an evaporite mineral formed as precipitate when sea water evaporates. Thick deposits accumulate in bays and in regions that have restricted access to the open ocean; deposition also occurs in salty inland seas or lakes (Jones and Jones, 2006). Frequently, there is an enclosure of inclusions of brine, clays, iron oxides, organic matters etc. Gypsum can also be found in playa lakes, salt pans, desert soils and volcanic vents (Mange and Maurer, 1992). As bedded sedimentary formations interstratified with limestone, red shale, marl and clays, gypsum can be associated with other minerals such as Halite, celestine, calcite, aragonite, anhydrite, dolomite, magnesian limestone, and in condition that have not produced salt, as in sulphur deposit (Battey, 1981; MDP, 2005).

Gypsum consists of a matrix of interlocking elongated crystals. There are two molecules of water chemically bound with calcium sulphate in an orthorhombic crystalline mineral structure. When the mineral is heated at temperature between 100°C - 170°C , losses one-third of its water of crystallization to form hemihydrates ($\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$), also called plaster (Anthony *et al.*, 2003; Manias *et al.*, 2013). When plaster is made wet it is hydrated back to gypsum, forming a hard cast which set in 5 – 20 minutes (Brown *et al.*, 2015.). Equation [1] illustrate the process as reported by Indian Institute of Technology (IIT) (2006).



Paris can easily be converted back to gypsum in the presence water liberating heat and forming a hard cast. This property makes gypsum a very useful as a casting material in the field of orthopaedic surgery, interior designs for building and cement production.

According to the Ministry of Solid Minerals Development (2000) and Federal Ministry of Trade and Investment (2011), there are about one billion tonnes of gypsum deposit spread over many states in Nigeria including Nafada/Bajoga in Gombe State, Fika in Yobe State, Guyuk/Gwalura in Adamawa State and Igankoto in Ogun State (Irahbor *et al.*, 2013). Despite the abundance of gypsum and other material needed for the production of Plaster of Paris (POP) in the country, the country relies heavily on the importation of orthopaedic plaster of Paris bandage. According to Raw Materials Research and Development Council (RMRDC) as reported by Daily Trust on November 21, 2015, Nigeria has spent about 12.9 billion naira on the importation of Plasters in the 3 years.

The solubility of different forms of gypsum in different media has been studied extensively. Most kinetics studies of gypsum dissolution in water revealed that rate is controlled by reaction on the surface of the mineral (Lebedev, 2015). The study of

solubilities of calcium sulphate dihydrate, hemihydrate, and anhydrite in concentrated HCl, CaCl_2 and their mixed aqueous solution using classic isothermal dissolution method has been done by Li and Demopoulos (2005). It was reported that the solubility of CaSO_4 phases increase with concentration and temperature. The solubility of gypsum in other media such as H_2SO_4 /Manganese sulphate media and in ternary systems of $\text{CaSO}_4 + \text{MSO}_4 + \text{H}_2\text{O}$ through isothermal solution saturation at 348.1 K and 363.1 K. Cobalt and Nickel were the metals used (Farrah *et al.*, 2007; Wang *et al.*, 2015). However, no previous work was found on the study of leaching kinetics of gypsum especially in HCl media and the quantitative purification of the mineral in the acid media.

In the leaching of minerals, different oxidizing reagents are used as the leaching media, these reagents include hydrochloric acid, sulfuric acid, nitric acid and other oxidizing agents (Baba *et al.*, 2014). The aim of this study is to establish the physicochemical condition for the leaching of Nigerian gypsum ore by hydrochloric acid, which can be used to predict possible condition for the production of highly pure gypsum. Pure gypsum free of gangue is white and is a valuable compound for the production of Plaster of Paris used for orthopaedic surgery and interior decorations.

2.0 EXPERIMENTAL

2.1 Materials, Sample collection, Preparation and characterisation.

The gypsum ore sample used for this research work was obtained from a gypsum quarry site in Potiskum, Yobe State, Nigeria. The sample was pulverized and sieved to produce four particle size fractions: $-90 + 63\mu\text{m}$, $-112 + 90\mu\text{m}$, $-180 + 112\mu\text{m}$, and $-250 + 180\mu\text{m}$. All experiments were performed with particle size fraction of $-90 + 63\mu\text{m}$ unless otherwise stated.

The characterization of gypsum ore before and after leaching at optimal conditions were carried out using EDX3600B Skyray X-ray fluorescence, GBC enhanced mini-materials analyser (eMMA) X-ray diffraction and Leo 1450 Scanning electron microscopy.

Chemie Lobal analytical grade Hydrochloric acid and distilled water were used in the preparation of all solutions

2.2 Leaching Procedure

This procedure was carried out in a 1L glass reactor equipped with a magnetic stirrer. The reactor filled with the 500ml of 0.2 M HCl and heated to 80°C . 5 g of the gypsum ore was introduced into the reactor and covered with a glass lid. The solution was stirred at the rate of 400 rpm with the aid of the magnetic stirrer for various contact time of 10, 30, 60 and 120 minutes. At the end of each period, the solution was cooled and filtered. The residue was washed with distilled water and oven dried at about 55°C for one hour and weighed to obtain the fraction of gypsum dissolved. The same procedure was repeated for 0.5 M, 1.0 M, 2.0 M 4.0 M and 6.0 M respectively. The concentration that gave the maximum dissolution was

Table 1: Chemical composition of raw gypsum (RWG) sample

Compound	CaO	SO ₃	SiO ₂	TiO ₂	Fe ₂ O ₃	MnO	Al ₂ O ₃
Wt %	46.23	50.48	1.253	0.044	0.369	0.039	1.624

The percentage purity of the gypsum ore sample was estimated to be 86.9% using the method described by Tao (2012).

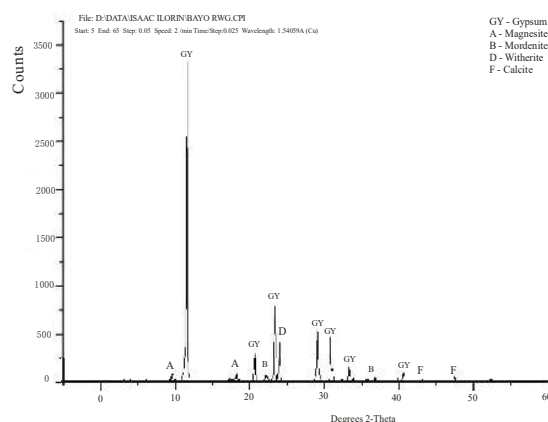


Fig 1: XRD Pattern of the initial gypsum sample showing different phases present

3.1.3 Morphological Characterization of Raw Gypsum Ore (RWG) By Scanning Electron Microscopy-Energy Dispersive Spectroscopy (SEM-EDS)

The microstructure, surface morphology and elemental percentage composition of raw gypsum ore (RWG) was characterized with Scanning Electron Microscopy-Energy Dispersive Spectroscopy (SEM-EDS). The equipment model is Leo 1450 with LaB₆ filament. The samples were viewed at 200

subsequently used for the optimization of other leaching parameters such as gypsum ore particle size ($-90 + 63\mu\text{m}$, $-112 + 90\mu\text{m}$, $-180 + 112\mu\text{m}$, and $-250 + 180\mu\text{m}$), solid-liquid ratio (10 g/L, 20 g/L and 40 g/L) and reaction temperature of 32 to 80°C (Gharabaghi *et al.*, 2013; Baba *et al.*, 2014). The residue obtained was characterized with XRD and SEM-EDS.

3.0 RESULT AND DISCUSSION

3.1 Characterisation of Raw Sample

3.1.1 Chemical Analysis by X-Ray Fluorescence

The chemical composition of the gypsum sample, obtained by X-ray Fluorescence and expressed as oxides wt.%, is shown in Table 1. The major oxides detected are calcium, sulphur, aluminium and iron oxide. The quantity of manganese oxide found was at trace level.

3.1.2 Phase Characterisation with X-Ray Diffraction

The ore phase characterised by X-ray diffraction revealed that the ore is rich in gypsum complementing the result of the chemical analysis by X-Ray Fluorescence. The phases were identified using the Joint Committee on Powder Diffraction Standard File number. The compound present in the ore include: Gypsum (01-070-0982), Magnesite (36-0383), Mordenite (49-0924), Witherite (5-0378), and Calcite (5-0586). Other minor phases that occurred in low to trace levels include Anatase (21-1272) and Chrysotile (25-0645) (Zelati *et al.*, 2011; Shen *et al.*, 2012; Intarpong *et al.*, 2013; Lafuente *et al.*, 2014; Lopez-Delgado *et al.*, 2014).

X and 1.0 KX magnification, 13 mm working distance and were carbon coated. The element analysis was done with a Brinker X-Flash detector using Esprit 1.82 software. The micrographs at both magnifications are given in Figures 2.

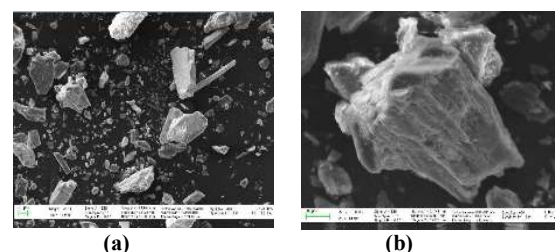


Fig 2: SEM image of Raw Gypsum Ore (RWG) at (a) 200 X magnification (b) 1.0 KX magnification

The image in figure 2(a) shows particles of different topography, while some seems to be homogeneous with few deposits of different phases on their surfaces others consist entirely of heterogeneous phase. At a higher magnification of 1.0 KX, the image in figure 2(b) shows clearly that the particle is a conglomerate deposition of different constituents. These imply that RWG is a heterogeneous material consisting of different phases (compounds). This supports the result obtained by X-ray diffractometer where other phases such as calcite, witherite, modernite and others were identified.

The spectrum of the elemental analysis by Energy Dispersive Spectroscopy in figure 3 shows that calcium, sulphur and oxygen are the most abundant elements in RWG. This is in consonant with that of X-ray Fluorescence and phase identification of X-ray Diffraction.

From the aforementioned characterisation, it can be concluded that RWG is indeed gypsum ore with impurities present. These impurities are what is responsible for brown colour and will impair the effectiveness of the material if directly used without purification.

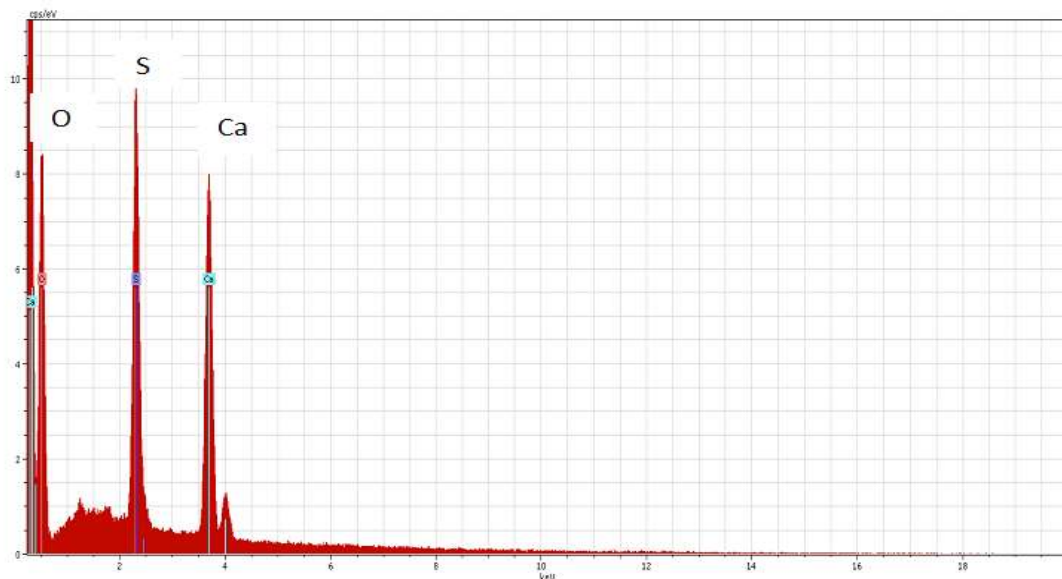


Figure 3: Electron Dispersive Spectroscopy Spectrum of raw gypsum ore (RWG)

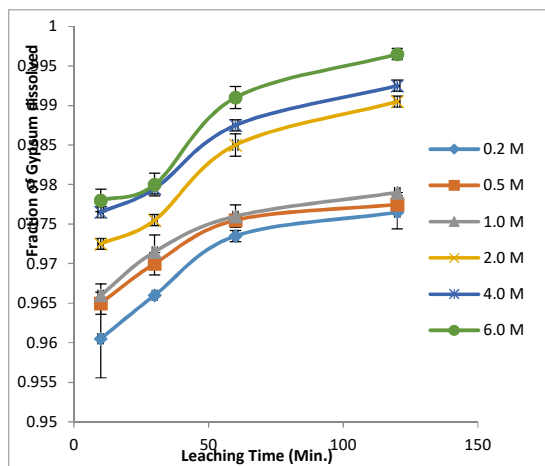


Fig. 4: Plot of fraction of gypsum dissolved versus leaching time at different concentrations of HCl. *Experimental conditions:* solid-liquid ration: 10g/l; stirring rate: 400rpm; particle size: -90 + 63 μm ; temperature: 80°C.

The results indicated that gypsum rapidly dissolves up to about 96% in a short time even at concentration as low as 0.2 M. A significant increase in dissolution was observed between 1.0 M and 2.0 M concentration of the acid. The leaching rate further increased with increase in acid concentration. This result indicates that gypsum dissolution is controlled by the hydrogen ion $[\text{H}^+]$ concentration in the solution. As indicated in the plot,

3.2 Dissolution Kinetics of Gypsum Sample in Hydrochloric Acid Solution.

3.2.1 Effect of Acid Concentration

The effects of acid concentration were studied in the range of 0.2 M – 6.0 M acid concentration at 80°C using -90 + 63 μm particle size with a stirring speed of 400 rpm. The fraction dissolved is plotted against leaching time for the different concentration of the acid as shown in figure 4

error margin was computed over a range of three values for each point on the plot.

3.2.2 Effect of Particle Size

The effect of particle size on the rate of gypsum dissolution in hydrochloric acid was studied over the range of four particle sizes: -90 + 63 μm , -112 + 90 μm , -180 + 112 μm , and -250 + 180 μm . Figure 5 gives a graphical impression of the effect.

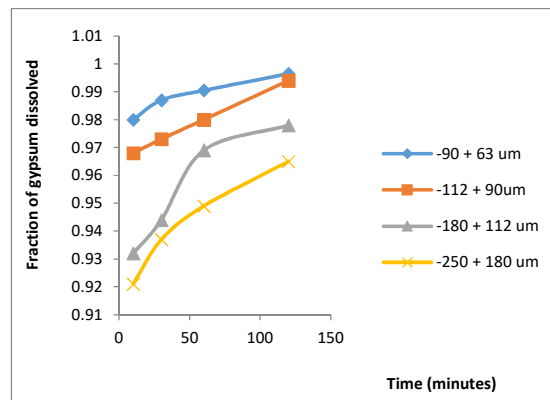


Fig. 5: Plot of fraction of gypsum dissolved versus leaching time at different particle sizes. *Experimental conditions:* solid-liquid ration: 10g/l; stirring rate: 400rpm; $[\text{HCl}] = 6.0 \text{ M}$; temperature: 80°C.

Figure 5 shows the effect of particle size on the dissolution rate of gypsum. It was observed that the rate decreases with increase in particle size because an increase in surface area will give rise

to a higher reaction rate as the solution portions are made more accessible to the solvent (Hu, 2016). The fraction of gypsum dissolved increased gradually over time for particle size -112 + 90 μm , -180 + 112 μm , and -250 + 180 μm . This increase is less pronounced for particle size : -90 + 63 μm .

In general, the particle size of sample has an important influence on the rate of dissolution. The smaller particle size has the faster extraction rate. The finer the particle size was, the greater geometric surface area and degree of contact surface between the acid solution and the particles were. In addition to the importance of size reduction, the surface area per unit weight of the sample increases causing greater amount of gypsum to be liberated from the matrix of the raw gypsum rock (Gharabaghi *et al.*, 2013).

3.2.3 Effect of Temperature

A number of experiments were also conducted to study the effect of temperature on the dissolution rate of gypsum in HCl acid. The reaction conditions are as follows: [HCl] = 6.0 M at 80°C using -90 + 63 μm particle size with a stirring speed of 400 rpm. Figure 4.3 gives the graphical representation.

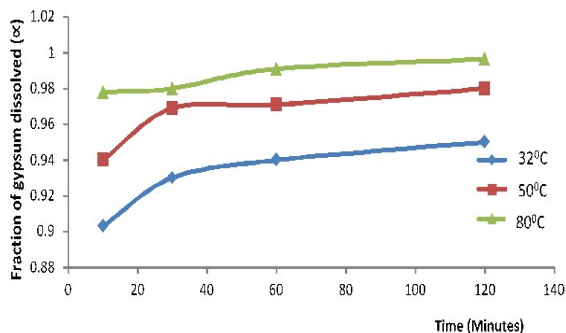


Fig. 6: Plot of fraction of gypsum dissolved versus leaching time at different temperatures. Experimental conditions: solid-liquid ratio: 10g/l; stirring rate: 400rpm; particle size: -90 + 63 μm ; [HCl] = 6.0 M.

It can be seen from figure 6 that about 90% dissolution was achieved at temperature as low as 32°C even within ten minutes of dissolution. Leaching rate only increases slightly with increase in temperature. At 50°C, it can also be observed that apart from the surge observed after 30 minutes, there was no further increase in rate anymore. Whereas at 80°C, there was no increase in leaching rate until the reaction time exceed 30 minutes after which only slight increase was observed. In general temperature has slight effect on the dissolution kinetics of gypsum in hydrochloric acid.

3.2.4 Effect of Solid-Liquid Ratio

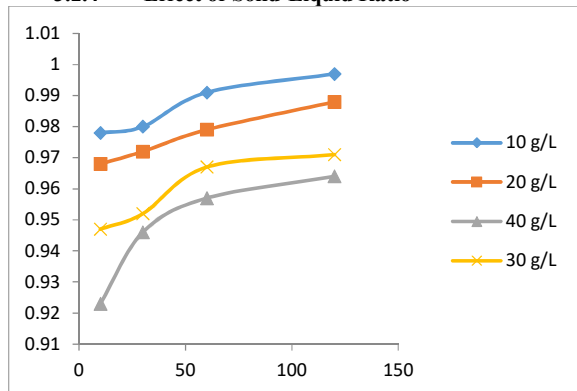
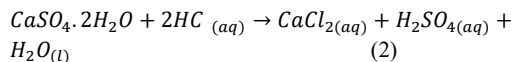


Fig. 7: Plot of fraction of gypsum dissolved versus leaching time at different Solid-Liquid Ratio. Experimental conditions: particle size: -90 + 63 μm ; [HCl] = 6.0 M; Temperature 32°C.

3.3 Analysis of Dissolution kinetics by Shrinking Core Models

The shrinking core model is always applied to describe the leaching kinetics where there is a reduction in both the mass and the particle size of the solid during leaching (Baba *et al.*, 2014).

The overall reaction for dissolution of gypsum by hydrochloric acid may be as follows:



For the dissolution kinetics of gypsum by HCl, the three established kinetic models were tested with all the experimental data expressed in fig 4 – 7. These are diffusion, chemical and mixed controlled kinetic model. If the reaction rate is controlled by diffusion through product layer, chemically or by both (mixed), integrated rate equation (3), (4) or (5) holds respectively.

$$1 - \frac{2}{3}(1 - \alpha)^{\frac{2}{3}} = \frac{2MDC}{\beta\rho\delta}t = K_d t \quad (3)$$

$$1 - (1 - \alpha)^{\frac{1}{3}} = \frac{kC}{r_0\rho}t = K_c t \quad (4)$$

$$1 - (1 - \alpha)^{\frac{1}{3}} + \frac{\gamma}{6} \left[(1 - \alpha)^{\frac{1}{3}} + 1 - 2(1 - \alpha) \right]^{\frac{2}{3}} = K_m t \quad (5)$$

These models were compared as shown in table 2 and after statistical analysis, it was discovered that Chemical controlled model best fit the data.

After statistical analysis, it was discovered that Chemical controlled model best fit the data. According to the equation, a plot of $1 - (1 - \alpha)^{\frac{1}{3}}$ against leaching time is a straight line with slope K_c when the process is diffusion controlled as shown in figure 4.

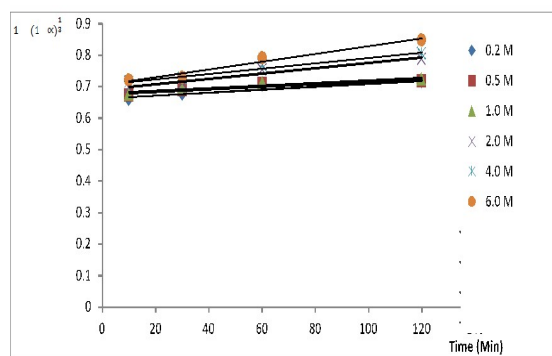
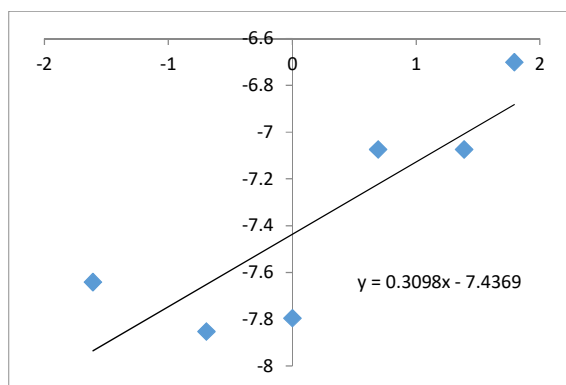


Figure 8: plot of $1 - (1 - \alpha)^{\frac{1}{3}}$ against leaching time at different HCl Concentration.

The experimental rate constants, K_c were evaluated from the slope of figure 8. the values were then then used to plot $\ln K_c$ against $\ln[\text{HCl}]$ as shown in figure 9

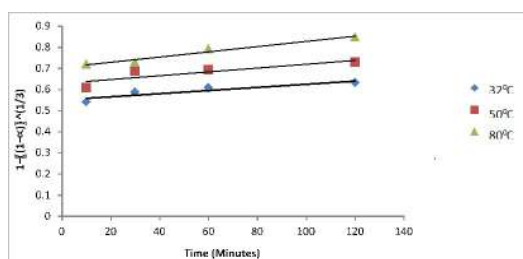
Table 2: Shrinking Core Model Comparison.

Parameters	Kinetic Models					
	Diffusion Control $1 - \frac{2}{3} \alpha - (1-\alpha)^{\frac{2}{3}}$		Chemically Controlled $1 - (1-\alpha)^{\frac{1}{3}}$		Mixed Controlled $1 - (1-\alpha)^{\frac{1}{3}} + \frac{1}{6} (1-\alpha)^{\frac{1}{3}} + 1 - 2(1-\alpha)^{\frac{2}{3}}$	
	$k_d \times 10^{-4}$	R_d^2	$k_c \times 10^{-4}$	R_c^2	$k_m \times 10^{-4}$	R_m^2
Concentration (M)						
0.2	2.059	0.877	4.815	0.883	9.992	0.876
0.5	1.642	0.847	3.892	0.852	7.958	0.846
1.0	1.720	0.885	4.115	0.893	8.334	0.885
2.0	3.214	0.952	8.470	0.961	15.722	0.953
4.0	3.079	0.959	8.475	0.969	15.192	0.961
6.0	4.129	0.949	12.30	0.965	20.859	0.955
Order of Reaction	0.2	0.660	0.3	0.716	0.2	0.667
Temperature (°C)						
32	3.548	0.821	3.548	0.828	18.183	0.812
50	3.985	0.726	3.985	0.749	19.489	0.722
80	4.129	0.949	4.128	0.965	20.859	0.955
Activation Energy	2.6 KJmol ⁻¹	0.847	9.6 kJ/mol	0.999		
Particle size						
-90 + 63 um	3.394	0.967	11.835	0.995	19.652	0.987
-112 + 90 um	4.620	0.993	12.490	0.985	22.788	0.992
-180 + 112 um	3.392	0.937	7.573	0.945	16.621	0.934
-250 + 180 um	2.432	0.814	4.970	0.817	12.678	0.807
Plot of k_d Vs $1/r^2$		0.989				
Plot of k_d Vs $1/r$				0.913		
Solid-Liquid Ratio (g/L)						
10	4.309	0.958	13.015	0.973	21.880	0.964
20	6.893	0.916	14.148	0.923	36.378	0.900
40	12.88	0.998	27.145	0.993	85.042	0.981

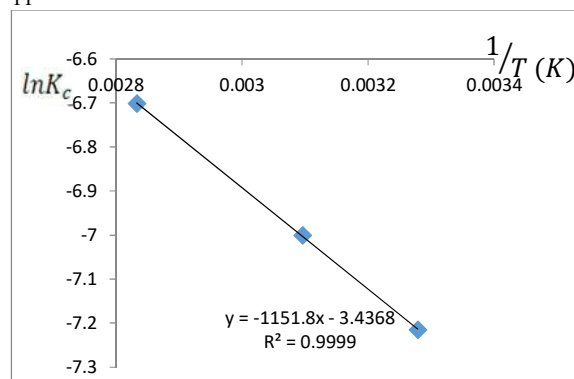
**Figure 9: plot of $\ln k_c$ against $\ln[\text{HCl}]$**

The slope of figure 9 was calculated to be 0.3. This indicates that the reaction order with respect to HCl leaching for which its concentration is 6M is 0.3.

The chemical controlled model was also used to linearize figure 6. The linearity of the data is shown in figure 10.

**Figure 10: Plot of $1 - (1-\alpha)^{\frac{1}{3}}$ against leaching time at different temperature**

The apparent K_c were determined from the slopes of the straight lines in figure 10 and were used to plot Arrhenius plot of figure 11

**Figure 11: Plot of $\ln K_c$ against $1/T$**

From the Arrhenius plot of figure 11, the activation energy was calculated to be 9.6 kJmol⁻¹. This value suggests diffusion controlled mechanism as against the chemically controlled mechanism from statistical analysis. However, it has been argued that the rate controlling mechanism of heterogeneous dissolution reactions is better predicted from plots of the kinetic equations rather than from the activation energy value (Olanipekun, 1999; Baba *et al.*, 2009). The low value of activation energy also suggests that the reaction between gypsum and hydrochloric acid proceed rapidly to product. This can be made evident in figure 4 – 7 where about 90% gypsum ore reacts with the acid in ten minutes. The value further suggests also that dissolution of gypsum in hydrochloric acid does not require large quantity of heat.

The plot of K_c against the inverse of square of particle radii ($1/r^2$) gave a linear relationship as shown in figure 12. This further proves that the reaction is chemically controlled.

3.4 Characterisation of Leached Residue from Dissolution Studies

The leached residue (LR) was analysed with GBC enhanced mini-materials analyzer (eMMA) X-ray Diffractometer. The solid residual products obtained from the leaching of 10 g/L gypsum ore at optimum condition of 6.0 M, 80 °C, 400 rpm, superimposed with the raw gypsum (RWG) sample is presented in figure 18.

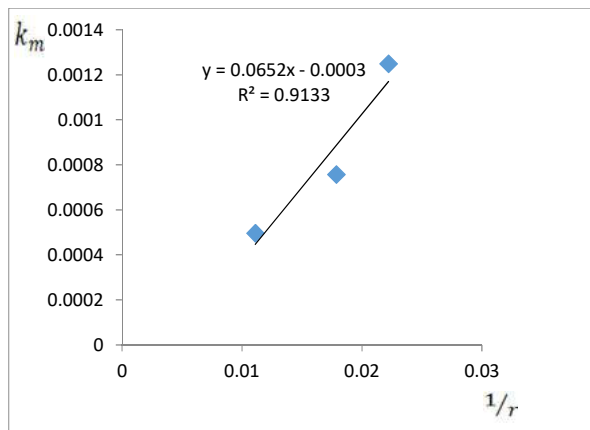


Figure 12: plot of K_m against $(1/r)$

It was observed that as at 6.0 M HCl concentration, gypsum had been completely leached as no gypsum phase was seen in the XRD pattern. The phases that are predominant in the leached residue include Magnesite (36-0383), Mordenite (49-0924), Witherrite (5-0378), Anatase (21-1272) and Quartz (46-1045) (Zelati *et al.*, 2011; Shen *et al.*, 2012; Intarpong *et al.*, 2013; Lafuente *et al.*, 2014). The phase found in the leached residue (figure 18) are the just the impurities in the raw sample with no trace of the gypsum phase. This implies that the compound of interest has been completely leached at the stated optimum condition.

The microstructure, surface morphology and elemental percentage composition of the gypsum recovered from the hydrochloric acid leached liquor was also characterized with Leo 1450 Scanning Electron Microscopy with Energy Dispersive Spectroscopy (SEM-EDS). The equipment

description, sample preparation and procedure are the same as stated in section 4.1.3. The micrographs at 200 X and 1.0 KX magnifications are given in figure 14. The images show particles of similar topography with those of the raw sample in figure 2. Suggesting that the leached residue is also heterogeneous in nature consisting of different phases.

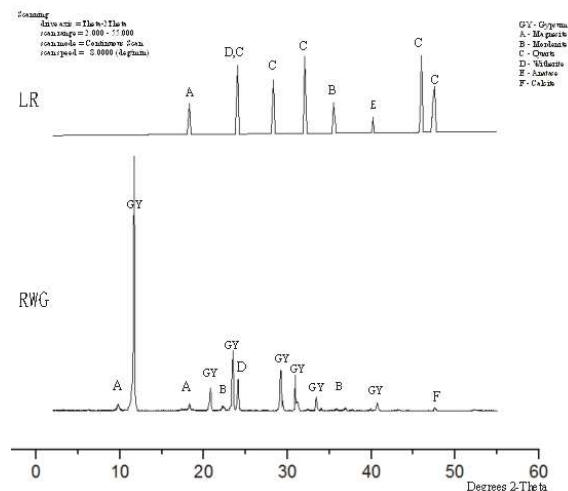


Figure 13: XRD Pattern of 10 g/L gypsum leached residue at 6.0 M HCl, 80 °C, 400 rpm

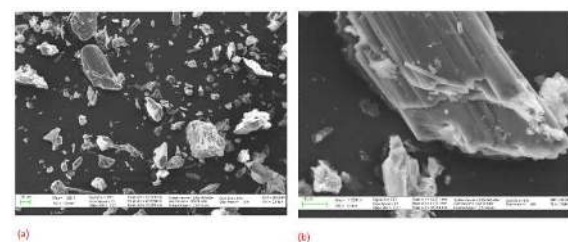


Figure 14: SEM image of leached residue (LR) at (a) 200 X and (b) 1.0 KX magnification

The spectrum of the elemental analysis by Energy Dispersive Spectroscopy in figure 15 shows that Silicon, Aluminium and Iron are the abundant element in the residue.

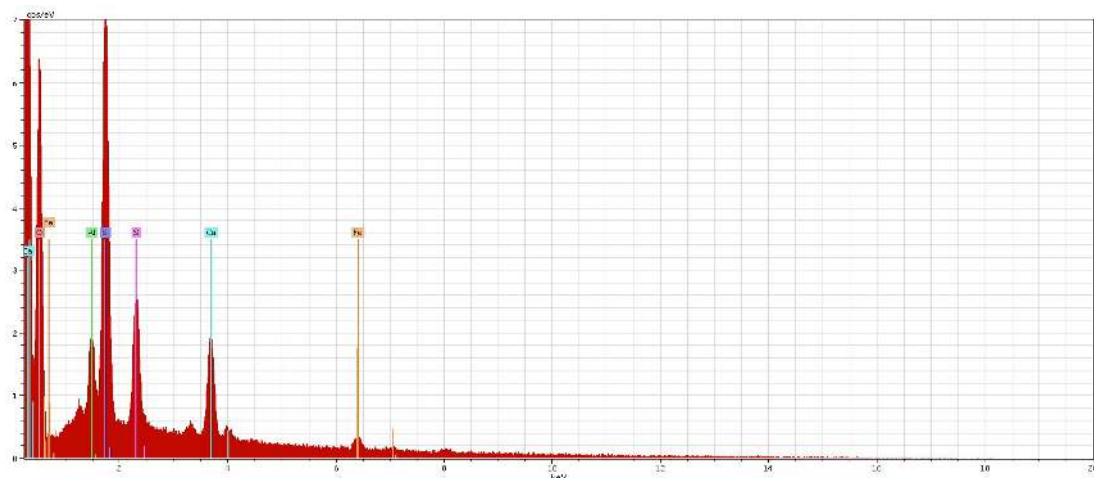


Figure 21: Electron Dispersive Spectroscopy Spectrum of leached residue (LR)

4.0 CONCLUSION

This study examined the dissolution kinetics of gypsum ore in hydrochloric acid. The results obtained showed that the

reaction rate increases with hydrogen ion $[H^+]$ concentration, and reaction temperature but decreases with particle size and solid-liquid ratio. The shrinking core model that best described

the dissolution kinetics was estimated to be chemically controlled model. The reaction order with respect to $[H^+]$ ion concentration was found to be 0.3 and a value of 9.6 kJ/mol was obtained as energy of activation, E_a , for the dissolution process.

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A COMPARATIVE STUDY OF THE CHEMICAL COMPONENT OF THE EXTRACTS OF YOUNG AND OLD ROOT OF *AZADIRACHTA INDICA* GROWN IN ZARIA

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ABSTRACT

This study was aimed at investigating comparison of the chemical component of crude extract of young and old root of *Azadirachta indica*. The chemical component was extracted using solvent extraction technique. Thin layer chromatography (TLC) was used to ascertain the complexity of the component present in the crude extracts, a qualitative phytochemical screening, cytotoxicity test and antimicrobial test were carried out on the young and old root extracts. (TLC) of both extracts revealed two prominent spot each of approximately the same retention factor. The cytotoxicity test of the young root showed that it's mediumly toxic with a LC_{50} value of 40.626 μ g/ml while the old root extract is highly toxic with a LC_{50} value of 64.585 μ g/ml which actually is the prominent difference between the extracts. The phytochemical result of the extracts showed a similar result of the secondary metabolites tested which include alkaloid, cardiac glycosides, tannin, saponins and steroids.

Introduction

Fossil records date human use of plants as medicines at least to the middle Paleolithic age some 60,000 years ago (Soleek and Shaidar 1975). From that point the development of traditional medical systems incorporating plants as a means of therapy can be traced back only as far as recorded documents of their likeness. However, the value of these systems is much more than a significant anthropologic or archeologic fact. Their value is as a methodology of medicinal agents, which according to the World Health Organization (WHO), almost 65% of the world's population has incorporated into their primary modality of health care (Farnsworth N.R et al., 1985). The goals of using plants as sources of therapeutic agents are;

In 2002, at the world neem conference, the idea of promoting neem as an industrial plant was put forward. Several industries including pharmaceutical, cosmetics and textile industries use neem oil. In India neem is highly exploited by many drug industries. Neem oil and powdered neem leaves are employed in various cosmetics preparation such as face creams, nail polish, nail oils, shampoos and conditioners (Jattan et al; 1995).

Neem cake a by-product of neem oil industry is used as livestock feed, fertilizer and natural pesticide. Neem oil is commonly used in soap production. Neem based tooth paste is widely used in Indian and European countries. It's a source for many oral hygiene preparations and dental care products. Neem bark yields gum and tannins which are used in tanning and dyeing etc. (Hekelbach et al; 2006). The present work is aimed at carrying out a comparative evaluation of the phytochemical, antimicrobial and cytotoxicity analysis of old neem root and young neem root

Experimental and Procedure

Apparatus and Glasswares

Sample bottles, extraction flasks, round and flat bottom flasks, conical flasks, micropipettes, TLC plate, TLC tanks, filter papers, funnels, distillation apparatus, test-tubes, aluminium foils, UV lamp, Soxhlet extractor, petri-dishes, test-tube rack, separating funnel, micropipette, spatula and rotary evaporator.

Reagents

Dichloromethane (DCM), Ethanol, picric acid, Petroleum spirit, Diethyl ether, vanillin reagent, 27% Hydrochloric acid, Wagner's reagent, Carbon tetrachloride, concentrated tetraoxosulphate (VI) acid, 5% lead acetate, distilled water and 10% Iron (III) chloride, Dimethylsulfoxide (DMSO), silica gel, brine, Acetic acid.

Sample Collection

The young and old root of *Azadirachta indica* was collected within Samaru metropolis and was evaluated for proper identification. Each of these fresh plants materials was chopped into smaller pieces and air dried at ambient temperature to ensure easy extraction. The chopped and dried plant material was soaked in dichloromethane in an extraction flask for two days to extract the chemical component which was concentrated to get the crude extract and was stored prior to analysis.

Thin Layer Chromatography of the Extracts

Thin layer chromatography was carried out on the extracts from the young roots and old roots of the plant. This was done by spotting these samples on a prepared TLC plate and developed using a mixture of petroleum spirit and diethyl ether (2:1). After the plate has been fully developed, it was viewed under the UV lamp at a certain wavelength to observe the spots on the plate. The TLC plate was then sprayed with vanillin reagent and heated on the hot plate to observe any colour reaction. The spray reagent was prepared as illustrated below:

- (i) 15ml of ethanol.
- (ii) 0.6g of vanillin.
- (iii) 2 drops of acetic acid.
- (iv) 2 drops of conc. H_2SO_4 .

Phytochemical Screening of the Extracts

A qualitative phytochemical screening of the extracts was done using a standard qualitative test method with appropriate reagent for the purpose of determining the various classes of secondary metabolites like alkaloid, cardiac glycosides, steroids, tannins, and saponins presence in the crude extracts.

Cytotoxicity Test of the Extracts

The toxicity of each extract was carried out using the brine shrimp lethality bioassay method (Simionatto et al 2005), knowing fully well that a highly toxic extract will have an adverse effect in the body system if used as drugs. This was done using the shrimp larvae.

The shrimp eggs were hatched in the laboratory using the artificial brine (sea water) prepared by dissolving 38 g salt per liter of water into shrimp larvae. Various concentrations of the extracts were prepared i.e. 1000ppm, 1000ppm and 1000ppm. 4.5ml of each of this concentration were put in three different test-tubes each. Ten shrimp larvae were introduced into each of these nine test-tubes and control test-tube after which the mortality rates were taken after 24 hours. The control test-tube was also set up containing only 5ml brine and two drops of dimethyl sulfoxide (DMSO) to enhance the solubility

of test material. The LC₅₀ values were determined at 95% confidence intervals was analyzed. The LD₅₀ values of the brine shrimps obtained for extracts of the plants studied were recorded.

Antimicrobial Assay of the Extracts

The antimicrobial assay of the extract was carried out in a microbiology laboratory under a standard and controlled experimental condition. This was done to ascertain which of the extracts will have the maximum micro-organism inhibitory property which can serve as tool to determine which of the extract can be potentially active in the synthesis of antimicrobial drugs to combat diseases caused by microorganism. Various bacterial and fungi were used for this study which includes: *Staphylococcus aureus*, *Pseudomonas aureginosa*, *Bacillus subtilis*, *Eschrichia coli*, *Salmolnellae typhi*, *Cadida albicans*, *Aspergillus niger*, *Rhizopus stolonifer*, *Penicillum nonatum*, *Klebbsiella pneumonia*.

Results and Discussion Results

Thin Layer Chromatography Analysis of the Extracts

The TLC of the two extracts showed a prominent yellow and brown spots with approximately the same Re (retention factor) of 0.74cm. This is shown in fig. 4.1 below:

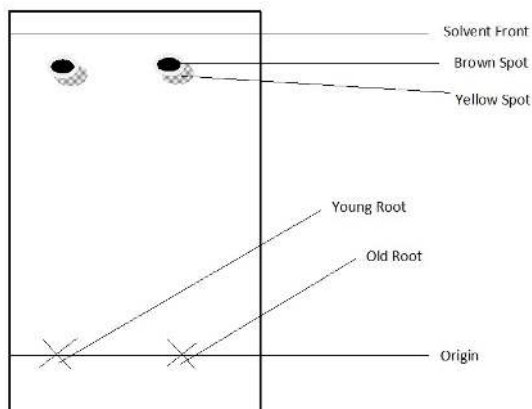


Fig 4.1: TLC of the extracts

The old root showed fluorescent with the same retention factor above the brown spot. When the plate was viewed under UV lamp at 366nm, the old root showed a fluorescent spot while the young root did not show any fluorescent spot. This is as shown in figure 4.2.

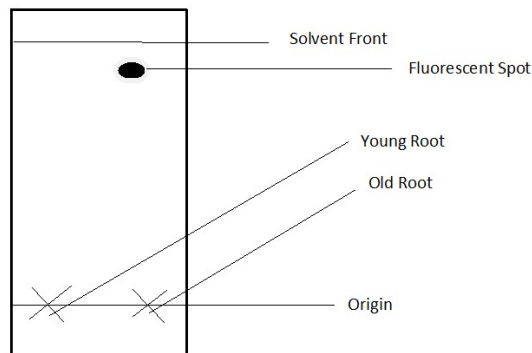


Fig. 4.2: Flourescence spot of the old root

Colour visualization test by vanillin spraying on the plate showed two dark green spots with the same retention factor. This is as shown in Fig 4.3:

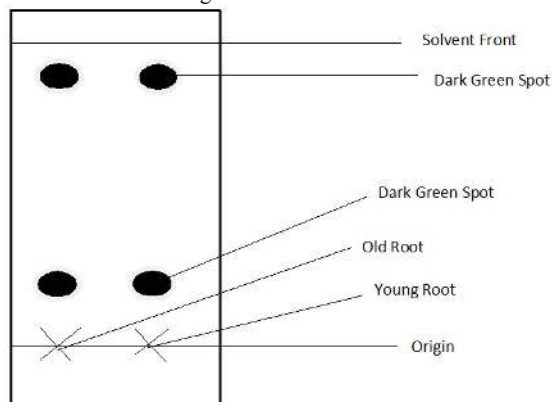


Fig 4: Colour reaction on the TLC plate

When the extracts were filtered from the plant materials, a golden brown filtrate of crude extract was obtained from the young root that turns yellow on concentration while a green filtrate of crude extract was obtained from the old root that turns to dark green on concentration.

Phytochemical Screening of the Extracts

Qualitative phytochemical screening of the young and old neem root extracts revealed the presence of alkaloid, cardiac glycosides, tannins, saponins and steroids is I as shown in the table below.

Table : Result of the phytochemical screening of the young root extract

Natural Product	Test	Observation	Inference
Alkaloid	Wagner's reagent	Brick-red Colouration	Alkaloid present
Alkaloid	Hager's reagent	Yellow colouration	Alkaloid present
Cardiac glycoside	Fehling reagent	Brick-red precipitate was formed	Cardiac glycoside present
Cardiac glycoside	1ml extract+CCl ₄ ; 1ml conc. H ₂ SO ₄	Brown colouration Formed	Cardiac glycoside Present
Tannins	FeCl ₃ solution	Blackish green colouration formed	Tannin present
Saponin	Frothing test	Frothing persist	Saponin present
Steroid	Ernulsification	Emulsion is formed	Steroid present

Table : Result of the phytochemical screening of the old root extract

Natural Product	Test	Observation	Inference
Alkaloid	Wagner's reagent	Brick-red Colouration	Alkaloid present
Alkaloid	Hager's reagent	Yellow colouration	Alkaloid present
Cardiac glycoside	Fehling reagent	Brick-red precipitate was formed	Cardiac glycoside present
Cardiac glycoside	1ml extract + CCl ₄ ; 1ml conc. H ₂ SO ₄	Brown colouration Formed	Cardiac glycoside Present
Tannins	FeCl ₃ solution	Blackish green colouration formed	Tannin present
Saponin	Frothing test	Frothing persist	Saponin present
Steroid	Ernulsification	Emulsion is formed	Steroid present

Result of the Cytotoxicity Test of the Extracts

The result of the cytotoxicity test of the young root extract is as shown in the table below Table : Result of cytotoxicity test of the young root extract

test-tube #	1	2	3	4	5	6	7	8	9
Concentration	1000ppm			1000ppm				1000ppm	
# Alive	0	0	0	7	5	0	7	8	7
# Dead	10	10	10	3	5	10	3	2	3
% Mortality	100	100	100	30	50	100	30	20	30%
	%	%	%	%	%	%	%	%	
Average	100%			60%			26.67%		

The average percentage mortality was used to estimate the lethal concentration at 50% (LC₅₀). From the evaluation, the LC₅₀ value gave 40.6261 μ g/ml which shows that the extract is mediumly toxic. The result of the cytotoxicity test of the old root extract is as shown in the table below.

Table : Result of cytotoxicity test of the old root extract

test-tube #	1	2	3	4	5	6	7	8	9
Concentration	1000ppm			100ppm			10ppm		
# Alive	0	0	0	3	1	2	5	4	6
# Dead	10	10	10	7	9	8	5	6	4
% Mortality	100	100	100	70	90	80	50	50	40
	%	%	%	%	%	%	%	%	%
Average	100%			80%			50%		

The average percentage mortality was used to calculate the lethal concentration at 50% (LC₅₀). From the evaluation, the LC₅₀ value gave 64.5851 μ g/ml which shows that the extract is highly toxic.

Antimicrobial Assay of the Extract

The result of the antimicrobial test carried out is as shown in the tables below

Table : Result of the antimicrobial test of the young root extract

S. a.	H.coli.	B. sub	Ps. A	Kleb.	Sal.	C. a	A. n.	Rhiz.	Pen.
20	18	10	14	10	10	12	12	18	18
18	14		10	-		10	10	14	14
14	10	-	-	-	-	-	-	12	12
10		-	-	-	-	-	-	10	10
-		-	-	-	-	-	-	-	-
-	-	-	-	-	-	-	-	-	-
-	-	-	-	-	-	-	-	-	-
34	32	34	36	34	32	22	20	22	20

Table : Result of the antimicrobial test of the old root extract

S.a	E.coli.	B. sub	Ps. A	Kleb.	Sal.	C. a	A. n.	Rhiz.	Pen.
20	18	10	14	10	10	12	12	18	18
18	14	12	10	-		12	10	14	12
12	10		-	-	-	-	-	10	12
10	-	-	-	-	-	-	-	10	10
-	-	-	-	-	-	-	-	-	-
-	—	—	—	—	-	—	—	—	—
-	-	-	-	-	-	-	-	-	-
34	32	34	36	34	32	21	20	21	21

KEY TO ANTIMICROBIAL TABLE OF RESULT

S.A - *Staphylococcus aureus*,
 Ps.a - *Pseudomonas aureginosa*,
 B.sub - *Bacillus subtilis*,
 E. coli - *Escherichia coli*,
 Sal - *Salmonella typhi*,
 C.a - *Candida albicans*,
 A.n - *Aspergillus niger*,

Rhiz - *Rhizopus stolonifer*,
 Pen - *Penicillium nonatum*,
 Kleb - *Klebsiella pneumonia*.

Discussion

The results obtained from TLC showed that both plant extracts (young and old root) contain an identical chemical component except a fluorescent spot that is absent in the young root.

The phytochemical screening revealed that both young and old root contains the same secondary metabolites tested for which include alkaloid, steroid, cardiac glycosides, saponins and tannins. This observation is similar to that reported by (Antherden 1960). In his experiment carried he observed the presence of tannin, glycosides, alkaloids and carbohydrates which he suggested would have been for the stimulating activity of medicinal plants.

The result of the cytotoxicity test of the young root extract showed that its mediumly toxic with a lethal dose concentration LC₅₀ value of 40.6261 μ g/ml while that of old root extract tends to be highly toxic with a LC₅₀ value of 64.5851 μ g/ml.

From the result of the antimicrobial test obtained from both extract, it showed that both young and old root extracts have a little antifungal activity but a prominent antibacterial activity against *Staphylococcus aureus*, *Escherichia coli*, *Rhizopus stolonifer* and *Penicillium noncitum*. This is similar to the report by (Kurian 1995) that the plant extract is active against *Staphylococcus aureus*, *Escherichia coli* and *Salmonella typhi* and he proposed that this is due to the presence of tannins.

Conclusion

The young and old root extracts of *Azadirachta Indica* showed some similarities from the thin layer chromatography. However, there exist a difference in the extracts when viewed under a UV lamp in which the old root gave a fluorescent spot at 366nm which is absent in young root extract. The old and young root extract also showed a similar antimicrobial activity against the microbes tested.

The difference in the old and young root extracts was from the cytotoxicity. Test in which the old root extract is highly toxic with a LC₅₀ value difference of 23.959 μ g/ml higher than that of the young root extract which is mediumly toxic. It can therefore be assumed that there is an increase in the toxicity level of the plant root as they grow.

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EFFICACY OF THE ETHANOLIC EXTRACT OF *ANDROGRAPHIS PANICULATA* AGAINST *TRYPANOSOMA BRUCEI BRUCEI* IN VITRO TEST

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ABSTRACT

An experiment was carried out on the anti-trypanosomal activities of *Andrographis paniculata* leaves extract. The crude extract was obtained using soxhlet extraction technique. The in vitro study of anti-trypanosomal activity of the crude extract was done using four (4) Wistar rats model. The assessment of invitro anti-trypanosomal activity was performed in 96 wells micro titre plates. To ensure that the effect monitored is that of the extract alone a set of control was included and a reference test was performed using a standard trypanocidal drug (Diminazene Diacurate). Phytochemical screening of the crude extract was carried out of which Alkaloids, Flavanoids, Tannis, Saponins, Terpenes and Glycosides were all positive. Also, haematological indices, weight and temperature of the animals were assessed. Invitro test carried out indicated that the crude extract has the ability to slow down the activity of the trypanosomes after 40/55 minutes out of the total 60 minutes duration. Therefore *A. paniculata* leaves can be used to inhibit *T. brucei*.

KEYWORDS: *Andrographis paniculata*, Ethanolic extract *Trypanosoma brucei brucei*, In vitro test.

INTRODUCTION

Trypanosomes are flagellate protozoans that inhabit the blood the lymph and various tissues of their host [6]. *Trypanosomiasis* is a disease of domestic animals, wild animals [5, 16]. *Trypanosomiasis* is a complex debilitating and often fatal disease caused by infection with one or more of the pathogenic tse-tse transmitted protozoan parasites of the genus *trypanosoma* [12]. It is transmitted by a vector called the tsetse fly [9] for several decades. *Trypanosomiasis* has continued to contribute adversely to the economic and social well-being of sub-saharan African. It is currently estimated that about 60 million people are at risk of Human African *Trypanosomiasis* (HAT) [11]. The most important species responsible for the disease complex commonly known as “nagana” in livestock includes, *Trypanosoma brucei brucei*, *T. Cong* [12]. African animal *Trypanosomiasis* represents one of the most serious veterinary problems in the world [13].

Trypanosoma brucei brucei is a species of Salivary trypanosome which causes African *Trypanosomiasis*, known also as sleeping sickness in humans and nagana in animals. *T. brucei* has traditionally been grouped into three subspecies namely:

- *Trypanosoma brucei brucei*
- *Trypanosoma brucei gambiense*
- *Trypanosoma brucei rhodesiense*.

Trypanosomiasis continues to represent a major threat to animal production in sub-saharan Africa. The disease is more devastating in terms of poverty and loss of agricultural production in affected areas [10]. These losses include reduction in herd size as a result of loss in body condition, drop in milks production, reduced work efficiency of draft animals and prevention of mixed farming [11]. Sheep and goats are seldomly found infected with Trypanosomes under natural conditions.

Andrographis paniculata which is also known as “Creat” in English or “King of bitters” is an annual herbaceous plant in the family *Acanthaceae*, native to India and Sri-lanka. It is widely cultivated in Southern and Southeastern, Asia, where it has been traditionally used to treat infections and some disease. Mostly the leaves and roots were used for medicinal purposes [15].

Andrographis paniculata is known on the Indian subcontinent as Chirayeta and Kalmegh in Urdu and Hindi Languages,

respectively is an annual plant, 1-3ft high. The slender stem is dark green, squared in cross – section with longitudinal furrows and wings along the angles. The lance – shaped leaves have hairless blades measuring up to 8 centimeters long 2.5 wide. The small flowers are borne in spreading racemes. The fruit is a capsule around 2 centimeters long and a few millimeters wide.

MATERIAL AND METHODS

SAMPLE COLLECTION

Leaves of *Andrographis paniculata* were been harvested from Barnawa, Kaduna metropolis and authenticated at biological science Department of Ahmadu Bello University, Zaria. The plant leaves were air-dried grinded into fine powder and kept in air – tight container with proper labelling.

EXTRACTION

PROCEDURE

About 50g of the dried powder sample was weighed and extraction process was carried out using 100cm³ of solvent (methanol) in soxhlet apparatus for 18 hours. Then the extract was concentrated by evaporation at 65°C for 8 hours and then air dried [17].

PHYTOCHEMICAL ANALYSIS

Phytochemical analysis of the crude extract of the plant was carried out using the below methods as described by [7, 14]. Test for presence of alkaloids, glycosides, tannis, saponins flavonoids and triterpenes were carried out.

QUALITATIVE ANALYSIS

Test for Alkaloids

About 0.5g of the methanolic plant extract was mixed in 8ml of 1% HCl, warmed and filtered. 2cm³ of the filtrate was treated separately with both reagents (Mayer's and Dragendorff). After which it was observed where the Alkaloids are present or absent in the turbidity of precipitates formation.

Test for Flavonoids

The filtrate (3cm³) was mixed with 4cm³ of 1% potassium hydroxide in a test tube and the colour was observed. A dark yellow colour indicated the presence of flavonoids

Test for Tannins

Methanolic plant extract (0.25g) was dissolved in 10ml distilled water and filtered 1% aqueous iron chloride (FeCl₃) solution was added to the filtrate. The appearance of intense green, blue or black colour Indicated, the presence of tannins in the test samples.

Test for Saponins

Methanolic plant extract (0.5g) was dissolved in boiling water in a test tube. Test cooling aqueous extracts was mixed vigorously to froth and the height of the froth was measured to determine the saponin contents in the sample.

Test for Terpenes

Methanolic plant extract (0.5g) was shaken with petroleum ether in order to remove the colouring material. Residue was extracted with 10ml chloroform and the chloroform layer was dried over anhydrous sodium sulphate 5cm³ of chloroform layer was mixed with 0.25cm³ of acetic anhydride and then two drops of concentrated sulphuric acid was added. Different colours were observed to indicate the presence of sterols or while the terpenes and triterpenes will be pink to purple.

Test for Glycosides

Methanolic plant extract (5cm³) was mixed with 2cm³ of glacial acetic acid containing one drop of ferric chloride (FeCl₃) solution, followed by the addition of 1cm³ concentrated sulphuric acids. Brown ring was formed at the interface which indicated presence of deoxysugar of cardenolides. A violet ring appeared beneath the brown ring while in the acetic acid layer a greenish ring was also form gradually throughout the layer.

EXPERIMENTAL ANIMAL

In this study, fifteen wistar rats weighing about 150g were purchased from the animal house of Nigerian Institute for Trypanosomiasis Research, Kaduna. The animals were housed in standard rat cages 13 hours/11hrs light /dark photo-period, maintained on standard pellet diet (Vital plc, Jos Nigeria) and water and labitum.

INFECTION OF ANIMALS

About 10² parasites were introduced intravenously into the rats in 0.1-0.2ml blood/PBS solution. Number of parasite /cm³ was estimated using the method of [3].

THE INVITRO TEST

The test was done as described by [2]. Exactly 10g of the plant extracts (Ethanolic) was weighted into Eppendorf tubes and first dissolved in 0.1ml of 20% dimethyl sulfoxide (DMSO) in phosphate Buffer, saline (PBS). Extract, concentration of

10.0mg/ml was prepared for the stock extract solution by appropriate dilution with phosphate Buffer Saline (PBS). Assessment of in vitro anti-trypanosomal activity was performed in 96 well micro titre plates (Flow laboratories INC, McLean, Virginian 22101, USA). In well of micro titre plates 20µl of blood containing about 20 – 25 parasites per microscopic, field (X40 magnification) was mixed with 5 µl of the extract solution of 20.0mg/ml and 10.0mg/ml to produce the two effective test concentration of 4mg/ml and 2mg/ml respectively. To ensure that the effect monitored is that of the extract alone, a set of control were included which also contain the parasites suspended in 2% DMSO only. For reference, test was also carried out using a standard commercial tyronocidal drug Diminazene. All analysis was performed in triplicates.

After 5 minutes incubation in closed eppendorf tube was maintained at 37°C about 2µl of test mixtures were placed on separate microscope slides, covered with cover slips and the parasites were observed every 5 minutes for a total duration of 60mins. Cessation of reduction in blood without extract was taken as a measure of anti-trypanosomal activity.

THERAPEUTIC MONITORING

Parasitaemia of each rat will be monitored every 48 hrs during the administration of the extract and the level will be estimated by rapid matching method of [3] as described by (Atawodi 2005). Parasitaemia level will be compared with untreated control animals and percentage inhibition of parasite will be assessed by the formula

$$\% \text{ Inhibition} = 100 - \frac{(\text{Parasitaemia of test})}{(\text{Parasitaemia of untreated})} \times 100$$

Assessment of the extract will also be based on survival period of the animals.

RESULTS

PHYTOCHEMICAL SCREENING

PHYTO-CONSTITUENTS	OBSERVATION	INFERENCE
ALKALOIDS	Mixture formed turbid precipitate	Alkaloids present
FLAVONOIDS	A dark yellow colour was formed	Flavonoids present
TANNINS	An intense green, blue colour was formed	Tannins present
SAPONINS	Froth was formed after heating	Saponins present
TERPENES	A pink- purple colours was formed	Terpenes present
GLYCOSIDES	Two layers were formed one violet the other greenish	Glycosides present

INVITRO TEST

S/N	Time (mins)	Extract concentration (mg/ml)						Reference Drug		
		4mg/ml			2 mg/ml			Control (Diminazene)		
		1 st	2 nd	3 rd	1 st	2 nd	3 rd	1 st	2 nd	3 rd
1	5	+++	+++	+++	+++	+++	+++	—	—	—
2	10	+++	+++	+++	++	++	++	—	—	—
3	15	+++	+++	+++	++	++	++	—	—	—
4	20	++	++	++	++	+++	++	—	—	—
5	25	++	++	++	++	++	++	—	—	—
6	30	++	++	++	+	+	+	—	—	—
7	35	++	++	++	+	+	+	—	—	—
8	40	++	++	+	+	+	+	—	—	—
9	45	++	+	+	++	++	++	—	—	—
10	50	+	+	+	++	+	+	—	—	—
11	55	+	—	—	+	+	+	—	—	—
12	60	+	—	—	+	+	—	—	—	—

Key: Very motile → +++; Motile → ++; Less motile → +; None motile → —

DISCUSSION

The result of this study (Phytochemical screening) clearly indicates that *Andrographis paniculata* leave extract contain the following bioactive substances Alkaloids, flavonoids, Terpenes, Glycosides, Tannis and Saponins which were all confirmed to be positive. Pytochemical screening also revealed that the major constituents of the extract are phenolic compounds.

From the above result in (Table 4.2) it can be noted that for the 4 mg/ml concentration of the crude extract, the parasite were still massive after 5 minutes but when viewed at 20 minutes the number of parasites dropped and became moderate. At 40 minutes the parasites reduced in number and moyility i.e its movement became very slow and at 55 minutes the parasites died off. It can therefore be confirmed that the crude extract is very active.

Also for the 2 mg/ml concentration of the extract the parasites were still massive and active at 5 minutes but later became moderate at 15 minutes and also became slow in their movement at 30 minutes and at 55 minutes no single parasite was found. However the In vitro evaluation carried out revealed that the crude extract of *Andrographis paniculata* can be used as a control measure against *T.brucei brucei* because of its high activity.

CONCLUSION

From the research work the pytochemical screening of the crude extract of *Andrographis paniculata* indicated the presence of the following bioactive constituents: Alkaloids, flavonoids, Terpenes, Glycosides, Tannis and Saponins which were all confirmed to be positive and therefore it can be concluded that *A.paniculata* is a good antioxidant. It was also confirmed that the extract contains anti-trypanosomal properties.

It is also interesting to note that the activity of the crude extract was high in both the 2 mg/ml and 4 mg/ml concentration of the extract. However the In vitro analysis carried out revealed that the crude extract of *Andrographis paniculata* can be used as a control measure against *T.brucei brucei* in wistar rats.

RECOMENDATION

More research should be carried out on the in vivo aspect of the work so as to obtain accurate result which could lead to the production of tablets for curing this endermic disease which has lead to low productivity in livestock in the sub Saharan Africa. Quantitative screening should be carried out on the crude extract of *A.paniculata* so as to ascertain certain constituents present in the leaves which could also help in cubing the problem

This research work should also be extended to higher animals such as sheep, goats, cattle etc because of their high susceptibility to the disease which of economic importance in sub Saharan Africa
More veterinary clinics should be established in endemic regions.

Finally serious attention should be given to this work so as to avoid other zoonotic diseases.

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