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SYNTHESIS AND CHARACTERIZATION OF PT-NIO/C AS POTENTIAL ELECTROCATALYSTS FOR FUEL CELL APPLICATION

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ABSTRACT

Three Platinum–Nickel Oxide supported on activated carbon (Pt-NiO/C) catalyst samples for methanol electro-oxidation reaction at the anode of a direct methanol fuel cell (DMFC) were prepared by precipitation, impregnation and reduction method using NaOH and $NaBH_4$ as precipitating and reducing agents, respectively. The catalyst samples were supported on activated carbon produced from coconut shell using chemical activation method with phosphoric acid as the activating agent. The Pt-NiO loading of the synthesized Pt-NiO/C electrocatalysts was from 0 – 30 wt%. Pore size distribution and surface morphology of the activated carbon were determined using N_2 adsorption Brunauer-Emmett-Teller (BET) analyzer and scanning electron microscope (SEM), respectively. XRD and BET analyses were used to characterize the Pt-NiO/C electrocatalysts. The BET results of the prepared activated carbon gave a surface area of 302.5 m^2/g and a pore volume of 0.518 cm^3/g. The XRD results showed successful preparation of activated carbon and appearance of the active species impregnated on it. The introduction of NiO reduced the particle size of Pt crystallites. The particle size and surface area of the produced Pt-NiO/C electrocatalysts as compared to commercial Pt-Ru/Vulcan 72R electrocatalyst was found to be 2.78 nm and 3.09 nm; and 100.85 m^2/g and 90.6 m^2/g, respectively. The electrical conductivity of the prepared electrocatalysts ranged from 4.68 S/cm to 5.76 S/cm. Based on the large specific surface area and good electrical conductivity values, the prepared electrocatalysts have potential to be used for the methanol electro-oxidation reaction at the anode of a DMFC.

Keywords*: Activated carbon, Catalyst support, Platinum-nickel oxide, Electrocatalyst, Fuel cell*

1.0 INTRODUCTION

Fuel cells are becoming subject of intense research due to their high energy conversion efficiency and low emissions (Gacutan *et al*., 2012). Fuel cells (FC) are electrochemical devices that use hydrogen (H_2), or H_2-rich fuels, together with oxygen from air, to produce electricity and heat through an electrochemical oxidation reaction (Mukhtar, 2011). Several different types of fuel cells have been developed and categorized according to fuels and electrolytes being used. These include alkaline fuel cell (AFC), polymer electrolyte membrane fuel cell (PEMFC), phosphoric acid fuel cell (PAFC), solid oxide fuel cell (SOFC), direct methanol fuel cell (DMFC), direct ethanol fuel cell (DEFC) and direct formic acid fuel cell (DFAFC) (Nedjeljko *et al*., 2015). The DMFC uses methanol (without having to first convert it into hydrogen) to generate power and heat by electro-oxidation reaction. It consists of two electrodes separated by a proton exchange membrane (PEM) and connected via an external circuit.

The methanol electro-oxidation reaction is catalyzed by platinum as the most active species for the reaction (Mukhtar *et al*., 2017). However, carbon monoxide is produced as an intermediate in the reaction, which poisons the Pt active sites. Pt poisoning can be overcome by alloying with materials less prone to CO poisoning, making the catalyst more stable. Therefore, the NiO will help in the conversion of CO to CO_2, which increases the shelf-life of the electrocatalyst. This will also reduce the amount of platinum usage and thus, the overall cost of the electrocatalyst. Electrocatalysts active species are usually dispersed on a support material for better performance. The most common supports as reported by Nedjeljko *et al*., (2015) are carbon black, binary carbon catalyst support (Vulcan XC-72 and Black pearl 2000), conducting polymers (eliminating the need for Nafion- layers or impregnation), carbon nanohorn and carbon nanotube hybrids which are produced at commercial scale. Almost any carbonaceous material with low organic volatile content, high elemental carbon content and of sufficient strength can be converted to an activated carbon to be used as catalyst support material (Mohammed and Dheyab, 2013). The choice of coconut shell over other waste raw materials was due to its availability, low cost and its good properties such as high carbon content and low ash content. These make it the preferred source for activated carbon used in the gold mining industry (Sudaryanto *et al.*, 2006). Due to these advantages it could be used to produce cheap electrocatalyst support for fuel cell application thereby reducing the overall cost of producing the electrocatalyst. Therefore, this paper reports the synthesis and characterization of nanostructured Pt-NiO/C electrocatalysts as potential anode electrode for DMFC application.

2.0 MATERIALS AND METHODOLOGY

2.1.1 Preparation of Activated Carbon from Coconut Shell

Coconut shell was obtained from Samaru, Zaria, Nigeria. The grey hard piece was washed with water to remove soil and fiber. It was then dried under the sun for 24 h in order to reduce the moisture content. The dried shells were crushed in a mortar to obtain a particle size of about 12-15 mm and were ground with a commercial miller and then sieved to a particle size of 125 µm.

2.1.2 Carbonization

The carbonization procedure reported by Mukhtar *et al.*, (2015) was followed. Eighty grams (80 g) of the prepared sample was placed in a stainless-steel tubular reactor and then into a horizontal tubular furnace (Carbolite) for carbonization. The carbonization process was carried out in an inert atmosphere using nitrogen gas of 99.9% purity, supplied at a rate of 2 mL/min under Standard Temperature and Pressure (STP) condition. After adjusting the nitrogen flow, the tubular furnace was switched on to allow the temperature rise to about 550 °C, which was the optimum carbonization temperature according to Mukhtar *et al.*, (2015). Once the desired carbonization temperature of 550 °C was attained, the heated sample was held isothermally at the set point for 1h before cooling down to room temperature under nitrogen flow. This same process was repeated for four other runs following similar procedure.

2.1.3 Chemical Activation

Chemical activation was done using an impregnation ratio of 1:1 on a mass basis. To obtain an impregnation mass ratio of 1:1 according to a study by Foo and Hameed, (2011), 10 g of carbonized coconut shell particles was poured into a beaker containing 10 ml phosphoric acid of 88 wt% purity. Then the mixture was stirred thoroughly and aged for 24 h before being dried in the oven at 110 °C for 24 h. 50 ml of 1 M KOH was poured into a beaker containing the impregnated activated carbon sample to wash it. The mixture was stirred thoroughly to remove the excess chemicals and separated using vacuum pump filtration. Subsequently, the samples were rinsed sequentially with distilled water until the pH of the wash solution fell in the range of 6-6.5. The solution pH was measured using a portable pH meter. The resultant samples were dried at 105 °C in the oven for 24 h.

2.2 Catalyst Synthesis

The concentration and the rate of addition of the nickel (II) nitrate hexahydrate and hexachloroplatinic (IV) acid hexahydrate solution were varied to obtain different calculated metal loadings of 7.5 wt%, 15 wt%, 22.5 wt% and 30 wt%. The Pt-NiO/C electrocatalysts were synthesized using a two-step method described by Amin *et al.,* (2012).

2.2.1 Impregnation of Nickel Oxide on Support

Nickel Oxide was supported on coconut shell activated carbon by precipitation method. The detailed steps of the catalyst synthesis were as follows: an appropriate amount of nickel (II) nitrate hexahydrate ($Ni(NO_3)_2.6H_2O$) was weighed and dissolved in a suspension of coconut shell activated carbon in distilled water. The added Nickel salt was calculated to prepare nickel oxide carbon support catalyst (NiO/C) powder containing 7.5 wt%, 15 wt%, 22.5 wt% and 30 wt% of the nickel oxide. Drops of 1 M NaOH solution were added to the mixture to maintain its pH value at 10 under constant stirring for 3 h. This induces the formation of small and uniform nanoparticles (Amin *et al.*, 2012). The resulting powder was then filtered using a vacuum pump filter and washed six times with distilled water and dried in an air oven at 80 ^{o}C for 6 h. Calcination step at 400 ^{o}C was performed in an electric furnace for 3 h to form NiO/C catalyst.

2.2.2 Impregnation of Pt on the Synthesized NiO/C

The loading of Pt was carried out on the synthesized NiO/C powder produced by varying its amount such that; 7.5 wt% NiO/C was loaded with 22.5 wt% Pt, 15 wt% NiO/C was loaded with 15 wt% Pt and 22.5 wt% NiO/C was loaded with 7.5 wt% Pt. The Pt was synthesized by the reduction/impregnation method. The corresponding weight of hexachloroplatinic (IV) acid hexahydrate solution ($H_2PtCl_6.6H_2O$) based on each of the outlined catalyst loading was dissolved in a suspension of NiO/C powder in distilled water. There was continuous stirring for 1 h at 70 ^{o}C which was followed by the addition of drops of 1 M NaOH solution to adjust the pH value at 11. The reduction step was performed by adding Sodium Borohydride ($NaBH_4$)

slowly to the mixture with continuous stirring for 3 h. The molar ratio of Pt salt to sodium borohydride was kept at 1:70 (Amin *et al*., 2012).

The prepared Pt-NiO/C catalyst was then filtered using a vacuum pump filter: washed six times with distilled water and an oven at 80 °C for 6 h.

The five different electrocatalyst samples prepared were:

NiO/C: (30 wt% NiO and 70 wt%C)
PtNiO-1/C: (7.5 wt% Pt, 22.5 wt%NiO and 70 wt%C)
PtNiO-2/C: (15 wt% Pt, 15 wt% NiO/C and 70 wt%C)
PtNiO-3/C: (22.5 wt% Pt, 7.5 wt% NiO and 70 wt%C)
Pt/C: (30 wt% Pt and 70 wt%C)

2.3 Characterization

2.3.1 Proximate and Ultimate Analysis

The proximate and ultimate analyses of samples were measured using thermal gravimetric analyzer and elemental analyzer, respectively (available at the Institute of Agricultural Research (IAR), Ahmadu Bello University, Zaria).

2.3.2 Scanning Electron Microscopy

The surface morphology of the raw coconut shell sample, carbonized coconut shell sample and the produced coconut shell activated carbon were observed under Scanning Electron Microscopy using Hitachi S-4500 field emission SEM with a quartz PCI x-one SSD x-ray analyzer in the Department of Chemical Engineering, Ahmadu Bello University, Zaria.

2.3.3 XRD of the electrocatalysts

The crystalline phase of the prepared activated carbon and the synthesized electrocatalysts were studied using the Shidmadzu XRD-6000 Diffractometer at the National Geological Survey Agency, Kaduna. The XRD patterns were identified and analyzed by comparing their diffraction lines and intensities using the Joint Committee on Powder Diffraction Standards (JCPDS).

2.3.4 BET analysis

Quantachrome Nova 4200e BET machine was used to determine the specific surface area, pore diameter and pore volume of the electrocatalysts prepared using the N_2 adsorption-desorption technique at the Centre for Genetic Engineering and Biotechnology, Federal University of Technology, Minna.

2.3.5 Electrical Conductivity of Support and Synthesized Catalyst

The electrical conductivity of the coconut shell activated carbon produced and the synthesized electrocatalysts was determined by a Programmable LRC Bridge (HM8118; ROHDE & SCHWARZ) in the Department of Physics, Ahmadu Bello University, Zaria.

3.0 RESULTS AND DISCUSSION

3.1 Proximate and Ultimate Analysis

Table 1 gives the proximate analysis results of the raw coconut shell and activated samples. It is observed (as expected) that the percentage fixed-carbon significantly increased after thermal treatment and chemical activation process while the percentage volatile matter drastically decreased. This is attributed to the burning of the non-carbonaceous and volatile components present in the raw sample. It is also corroborated by the results of the ultimate analysis as indicated in Table 2. The inert environment of N_2 created during the carbonization process reduced the percentage of oxygen and increased the percentage of nitrogen.

Table 1: Proximate analysis of raw and activated carbon samples

Proximate Analysis	Raw sample (%)	Activated sample (%)
Volatile matter	70.82	26.46
Fixed carbon	20.18	69.29
Ash content	0.8	2.05
Moisture content	8.2	2.2

Table 2: Ultimate analysis of raw and activated carbon samples

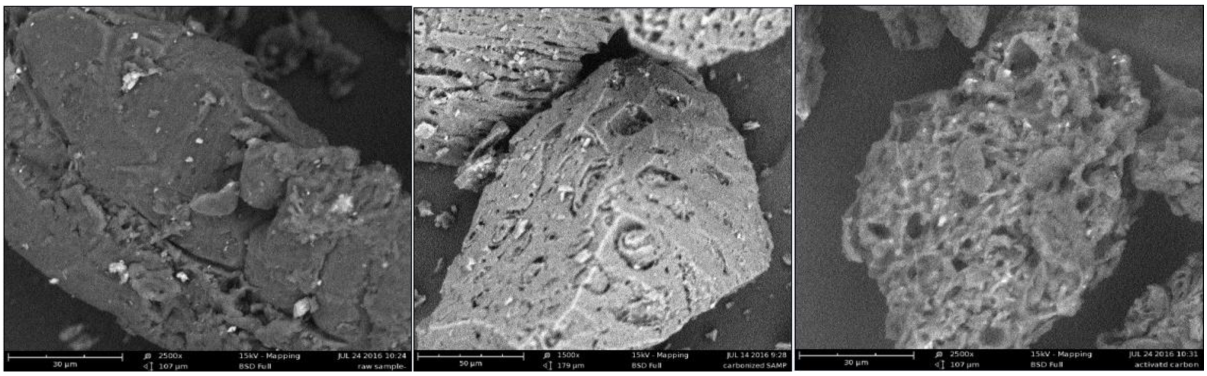
Ultimate Analysis	Raw sample (%)	Activated sample (%)
Carbon	49.62	80.13
Hydrogen	7.31	2.36
Nitrogen	0.22	1.10
Sulphur	0.10	0.06
Oxygen	42.75	16.35

3.2 Percentage Yield of Activated Carbon

The percentage yield of the produced activated carbon was determined as the ratio of the mass of activated carbon sample produced to the mass of raw sample used. The average percentage activated carbon yield of 23.29% obtained is within the range of the reported values in the literature (Tan *et al*., 2008).

3.3 Scanning Electron Microscopy (SEM)

SEM analysis was performed to elucidate the morphology of the samples' surface. Figure 1(a) shows the SEM image of the raw coconut shell sample, which exhibited irregular agglomerates of rod-like particles of coconut shell with an absence of pores. After carbonization at the reported conditions according to Achaw and Afrane, (2008), the carbonized coconut shell sample in figure 1(b) shows a more developed porous carbon with the presence of cavities and pore spaces as compared to that of the raw sample shown in figure 1(a). The development of pores during carbonization is due to the burning of the non-carbonaceous and volatile components present in the raw sample. This creates spaces thus resulting to the pore spaces observed in figure 1(b). An increase in the number of pores was observed after chemical activation with phosphoric acid as shown in figure 1(c). Phosphoric acid acts as the activating agent which helps in further development of the pores during the drying process. As shown in figure 1(c), the sample shapes were rod-like with holes and cave type openings on the surface of the produced activated carbon that would definitely have increased the surface available for the active species impregnation during the catalyst synthesis.



(a) **(b)** **(c)**

Figure 1: SEM image of the raw coconut shell sample (a), carbonized coconut shell sample (b), produced activated carbon (c)

3.4 BET Surface Area Analysis

Surface area is an important attribute of a solid catalyst that plays a vital role in its catalytic activity. The surface area of the produced activated carbon was determined using BET (Brunauer-Emmett-Teller) method. The average pore size of the coconut shell activated carbon produced was determined to be 29.76 nm with pore volume 0.518 cm^3/g. This implies that the coconut shell activated carbon produced has more mesopores. The specific surface area of 302.5 m^2/g obtained was within the range required for it to be used as a catalyst support material. This is similar to other support materials used in a related work by Amin *et al*., (2012) with specific surface area of 240 m^2/g using Vulcan XC-72 as support material and by Yoshiyuki *et al*., (2013) with specific surface area of 347 m^2/g using graphene oxide as support material.

3.5 XRD Result of Produced Activated Carbon

XRD was used to investigate phase transformation, crystallite size and shape of the samples. The diffraction patterns of the coconut shell activated carbon produced is shown in figure 2. It was obtained with Cukα radiation ($\lambda = 0.15406$ nm) in a 2θ scan range of 0^o – 60^o at a step interval of 0.2. The peaks with low and high intensity observed at 2θ value of 18^{o}and 24^{o}is attributed to the hexagonal graphite structure (001) and (002), respectively having (JCPDS) card number;75-1621. Figures 3, 4, 5, 6 and 7 show the X-ray diffraction patterns for the prepared catalysts; NiO/C, Pt/C, PtNiO-1/C, PtNiO-2/C and PtNiO-3/C respectively. X-ray diffraction analyses showed the presence of diffraction peaks for carbon (001) and (002), Nickel Oxide (111) and (200), and platinum (111) and (200). The peaks with low and high intensity observed at 2θ value of 18^{o}and 24^o clearly appeared in all the XRD patterns of NiO/C, PtNiO-1/C, PtNiO-2/C, PtNiO-3/C and Pt/C electrocatalysts. However, they are of lower intensity as compared to the XRD pattern intensity of the activated carbon produced in figure 3. This may be as a result of the partial coverage of the carbon surface by deposited Pt, NiO and PtNiO active species. Moreover, Pt/C and all the Pt–NiO/C samples showed two distinct diffraction peaks for platinum representing a typical face centered-cubic (f.c.c.) crystal structure of platinum. They are located at about 2theta (degree) values 39^o and 46^{o}corresponding to Pt(111) and Pt(200) planes respectively to demonstrate the presence of Pt in the metallic form(JCPDS: 01-1194).

The XRD pattern of the synthesized NiO/C when compared to the XRD standard values (JCPDS: 47-1049) agrees with the diffraction peaks of NiO which is consistent with reported XRD pattern. In the XRD pattern for NiO, crystallographic planes such as (111) and (200) located at 2theta (degree) values of 37^o and

43° were observed, which indicates NiO particles crystallization.

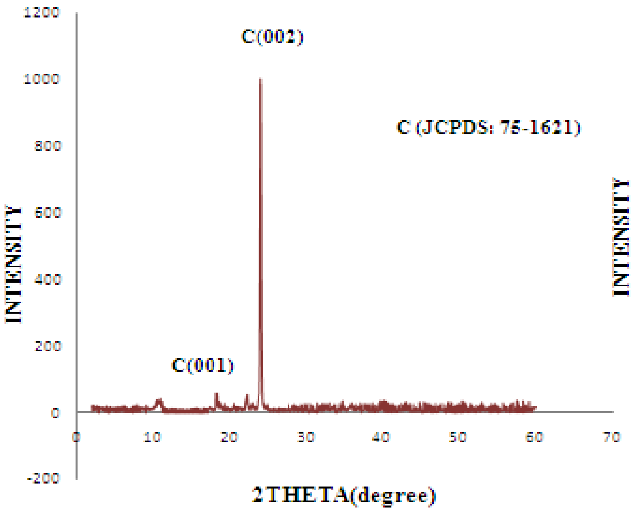


Figure 2: XRD Pattern for the Activated Carbon Synthesized (100wt%C)

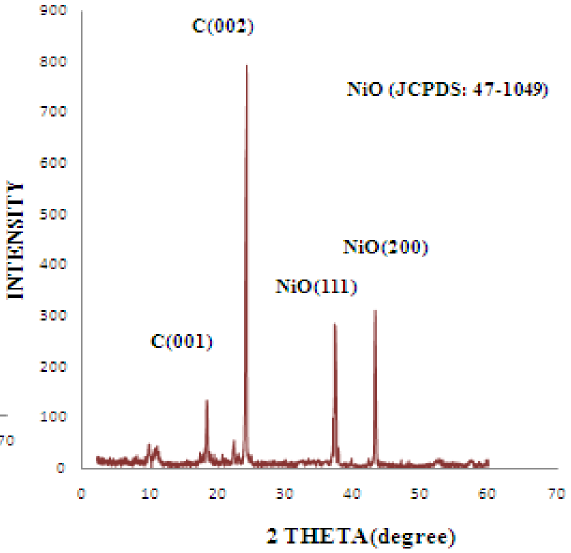


Figure 3: XRD Pattern for synthesized NiO/C (30wt%NiO, 70wt%C)

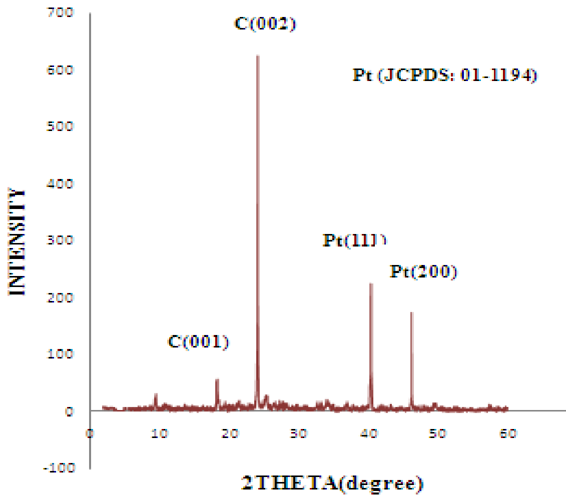


Figure 4: XRD Pattern for the Pt/C Synthesized (30wt%Pt, 70wt%C)

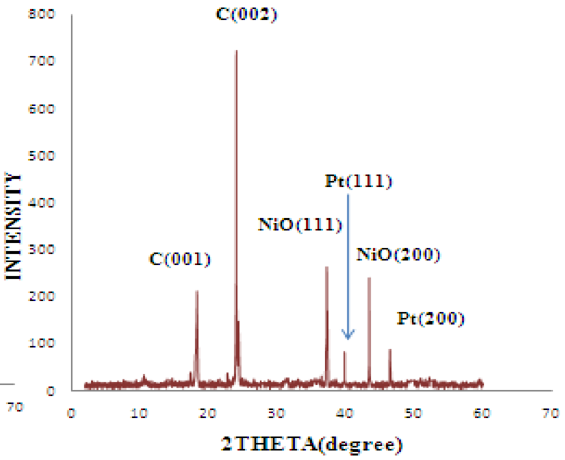


Figure 5: XRD Pattern for the PtNiO-1/C Synthesized (7.5wt%Pt, 22.5wt%NiO, 70wt%C)

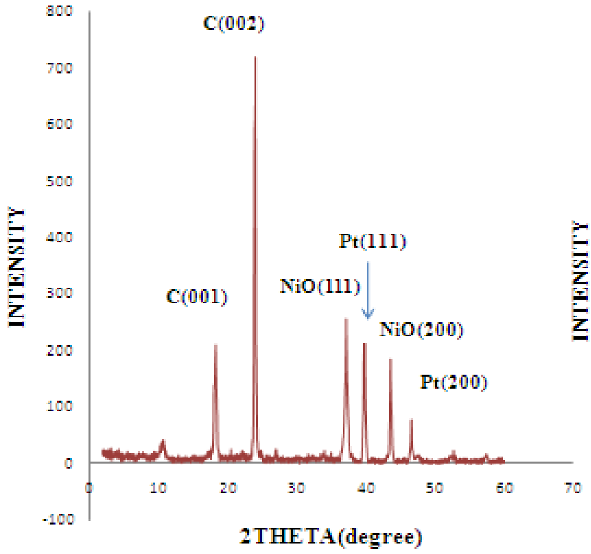


Figure 6: XRD Pattern for the PtNiO-2/C Synthesized (15wt%Pt, 15wt%NiO 70wt%C)

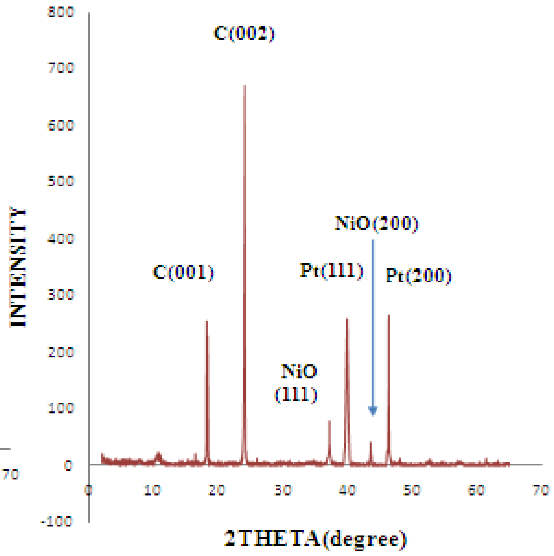


Figure 7: XRD Pattern for the PtNiO-3/C Synthesized (22.5wt%Pt, 7.5wt%NiO, 70wt%C)

3.6 Electrical Conductivity of the Support and Synthesized Electrocatalyst

Figure 8 shows the electrical conductivity values of the produced electrocatalyst.

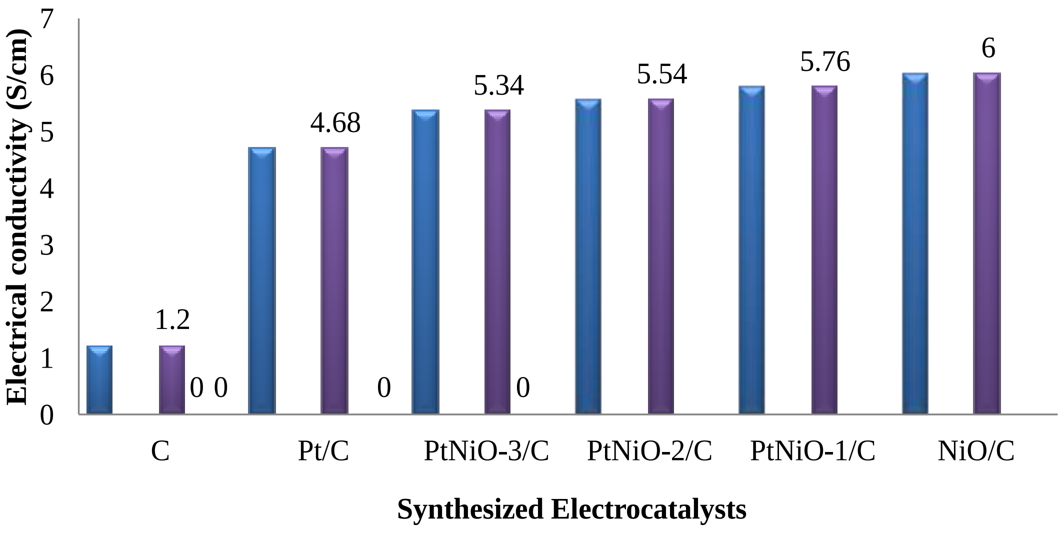


Figure 8: Electrical Conductivity of the Synthesized Electrocatalysts

The results show that the plain activated carbon produced had the least electrical conductivity value of 1.2 S/cm while an increment in the electrical conductivity of the electrocatalyst samples with increase in the metal loading (especially nickel oxide) was observed. The low electrical conductivity of the produced coconut shell activated carbon is attributed to the amorphous nature of carbonaceous material (Anne, 2017). After the impregnation of the active species on the produced coconut shell activated carbon, the result shows an increase in the electrical conductivity for the synthesized electrocatalysts from 4.68S/cm for Pt/C to 6.0 S/cm for NiO/C. This is attributed to the relatively high electrical conductivity of the active species (nickel and platinum) present in the synthesized electrocatalysts samples.

3.7 Comparative Analysis of Synthesized Electrocatalysts with the Reported Electrocatalysts

The comparative analysis of the synthesized electrocatalysts with the reported electrocatalysts was carried out using the important properties shown by a typical direct methanol fuel cell anode electro-oxidation catalyst. Table 3 shows the BET surface area of the prepared electrocatalysts after the impregnation of active species. The particle size of the produced electrocatalysts was calculated using the Scherer's equation;

$$d = \frac{0.9\lambda}{\beta cos\theta max} \qquad (1)$$

Where d is average diameter (nm), λ is wavelength of X-ray (0.154nm), β is full width at the diffraction at half maximum (rad) and θmax is angle at the position of the peak maximum (degree).

As indicated in Table 3, the presence of NiO helped the formation of small sized electrocatalysts particles. This agrees with the results obtained by Amin *et al*., (2012) who prepared carbon dispersed Pt–nickel oxide nanocatalysts on Vulcan XC 72R carbon and found that the addition of NiO to Pt/C catalyst greatly decreased Pt particle size from 9.8 to 4.9 nm. Wang *et al*., (2010) also prepared carbon dispersed Pd–nickel oxide nanocatalysts and found that the addition of NiO to Pd/C catalyst greatly decreased Pd particle size from 59.6 to 7.0 nm. Kim *et al*., (2010) likewise observed the reduction of Pt crystallite size from 2.0 to 1.6 nm when NiO was supported on Vulcan carbon. The diffraction peaks of NiO are present in all XRD patterns of Pt–NiO/C catalysts. This is attributed to the relatively large amount dispersed on the coconut shell activated carbon support (7.5wt %) unlike its absence from the XRD patterns of the electrocatalyst synthesized by Amin *et al*., (2012) when 5 wt. % was dispersed on Vulcan carbon support.

Table 3: Specific surface area and particle size of produced electrocatalysts compared with the reported electrocatalysts

.Electrocatalyst	Specific surface area (m^2/g)	Particle size (nm)	References
NiO/C	53	13.4	Present work
Pt/C	60.13	6.29	Present work
PtNiO-1/C	68.4	4.1	Present work
Pt-NiO-2/C	90.8	2.71	Present work
PtNiO-3/C	100.85	2.78	Present work
NiO/Vulcan	74	12.2	Rifaya *et al*., (2012)
Pt/Vulcan	67	9.8	Josef *et al*., (2014)
Pt-NiO/Vulcan	78	4.9	Amin *et al*., (2012)
PtRu/GO	96.4	2.9	Yoshiyuki *et al*., (2013)
PtRu/Vulcan	90.6	3.09	Yoshiyuki *et al*., (2013)

The specific surface area of the synthesized electrocatalysts was obtained using BET adsorption and desorption isotherm at -196 ^oC of Nitrogen gas. The values obtained varies respectively from 53.0 m^2/g for NiO/C, 60.13 m^2/g for Pt/C, 68.4 m^2/g for PtNiO-1/C, 90.8 m^2/g for PtNiO-2/C and 100.85 m^2/g for PtNiO-3/C. These sharp decrease in specific surface area as against a specific surface area of 302.5 m^2/g for the coconut shell activated carbon used as carbon support materials may be as a result of active species deposition inside the pore spaces. The result is similar to that of Yoshiyuki *et al*., (2013) whose electrocatalysts specific surface area when graphene oxide was used as support decreased from 347 m^2/g to 96.4 m^2/g with a particle size of 2.9 nm and when Vulcan XC 72R carbon was used as support decreased from 237 m^2/g to 90.6 m^2/g with a particle size of 3.09 nm. Thus, the synthesized electrocatalysts is within the acceptable range of electrochemical surface area required for an electrocatalyst to be used as an anode electro-oxidation catalyst for a direct methanol fuel cell.

4.0 CONCLUSION

Activated carbon from coconut shell was produced using chemical activation method with a percentage yield of 23.29%. The SEM results showed the surface morphology and the formation of pores on the activated carbon produced. The BET results showed a high surface area of 302.5 m^2/g and a pore volume of 0.518 cm^3/g, which makes it a suitable electrocatalysts support material for fuel cells application. NiO and Pt were successfully impregnated separately on the prepared activated carbon and jointly as dual active species on the activated carbon to form Pt-NiO/C. The XRD results showed successful preparation of activated carbon and appearance of the active species impregnated on it. The synthesized Pt/C, Pt-NiO-3/C, Pt-NiO-2, PtNiO-1 and NiO/C electrocatalysts had electrical conductivity values of 4.68 S/cm, 5.34 S/cm, 5.54 S/cm, 5.76 S/cm and 6.0 S/cm, respectively. The comparative analysis of the synthesized electrocatalysts with the reported electrocatalysts in the literature indicate that the produced electrocatalysts have potential to be used for the methanol electro-oxidation reaction at the anode of a direct methanol fuel cell.

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EFFECT OF LOCALLY SYNTHESIZED CEMENT RETARDER ON THE SETTING TIME AND RHEOLOGICAL PROPERTIES OF CEMENT SLURRY

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ABSTRACT

Cementing operation in oil and gas industries is an important operation in wellbore construction. In order to achieve successful cementing operation, additives are used for the designing of these cement slurries to meet the American Petroleum Institute (API) specifications. This study was carried out using API recommended practice 13B-2 (1997), to determine the effect of the synthesized cement retarder at concentrations of 0.01 gal/sk, 0.04 gal/sk, 0.07 gal/sk and 0.10 gal/sk on the setting time and rheological properties of the cement slurry. The test results obtained at various concentrations showed the setting time as: 3:06 hrs , 4:06 hrs, 5:28 hrs and 12:18 hrs and the yield point which represent the rheological values as: 78 Ib/100ft2 , 62 Ib/100ft2, 13 Ib/100ft2, and 9 Ib/100ft2. The results obtained revealed a retarding tendency of the synthesized cement retarder as the concentrations increased and a decrease in the yield point as observed in the The statistical analysis using analysis of variance (ANOVA) single factor also showed a significant difference on rheological property as the concentration increases.(Fcal >F critical).

***Keywords**: Setting time, synthesized cement retarder, Rheology, API Specification.*

1. INTRODUCTION

Cementing operation is the placing of oil well cement slurry in between the formation and casing to achieve adequate zonal isolation of the well. The objectives of the operation is to prevent the formation of fluid like gas and water from communicating from one zone to another in the well, to support the casing, to prevent casing from corrosion, to prevent casing from shock loads while drilling, to prevent blowouts, to achieve seal off lost circulation or thief zones and for well abandonment. Well cementing is one of the major operations that is carried out during oil well construction (Lootens et al, 2004) therefore, cement slurry of high grade is needed so as to achieve economically and safely crude oil production over the lifetime of the well (Ridha et al, 2010), And to secure the extended durability of wellbore by providing a high-quality casing (Pourafshary et al, 2009; Ershadi et al, 2011). When complete zonal isolation is not achieved and there is a weak bond between the cement and the casing and/or the cement with the formation, it may cause the well not to produce to its full potential as there will be oil spills (Calvert, 2006). In well cementing, poor cement slurry design and poor cementing operation can adversely affect the production of crude oil. Some of the effects of poor cementing operation and poor slurry design can lead to oil spills which have an environmental effect (Lootens et al, 2004) that causes death to aquatic lives and land pollution causing low production of agricultural produce, making the environment inhabitable to humans as it causes some respiratory diseases and is also responsible for loss of world oil reserves.

1.2 Chemistry of Portland cement slurry reaction

The predominantly used cement in cementing oil well is Portland cement. The four important clinker phases found in Portland cement are dicalcium silicate (C_2S), tricalcium silicate (C_3S), and tetra calcium aluminoferrite (C_4AF), tricalcium aluminate (C_3A),; the clinker is mixed with gypsum (CH_2). (Michaux, et al, 1990). In The formulae above C represents CaO, S represents SiO_2, A represents Al_2O_3, F represents Fe_2O_3 and H represents H_2O in chemistry abbreviations,(Young and Hansen, 1987). The chemical reactions that results between water and cement are complex. Each parts of the Portland cement undergo hydration process by a unique chemical reaction routes and at various reaction kinetics. The chemical reactions, nonetheless, depends on one another due to the chemistry of the cement and the closeness of the parts. When this reactions takes place it usually result to energy being giving out or producing heat. The gradual changes and build up that occurs in hydration is sketched in (Figure 1.1)

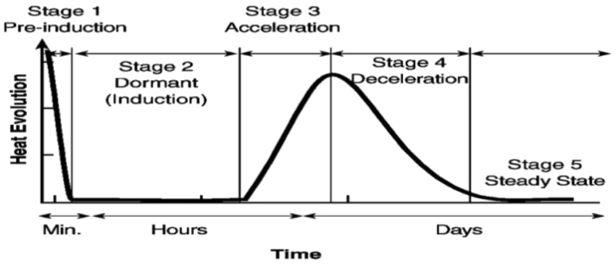

Figure 1.1. Heat evolution schematic for Portland cement at 20°C.(Nelson, 1990)

Five principal chemical reactions occur instantly between water and cement in a mixture

Once they are in contact. The reactions are: (i) dissolution of parts of the clinker sulphates (ii) dissolution of parts of the gypsum, generating a basic or an alkaline solution that is rich in sulphates. Immediately when mixing is over, the Tricalcium aluminate (C_3A) component-the one that react most among the components undergo chemical reaction with the water to develop a gel-like solution that is rich in aluminate as shown in the chemical reactions equations below.

$$2C_3S + 6H \longrightarrow C_3S_2H_3 + 3CH$$

$$2C_2S + 4H \longrightarrow C_3S_2H_3 + CH$$

$$2C_3A + 27H \longrightarrow C_2AH_8 + C_4AH_{19}$$

$$2C_3A + 27H \longrightarrow 2C_3AH_{12} + 15H$$

The gel undergoes reactions with sulphate produced as a result of dissolution of some parts of the clinker sulphate in the mixture to form a minute rod-like structure of ettringite. The Tricalcium aluminate (C_3A) hydration process is usually a heat evolution process that last for a few period. And is immediately taken over by a duration of some hours of comparably low energy production. This period is known as the induction period. The early stage of the induction period last for between 2-10hours which will be enough time for the cementing operation that is if not retarded with a cement retarder and depending on the environmental conditions. As the induction time continues, the slurry turns very hard to be pumpable. At the completion of the induction time, the C_3S and C_2S in the Portland begin to undergo hydration, with the building up of calcium hydroxide and calcium silicate hydrate. At the same time the strength of the cement is developing too. The cement particles begin its reaction within the surface insides and causes the anhydrous cement grains turns smaller. The tricalcium aluminate (C_3A) hydration at same time progresses, as new crystals is easily reachable to water. The time of highest energy evolution happens usually in average of 15hours from when it was intermingled and slowly dies off. In a mixture having cement particles as major cementitious particles, the main strength development attained happens usually within 30days. Ferrite hydration begins immediately water is introduced, and gradually reduces thereafter, and this could be because of formation of a film gel of iron hydroxide, covering the iron and behaving as a hindrance for any other future chemical reaction. The rate of reaction between water and cement particles can be altered by additions of chemicals known as additives (Lu et al, 1993)

1.3 Cement additives

There are over 100 cement additives in the oil and gas industries, these additives are classified into eight (8) categories namely: Retarder, accelerator, Fluid loss, Lost circulation material, weighting Agent, Extender, Dispersant and special Additives such as Antifoams.

1.3.1 The Retarder as an Additive.

The chemical Additives which helps to slow down the setting time of the cement slurry is known as retarder, the predominantly used additives as cement retarder in the oil industries are Cellulose, lignosulphonates, and sugar extracts. The most abundant retarders are gotten from wood pulp. They comprise Calcium and sodium salts of lignosulphonic acids and contain some saccharides. They are believed to attach onto initial layer of calcium silicate hydrate (C-S-H) gel, causing it to be hydrophobic and prolonging the induction period. Added in concentrations of 0.1 to 1.5 percent BWOC, they retard hydration at temperatures up to 122^{o}C (250^{o}F). When treated with other chemicals such as borax, lignosulphonates can be used at temperature of up to 315^{o}C (600^{o}F).

Hydroxycarboxylic acids, such as glucoheptonate and gluconate salts, also retard hydration of cement but are not used when the bottom-hole temperature is below 93^{o}C (200^{o}F). Cellulose sources like carboxymethyl hydroxyethyl cellulose (CMHEC) have been used for many years as cement retarder. In order to achieve a good cementing operations several cement slurry designs are carried out, however this study tend to look into the other effects such as setting time and the rheology of the cement slurry formulated with the locally synthesized cement retarder

2. MATERIALS AND METHODS

A series of tests were performed to evaluate the performance of the synthesized cement retarder which was obtained from sawdust by hydrolysis process and sulphonation reaction using sodium hydroxide, 98% sulphuric acid and sodium bisulfite (Setiati et al, 2017) on thickening time and rheological properties. All tests were conducted in line with the specification for materials and testing for Well Cements (Anon, 1997). The testing conditions are specified in Table 1.

2.1 Slurry preparation

The slurries were prepared according to the API specification 10A standard (1995). The slurry composition is shown in Table 2. Dyckerhof-G cement and water content of 46% by weight of cement (BWOC) were used and the following laboratory test; thickening time and rheology were carried out at the various concentrations of the synthesized cement retarder.

2.2 Thickening (Setting) time Test

The thickening time or setting time test indicates how long the cement slurry will remain in fluid state before it hardens or becomes unpumpable (Alp et al, 2013). In order words, the duration after initial mixing when the cement can no longer be pumped (Salam et al, 2013). Consistency of cement slurry is expressed in Bearden units of consistency (Bc). The Thickening Time (TT) test was performed using a High-Pressure- High-Temperature (HPHT) Consistometer rated at a pressure of up to 206.8 MPa (30 000 psi) and temperatures of up to 204^{o}C (400^{o}F). The cement slurry was mixed according to API procedures and then placed in a slurry cup into the consistometer for testing. The testing pressure and temperature were controlled to simulate the conditions the slurry will encounter in the well. The test concluded when the slurry reached a consistency considered unpumpable in the well. The time it take the cement slurries to reach 40Bc, 70Bc and 100Bc consistency were recorded (Anon,1997).

2.3 Rheology testing

The rheological property of cement slurries when ascertained helps to correctly predict the frictional pressures that occur when pumping the different fluids down the well. The rheology of fluids also has a major effect on solids setting and frees fluid properties and also on the friction pressures (Joel, 2009). Since rheological testing is typically conducted at atmospheric pressure, the maximum temperature is limited to about 190°F (Anon,1997) After blending, the slurry was conditioned using atmospheric consistometer to simulate the well condition of 120^{o}F for 20 minutes. The conditioned slurry was poured into the viscometer cup and the bob of the viscometer was inserted into the cup and the thermometer of the viscometer was also inserted to record the temperature of the slurry. The Fan viscometer was turned on for 15 minutes. The shear rate and the shear stress behaviour of the slurry were determined. The viscosity was measured in centipoises (cP) usng the Fann viscometer and the readings were recorded.

Fig 2 HTHP Consistometer

3 RESULTS AND DISCUSSION

Table 1: Test Physical Parameter Data

TVD =6500ft (1981m); MD =7900ft(2408m)					
S/No		1	2	3	4
BHST	^{o}F	164	164	164	164
BHCT	^{o}F	120	120	120	120
BHP	Psi	3000	3000	3000	3000
Ramp time	Min	11	11	11	11

TVD stands for the True vertical Depth of the well and MD stands for measured depth. In estimating the physical parameter which gives the information about the well conditions such as the well temperature, pressure, ramp time the TVD is used, reason being that pressure at the same level is the same. Table 1 show the physical parameter which is keyed into the HTHP Consistometer to mimic the well condition in the field. As shown in table 1, the temperature at which the test were conducted was 120^{o}F, the downhole pressure was 3000psi and the ramp time which is the time it takes the consistometer surface temperature to reach the downhole temperature was 11mins.

Table 2: Additives Concentration and Slurry Composition

Additives	specific gravity	1	2	3	4
Dyckerhoff-G cement (%BWOC)	3.172	100	100	100	100
Synthesized cement retarder(GAL/SK)	1.23	0.01	0.04	0.07	0.1
Defoamer(GAL/SK)	0.902	0.014	0.014	0.014	0.014
Water type	Lab water				
Chloride content (ppm)	1	200	200	200	200
Water requirement (GAL/SK)		5.04	5.02	5	4.97
Mixing fluid(GAL/SK)		5.06	5.07	5.08	5.09
Yield(CUFT/SK		1.152	1.153	1.154	1.155
Slurry weight(PPG)		15.8	15.8	15.8	15.8

Table 2 shows the additives concentrations and the slurry composition, the defoamer helps to remove the air bubbles in the cement slurry and prevent pump cavitation during cementing operations, for 15.8ppg slurry it is usually added at 0.014gal/sk for effective removal of the air bubble, the water used was the laboratory water with chloride content of 200ppm.

Table 3: Setting Time Test Result

Consistency (BC)	**Concentration(gal/sk)**	**Setting Time(hrs:mins)**	**Neat slurry setting time(hr:mins)**
40BC	0.01	02:30	01:30
	0.04	03:41	
	0.07	04:42	
	0.1	11:56	
70BC	0.01	02:47	01:45
	0.04	03:57	
	0.07	05:01	
	0.1	12:01	
100BC	0.01	03:06	02:05

Consistency (BC)	Concentration(gal/sk)	Setting Time(hrs:mins)	Neat slurry setting time(hr:mins)
	0.04	04:06	
	0.07	05:28	
	0.1	12:18	

Table 3 shows that the locally produced cement retarder has a retarding ability when compare with the neat slurry as shown in the table, at 40BC for the retarded slurry it took the slurry 2hours 30mins while for the neat slurry it took about 1 hours 30mins, at 70BC the time was 2hours 47mins while for the neat slurry it was 1hour 45mins and for 100BC the time was 3hours 6mins whereas for the neat slurry it was 2hours 5mins. The table 3 has also shown that increase in concentration of the locally synthesized cement retarder leads to increase in the setting time and This might be due to the building of a coating film on the cement particles making it less permeable and the development of the CH nuclei poisoned which would lead to increase in induction period and this means that the slurry will remain in the pumpable state throughout the induction period (Young, 1976), though the retardation process delay the setting time of the cement slurry and slow the rate of strength development but does not necessary decrease the strength developed. (Joel, 2009). The concentration of cement retarder for a retarding process depends on the type of cement, the temperature, the water to cement ratio and the volume of cement slurry to be designed for a particular operation, therefore the concentration recommended is based on operational demand but it must not exceed 0.4gal/sk as concentration above this will lead to over dispersed slurry causing settling of the cement slurry particles.

Table 4: Rheology result @Surface Temperature (120^{0}F)

Rpm		0.01	0.04	0.07	0.1
300	cP	123	96	52	33
200	cP	111	83	35	22
100	cP	93	72	30	17
60	cP	70	53	20	12
30	cP	45	34	18	9
6	cP	24	26	15	7
3	cP	18	19	10	4
PV	cP	45	36	33	24
YP	(lbf/100ft2)	78	62	13	9

Table 4 shows the rheology of the slurry at 120^{o}F it was observed that as the concentration of the retarder increases the yield point decreases, which was in agreement with the findings from (Joel, 2009). For good cement slurry from operational point the slurry yield point must not be less than 6 lbf/100ft2. This is very important to avoid settling down of the cement particles.

Table 5: Statistical analysis using single factor ANOVA

SUMMARY

Groups	*Count*	*Average*	*Variance*
123	8	60.5	1088.857
96	8	48.125	526.6964
52	8	21.75	92.5
33	8	13	52.57143

ANOVA

Source of Variation	SS	MS	F	P-value	F crit
Between Groups	11833.84	3944.62	8.961851	0.00025	2.94669
Within Groups	12324.38	440.156			
Total	24158.22				

Table 6 shows that there is a significant difference ($p < 0.05$) in the rheology of the cement slurry as the concentration of the retarder increased.

4. CONCLUSIONS

The test results shows the following

- That the locally synthesized cement retarder has the capacity to retard dyckerhoff- G cement prepared at 15.8ppg with water content of 46%BWOC
- That the yield point of the cement slurry decreases as the concentration of the locally synthesized cement retarder increases
- That the concentrations of the cement retarder depend on the type of cement, the volume of cement slurry required for the given operation and the temperature of the well.
- That the concentration of the retarder must not exceed 0.4gal/sk to avoid settling down of the cement particles due to over dispersion.

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EVALUATION OF GROUNDWATER CONTAMINATION STATUS IN IGANDO AREA OF LAGOS STATE, NIGERIA

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ABSTRACT

The integrity of groundwater is very important to determine its suitability for drinking. The status groundwater contamination of Igando area of Lagos State was evaluated. Groundwater samples were taken from 16 different locations in Igando using treated 1 litre plastic bottles. The samples were labeled GW 1 to GW 16 and they were analysed for the following parameters: calcium (Ca^{2+}), magnesium (Mg^{2+}), manganese, (Mn^{+}) potassium (K^{+}), sodium (Na^{+}), iron (Fe^{2+}), boron (B^{3+}), total hardness (TH), total dissolved solid (TDS) and chloride (Cl^{-}) using the standard methods for the examination of water and wastewater as prescribed by the American Public Health Association. Analysis of variance (ANOVA) was carried out on the data obtained from groundwater analysis with the aid of an in-built Microsoft excel version 2007. The results of the analysed parameters in groundwater samples investigated from locations 1 – 3, 7 and 9 were below the values stipulated in the guidelines for drinking water by World Health Organisation (WHO). The contamination factors of the analysed parameters in groundwater samples from locations 1 – 3 ranged between 0.02 and 0.36. The modified degree of contamination of groundwater from locations 1 – 3 were 0.09, 0.11 and 0.15 respectively while that of locations 7, 9 and 12 were 17.46, 21.16 and 15.77 respectively. The water quality index of groundwater from locations 1 – 3 were 0.19, 0.62 and 0.14 respectively while that of locations 7, 9 and 12 were 7.08, 8.50 and 6.42 respectively. The pollution load indexes of groundwater from all the locations considered varied between 0.07 and 0.80 except that from location 16 which was 1.05. The ANOVA showed that the mean concentrations of parameters investigated are not different at 5 % significant level while the correlation coefficient matrix revealed the parameters investigated were positively and negatively correlated. It was concluded based on the analysed parameters that only groundwater from locations 1 – 3 were fit for drinking. It was also revealed that using only WHO standard for drinking water to evaluate the status of groundwater can be misleading but also contamination factor, modified degree of contamination and water quality index should also be carried out

***Keywords**: Analysis of variance, contamination, evaluation, groundwater and status.*

1.0 INTRODUCTION

Groundwater is water present below the ground surface that saturates the pore space in the subsurface. It is the major source of potable water in both rural and urban areas of Nigeria (Olatunji *et al*., 2015). The sustenance of life in nature is made possible by water (Edori *et al*., 2016). The availability of safe drinking water is a major problem in the world especially in Africa and Asia (WHO, 2004 and Edori *et al*., 2016).). Most groundwater is cleaned but can be polluted or contaminated (Gibat, 1991). Groundwater is contaminated when concentrations of chemicals, nutrients or elements in water become more than its natural, normal, acceptable or recommended concentrations. It is polluted when the contamination goes on to harm living organisms.

Today, contamination of groundwater is one of the major problems in the world (Hazem and Talaat, 2017). Several works have been carried out on groundwater contamination (Ideriah *et al*., 2007; Longe and Balogun, 2010; Ernest *et al*., 2010; Akoteyan *et al*., 2011; Afolayan *et al*., 2012; Olafisoye *et al*., 2013; Oyedami *et al*., 2013; Idowu and Olubunmi, 2013; Ilaboya *et al*., 2014; Olatunji *et al*., 2015 and Edori *et al*., 2016). Akoteyon (2012) evaluated groundwater quality in Igando area of Lagos State using contamination factor but neglected pollution load index and water quality index as well as the analysis of variance of the metals analysed The work revealed the groundwater in Igando area was not contaminated. Idowu and Olubunmi (2013) also evaluated groundwater quality in Igando area of Lagos State. However, only TDS, electrical conductivity, chloride, nitrate oxide, zinc and iron were considered. The contamination status of the groundwater was not carried out. Salami and Susu (2015) predicted the groundwater contaminants concentrations in Igando area of Lagos State using two dimensional model. The work did not consider the contamination status of the groundwater.

Therefore the aim of this work is to evaluate the groundwater contamination status in Igando area of Lagos State using contamination factor, modified degree of contamination, water quality index and pollution load index with a view of carrying out the ANOVA and establishing the correlation coefficient matrix for the parameters under consideration. The need for protection and continuous monitoring of groundwater status cannot be overemphasized (Olatunji *et al.*, 2015). There are three landfill sites in Igando of Lagos state out of which two are operational and the remaining one is closed. It is imperative that the groundwater in Igando area of Lagos State is evaluated to determine its present status as this will serve for data collection for policy makers and local authorities, tool to sanitise our environment and improve the quality of water consumed by the community.

2. THEORY

2.1 Contamination Factor

Contamination factor (CF) is the level of contamination of water by metals. It can be expressed using Equation (1) (Syed *et al.*, 2012).

$$CF = \frac{C_i}{B_i} \tag{1}$$

Where C_i is the measured concentration of a particular element in the groundwater sample and B_i is the concentration of the particular element in the background sample. The background sample is the WHO upper limit standard for concentration of element in drinking water (Edori *et al.*, 2016). Table 1 shows the different contamination factor level and class (Hakanson 1980 and Odunlami and Salami, 2017).

Table 1: Different Contamination Factor and Level Class

CF Class	Contamination Factor and Level
$CF \prec 2$	Low contamination factor
$2 \leq CF \prec 3$	Moderate contamination factor
$3 \leq CF \prec 6$	Considerable contamination factor
$6 \leq CF$	Very high contamination factor

2.2 Modified Degree of Contamination

Modified degree of contamination $\left({}_mC_d\right)$ summarises the combined effects of several quality parameters considered harmful to drinking water (Hazeem and Talaat, 2017). The Hakanson modified and generalized form of equation presented by Abrahim and Parker (2008) shown in Equation (2) is used for calculation of the overall degree of contamination at a given sampling site as follows (Syed *et al.*, 2012):

(i) The modified degree of contamination is defined as the sum of all the contamination factors for a given set of pollutants divided by the number of analysed pollutants.

(ii) The mean concentration of a pollutant element is based on the analysis of at least three samples.

$$\left({}_mC_d\right) = \frac{\sum_i^n CF}{n} \tag{2}$$

Where n is the number of elements analysed and CF is as defined in Equation (1). The modified degree of contamination allows the incorporation of many metals as possible as there is no upper limit. There are seven graduations for classification and description of modified degree of contamination according to Abrahim and Parker (2008). The different modified degrees of contamination are presented in Table 2.

Table 2: Different modified degree of contamination for groundwater

${}_mC_d$ Class	modified degree of contamination level
${}_mC_d \prec 1.5$	Nil to very low degree of contamination
$1.5 \leq {}_mC_d \prec 2$	Low degree of contamination
$2 \leq {}_mC_d \prec 4$	Moderate degree of contamination
$4 \leq {}_mC_d \prec 8$	High degree of contamination
$8 \leq {}_mC_d \prec 16$	Very high degree of contamination
$16 \leq {}_mC_d \prec 32$	Extremely high

${}_mC_d$ **Class**	**modified degree of contamination level**
	degree of contamination
$32 \leq {}_mC_d$	Ultra - high degree of contamination

2.3 Water Quality Index

The unit weight of a particular element (W_i) is calculated using Equation (3) (Bangalore and Latha, 2008 and Olatunji *et al*., 2015).

$$W_i = \frac{K}{B_i} \tag{3}$$

Where B_i is as defined in Equation (1). *K* is a constant of proportionality which is taken to be unity for simplicity (Olatunji *et al*., 2015). The water quality index (WQI) is calculated using Equation (4).

$$WQI = \frac{\sum\left(CF \times W_i\right)}{\sum W_i} \tag{4}$$

Where *CF* is as defined in Equation (1). The numerical value of WQI less than 1 implies that the water is fit for drinking and a numerical value greater than or equal to 1 indicates that the water is unfit for drinking (Bangalor and Latha, 2008).

2.4 Pollution Load Index

The pollution load index (PLI) developed by Thomilson *et al*., (1980) is presented in Equation (5). PLI is aimed at providing a measure of the degree of overall contamination at a sampling site (Mmolawa *et al*., 2011). It is also used for detecting pollution which permits a comparison of pollution levels between sites and at different times (Syed *et al*., 2012). The PLI gives an estimate of the metal contamination status. A PLI value less than 1 denotes the water is not polluted, a PLI value of 1 means only the baseline level of pollution is present and a PLI value greater than 1 indicates the water is polluted.

$$PLI = \sqrt[n]{CF_1 \times CF_2 \times CF_3 \times \ldots CF_n} \tag{5}$$

3.0 MATERIALS AND METHODS

3.1 Study Area

Igando is situated in Ikoyun/Igando Local Council Development Area of Alimosho Local Government of Lagos State, Nigeria. It is located between latitude 6^o 31 0' N to 6^o 31 30' N and longitude 3^o 15 0' E and 3^o 15 30' E (Akoteyon, 2012). The climate of Igando and its environs is a warm tropical type having little seasonal variation and the annual mean temperature is around 30^oC while humidity is about 75 % with a steady vapour pressure (Idowu and Olubunmi, 2013). It occupies an area of about 25.1 sq km. It is bound by Ifako – Ijaye, Agege and Ikeja Local Government in the east and Oshodi/Isolo, Amuwo – Odofin and Ojo Local Government areas in the southern part while river owo demarcates it from Ado – Odo/Ota Local Government of Ogun State (Akoteyon, 2012). There are 3 landfill sites in the area out of which two are operational and the remaining is closed. The major source of drinking water in Igando is groundwater source. There is a presence of a state mini water works which also depend on groundwater source. A state general hospital is also presence in the area which provides health services to the people in Igando and its environ. The soil is red and laterite in nature.

3.2 Location of Position of Sampling Points

The locations of all the sampling points were coordinated using Global Positioning System (GPS) in order to identify the sampling points universally. The coordinate list in Minna data of the sampling points is presented in Table 3.

Table 3: Coordinate List of sampling point in Minna Datum

Location	Eastings (m)	Northings (Meter)	Orthometric Heights (m)
1	528001.270	725659.533	35.173
2	527866.697	725528.750	34.540
3	527874.639	725581.834	34.879
4	527883.005	725600.306	35.035
5	528118.000	725652.000	38.098
6	528192.584	725584.061	34.698
7	528110.278	726137.063	37.982
8	528164.000	726145.000	38.269
9	528166.767	726345.164	38.302
10	528032.334	726199.452	37.630

Location	Eastings (m)	Northings (Meter)	Orthometric Heights (m)
11	528223.586	726344.494	36.393
12	528258.606	726302.929	36.519
13	528023.000	726261.000	37.265
14	527973.288	726202.786	37.435
15	527870.063	726416.404	36.286
16	527780.610	726250.378	34.539

3.3 Sampling and Analysis

Groundwater samples were collected in the month of August, 2017 using 1 litre plastic bottles which had been cleaned by soaking in 10 % nitric acid and rinsed with distilled water in order to avoid contamination and allowed to dry before use. At the sampling locations, the bottles were rinsed three times with water to be sampled prior to filling and they were labeled GW 1 – GW 16. The samples were quickly transferred to the analytical laboratory of University of Lagos for analysis using the standard methods for the examination of water and wastewater as prescribed by American Public Health Association (APHA, 1994). The parameters analysed were Ca^{2+}, Mg^{2+}, Mn^{+}, K^{+}, Na^{+}, Fe^{2+}, B^{3+}, TH, TDS and Cl^{-}. All experiments were carried out in triplicate and the results were found reproducible within ± 3% error. The data were statistically analysed by setting up and calculating a correlation coefficient matrix and a one way ANOVA using the in-built solver tool in Microsoft Excel version 2007.

4.0 RESULTS AND DISCUSSION

Table 4 presents the numerical values of groundwater samples from Igando of Lagos State. The concentrations of parameters analysed in groundwater samples from locations 1 – 3, 7, 9 and 12 were below the values stipulated by WHO for drinking water. The concentrations of manganese, iron and boron in groundwater sample from location 4 were 0.08, 2.77 and 9.09 mg/L respectively. These values were higher than the WHO standard values of 0.05, 0.3 and 0.5 mg/L for manganese, iron and boron respectively for drinking water. In locations 5 and 6, the values of manganese were 0.09 and 0.1 mg/L respectively which were higher than the value of 0.05 mg/L stipulated by WHO for drinking water. The groundwater sample from location 8 has a value of 0.6 mg/L for boron which exceeded the stipulated value of 0.5 mg/L by WHO for drinking water. The groundwater samples from locations 10 - 11 have iron content of 1.10 and 0.7 mg/L respectively which are above the WHO limit for drinking water. The manganese and iron in groundwater samples from locations 13 – 16 varied between 1.78 and 8.80 mg/L and between 6.03 and 8.04 mg/L respectively. These values were above the WHO values of 0.05 and 0.3 mg/L for manganese and iron respectively. The high values of manganese and iron in groundwater samples from locations 13 – 16 may be attributed to the fact that these location are very close to the dumpsite. Considering the WHO standard for drinking water, groundwater from locations 1 – 3, 7 and 9 were fit for drinking while groundwater in locations 4 – 6, 8, 10 – 11 and 13 – 16 were unfit for drinking based on the parameters analysed. This is an indication that the dumpsites in the area have impacted negatively on the groundwater.

Table 4: Numerical values of groundwater samples from Igando of Lagos state

Locations	Parameters (mg/l)									
	Ca^{2+}	Mg^{2+}	Mn^{+}	K^{+}	Na^{+}	Fe^{2+}	B^{3+}	TH	TDS	Cl^{-}
1	1.80	0.43	0.01	0.36	5.80	0.05	0.01	3.60	29.00	6.90
2	1.73	0.45	0.04	0.09	7.60	0.03	0.02	3.57	27.50	8.94
3	1.79	0.44	0.01	0.14	9.90	0.04	0.03	3.51	30.10	11.70
4	16.07	0.54	0.08	13.97	6.49	2.77	9.09	17.86	23.97	88.06
5	1.79	0.49	0.09	0.03	8.80	0.02	0.05	3.57	29.30	10.32

Locations	Parameters (mg/l)									
	Ca^{2+}	Mg^{2+}	Mn^{+}	K^{+}	Na^{+}	Fe^{2+}	B^{3+}	TH	TDS	Cl^{-}
6	17.70	1.70	0.10	196.60	10.30	0.48	0.12	24.80	44.00	10.32
7	3.50	0.86	0.04	172.60	5.10	0.08	0.10	7.10	66.00	6.70
8	4.30	0.75	0.02	109.50	7.30	0.04	0.60	7.60	70.00	6.70
9	3.50	0.86	0.05	209.90	6.90	0.01	0.02	6.90	37.00	10.70
10	49.60	1.76	0.01	262.00	24.37	1.10	0.16	56.60	121.20	32.95
11	3.50	0.79	0.03	22.00	10.60	0.70	0.06	7.40	69.00	14.70
12	4.78	0.91	0.04	156.00	8.69	0.01	0.03	7.80	41.00	14.89
13	6.41	2.86	2.00	7.53	4.60	7.00	0.01	28.05	23.00	25.00
14	4.81	3.34	1.78	4.02	4.80	7.03	0.01	26.05	49.00	37.50
15	2.41	3.40	2.04	3.02	5.00	8.04	0.10	19.01	98.80	87.50
16	3.21	8.81	8.81	2.51	5.35	6.03	3.60	24.05	42.37	45.00
*WHO	70.00	2.00	0.05	1.00	200	0.30	0.5	100	500	200

*Source: WHO (2004)

Table 5 shows the contamination factors for parameters analysed in groundwater samples from Igando of Lagos State. The contamination factors were obtained using Equation (1). The contamination factor for the parameters analysed in groundwater samples from locations 1 - 3 and 5 were less than 2 which indicates that the groundwater samples from locations 1 – 3 and 5 were of no contamination. Groundwater samples from locations 13 – 16 were of very high contamination in term of manganese and iron because the contamination factors were higher than 6 and this was attributed to the proximate of locations 13 – 16 to the dumpsite. The contamination factor for potassium in groundwater samples from locations 7, 9 and 12 were 172.60, 209 and 156 respectively which indicates the groundwater samples from locations 7, 9 and 12 are of very high contamination. According the WHO standard for drinking water, groundwater samples from locations 7 and 9 may be fit for drinking however, the contamination factor of potassium are 172.60 and 209.90 respectively which showed the groundwater samples were contaminated.

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Table 5: Contamination factor for parameters analysed in groundwater samples from Igando of Lagos State

Locations	Parameters									
	Ca^{2+}	Mg^{2+}	Mn^{+}	K^{+}	Na^{+}	Fe^{2+}	B^{3+}	TH	TDS	Cl^{-}
1	0.03	0.22	0.20	0.36	0.03	0.17	0.02	0.04	0.13	0.03
2	0.02	0.23	0.80	0.09	0.04	0.10	0.04	0.04	0.09	0.07
3	0.03	0.22	0.14	0.14	0.05	0.13	0.06	0.04	0.06	0.05
4	0.23	0.27	1.60	13.97	0.03	9.23	18.18	0.18	0.05	0.44
5	0.03	0.23	1.80	0.03	0.04	0.07	0.10	0.04	0.06	0.06

Locations	Parameters									
	Ca^{2+}	Mg^{2+}	Mn^{+}	K^{+}	Na^{+}	Fe^{2+}	B^{3+}	TH	TDS	Cl^{-}
6	0.26	0.85	2.00	196.00	0.05	1.60	0.24	0.25	0.06	0.07
7	0.05	0.43	0.80	172.60	0.03	0.27	0.20	0.07	0.06	0.03
8	0.06	0.38	0.46	109.56	0.04	0.13	0.12	0.08	0.10	0.08
9	0.05	0.43	0.90	209.90	0.03	0.03	0.04	0.07	0.05	0.05
10	0.71	0.88	0.20	262.00	0.12	3.67	0.32	0.57	0.08	0.16
11	0.05	0.40	0.60	22.00	0.05	2.33	0.12	0.07	0.14	0.07
12	0.06	0.46	0.80	156.00	0.04	0.03	0.06	0.08	0.24	0.07
13	0.09	1.43	40.00	7.53	0.02	23.33	0.02	0.28	0.07	0.13
14	0.07	1.67	35.60	4.02	0.03	23.43	0.02	0.26	0.08	0.19
15	0.03	1.70	40.80	3.02	0.03	26.80	0.20	0.19	0.20	0.44
16	0.05	4.41	176.20	2.51	0.03	20.10	7.20	0.24	0.08	0.23

Table 6 presents the modified degree of contamination, water quality index and pollution load index of the studied groundwater samples. The modified degree of contamination, water quality index and pollution load index were generated using Equations 2, 4 and 5. The modified degree of contamination of groundwater samples from locations 7 and 9 were 11.21 and 21. 16 respectively which indicated that the groundwater samples from location 7 and 9 were of extremely high degree of contamination. The WQI of groundwater samples from locations 1 – 3 were less than 1 while that of locations 7, 9 and 12 were 7.08, 8.50 and 6.42 respectively which implied the groundwater samples from locations 7, 9 and 12 were unfit for drinking since the WQI were greater than 1. The PLI of groundwater samples from locations 1 – 15 were less than 1 while that of location 16 was greater than 1.

Table 6: Modified degree of contamination, water quality index and pollution load index of groundwater samples from Igando of Lagos State

Location	${}_mC_d$	WQI	PLI	Location	${}_mC_d$	WQI	PLI
1	0.11	0.19	0.07	9	21.16	8.50	0.19
2	0.15	0.62	0.07	10	26.89	10.40	0.80
3	0.09	0.14	0.07	11	2.58	1.57	0.28
4	4.42	4.21	0.70	12	15.77	6.42	0.21
5	0.25	1.36	0.08	13	7.29	32.98	0.48
6	20.20	9.05	0.55	14	6.54	29.59	0.50
7	17.46	7.08	0.26	15	7.34	33.85	0.66
8	11.21	4.53	0.27	16	21.10	134.36	1.05

Considering the WHO standard for drinking water, groundwater samples from locations 1 – 3, 7 and 9 can be deemed fit for drinking based on the parameters analysed in this work. However, in term of contamination factor, modified degree of contamination and water quality index, groundwater samples from locations 7 and 9 were unfit for drinking. This clearly shows that using only WHO standard to determine the status of groundwater for drinking can be misleading. Therefore, the need also for contamination factor, modified degree of contamination and water quality index. Based on the pollution index, groundwater in locations 1 – 3, 7, 9 and 12 can be deemed not polluted. Table 7 shows a one - way ANOVA for parameters investigated in groundwater samples from Igando. The F and F critical in this work were 0.05 and 1.75 respectively at 5% significant level ($\alpha = 5\%$). This implied that the mean concentrations of parameters investigated are not different at 5 % significant level.

Table 7: Analysis of variance of parameters investigated in groundwater samples

Source of variation	Sum of Square	Degree of freedom	Mean Square	F	F critical
Between Treatment	144	15	9.60	0.05	1.75
Residue	262,383.60	144	1,822.11		
Total	262,527.60	159	1,831.71		

Table 8 presents the correlation coefficient matrix for parameters investigated in groundwater samples

Table 8: Correlation coefficient matrix for parameters investigated in groundwater

Parameters	**Ca^{2+}**	**Mg^{2+}**	**Mn^{+}**	**K^{+}**	**Na^{+}**	**Fe^{2+}**	**B^{3+}**	**TH**	**TDS**	**Cl^{-}**
Ca^{2+}	1.00									
Mg^{2+}	- 0.02	1.00								
Mn^{+}	- 0.15	0.97	1.00							
K^{+}	0.60	- 0.20	- 0.32	1.00						
Na^{+}	0.86	- 0.19	- 0.28	0.56	1.00					
Fe^{2+}	- 0.07	0.71	0.63	- 0.43	- 0.36	1.00				
B^{3+}	0.14	0.18	0.25	- 0.22	- 0.14	0.17	1.00			
TH	0.84	0.42	0.26	0.36	0.58	0.45	0.11	1.00		
TDS	0.56	0.11	- 0.03	0.45	0.57	0.13	- 0.24	0.55	1.00	
Cl^{-}	0.19	0.39	0.34	- 0.12	- 0.12	0.68	0.65	0.39	0.23	1.00

The purpose of the correlation analysis is to measure the intensity of association observed between two variables. In the groundwater investigated, calcium had a weak negative correlation with magnesium, manganese and iron but a strong positive correlation with sodium. Magnesium had a strong positive correlation with manganese but a weak positive correlation with boron and chloride. The correlation observed among the parameters investigated was attributed to the likely reaction among them.

5.0 CONCLUSION

The evaluation of groundwater contamination status in Igando area of Lagos State has been carried out. Based on the guidelines for drinking water by WHO, groundwater samples from locations 1 – 3, 7 and 9 were fit for drinking while groundwater in locations 4 – 6, 8, 10 – 11 and 13 – 16 were unfit for drinking based on the parameters analysed. The contamination factor and the modified degree of contamination revealed the groundwater samples from locations 7 and 9 were of very high contamination and extremely high degree contamination which makes the groundwater samples from locations 7 and 9 unfit for drinking. The water quality index also showed that the groundwater samples from location 7 and 9 were unfit for drinking. This work revealed that using only WHO standard for drinking water to evaluate the status of groundwater can be misleading but also contamination factor, modified degree of contamination and water quality index should also be carried out. The one - way analysis of variance revealed the mean concentrations of parameters investigated are not different at 5 % significant level. The parameters analysed were positively and negatively correlated among themselves.

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OPTIMISATION OF ANAEROBIC DIGESTION TREATMENT OF PETROLEUM SLUDGE

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ABSTRACT

Anaerobic digestion treatment of petroleum sludge increases Nigerian gross domestic product and enhance sustainable development as it yields biogas and biosolids fertilizer. The potential of anaerobic digestion for the treatment of Petroleum sludge was proved by a reduction in Biochemical Carbonaceous Oxygen Demand (BCOD) of the sludge from 6080 mg/L to 20.40 mg/L and Total Hydrocarbon Content (THC) from 57000 ppm to 1500 ppm. Gas Chromatography and Mass Spectrophotometry (GC-MS) result showed a decrease in concentration of Polycyclic Aromatic Hydrocarbons (PAHs) from 37.1 mg/L to 0.32 mg/L Napthalene; 33.43 mg/L to 8.24 mg/L Anthracene and 33.97 mg/L to 9.86 mg/L Phenanthrene. Anaerobic digestion of 200 grammes of the sludge gave 10,500 m^3/d *biogas and 190 g biosolids with NPK value of 5.0 mg/kg Nitrate, 30.0 mg/kg Phosphate and 695.95 mg/kg Potassium. For 5 Tons per day of sludge plant capacity, economic analysis gave 2 years Pay Back Period (PBP) and 47 % Rate of Return on Investment (ROI). This show that a petroleum sludge anaerobic digestion plant if well managed could be economically viable in Nigeria. The plant should be located as a process unit in every Nigerian process industry, waste water treatment plant and sites where sludges are dumped.*

Keywords*: Polycyclic Aromatic Hydrocarbons; Biochemical Carbonaceous Oxygen Demand; Total Hydrocarbon Content; Spectrophotometry; Economic Viability*.

1.0. INTRODUCTION

The disposal of untreated petroleum sludge causes environmental and health hazards because of disease pathogens present in the untreated sludge. The treatment of sludge destroys the disease pathogens to enable an industry meet Environmental Protection Agency standards and regulations for treatment and disposal of sludge. Besides health related problems, disposal of untreated petroleum sludge onto land or water bodies causes land pollution, water pollution and destruction of ecosystem. Moreover, the treatment of sludge in anaerobic digesters yields the environmentally friendly and renewable energy source,biogas a substitute for natural gas and biosolids, a substitute for petrochemical based fertilizers. In Nigeria, the treatment and disposal of sludge in accordance with EPA specifications imposes a major challenge to the oil and gas industry. Winter (1984) states that anaerobic biogas digesters have historically been used for sewage sludge stabilization in Waste Water Treatment Plants (WWTP$_S$). Owabor and Owihiri (2011) give the priority pollutants as the Polycyclic Aromatic Hydrocarbons (PAHs) which are known to be in the priority list of EU and EPA due to their mutagenic and carcinogenic properties to be napthalene, phenanthrene and anthracene which can be used as representative of the PAHs.

Besides destroying disease pathogens in the sludge, anaerobic digestion treatment of sludge yields biogas and biosolids fertilizer hence saving the fuel needed to manufacture petrochemical based fertilizers (Appels *etal.*, 2008). Moreover, besides being cheaper, biosolids fertilizer is retained in the soil longer than petrochemical based fertilizers as it does not easily get leached.

Biogas produced from anaerobic digestion is useful for generating power for operating the plant, hence optimizing operational cost of the plant (Appels *etal.*, 2008). Although Nigerian natural gas reserve is exponentially increasing, biogas is more advantageous being a renewable energy source and more environmentally friendly as it produces less greenhouse emissions as it has less carbon. Moreover, adequate treatment prevents corrosion to user equipments. It is emphasized in Hakan *et al.* (2009) that other renewable energy sources lay claim to large areas of arable land thereby hampering food production. This technical paper describes anaerobic digestion Process for petroleum sludge treatment and its numerous economic advantages. Moreover, mathematical modeling, process optimization and troubleshooting of the anaerobic digestion plant are also included in the paper.

1.1. Process Description

1.1.1. Microbial Digestion

The thickened sludge was pretreated to disrupt chemical bonds of cell walls and membranes thus enhancing solubilisation of cell components. The sludge was degraded in anaerobic digester by microbial action in the absence of oxygen to biogas and NPK rich bio solids fertilizer. The supernatant from the digester and water from the thickener were recycled to the Waste Water Treatment Plant (WWTP) and the bio solids dried, pelletised and sent to bagging unit. Green and Perry (1997) gave Solid Retention Time (SRT) of 15 – 30 days, Hydraulic Retention Time (HRT) of 10 – 30 days, Temperature 30 – 38 °C, Mesophillic and 50 – 70 °C, Thermophillic. Boe (2006) give optimum pH for the *methanogenic* bacteria to be between 6.5 to 7.2.

1.1.2. Formation of Biogas

The formation of biogas from anaerobic digestion of petroleum sludge involve four basic steps (Appels *etal*.,2008): Hydrolysis, acidogenesis, acetogenesis and methanogenesis. Among these, hydrolysis is the rate limiting step. These steps are illustrated on Figure 1.

1.1.3. Biogas Up gradation

Impurities in the biogas are removed by Pressure Swing Adsorption (PSA) on activated carbon. Since adsorption takes place at high temperature and pressure, desorption is achieved by depressurizing. Moisture is removed from the biogas by drying. The active site of the adsorbent retains water vapour and other pollutants thus decreasing adsorbent life hence desorption is frequently carried out by depressurizing. Moreover, siloxanes are difficult to desorb from the adsorbent beds, so the adsorbent beds should be replaced regularly e.g weekly. The biogas is dried, compressed and sent to storage.

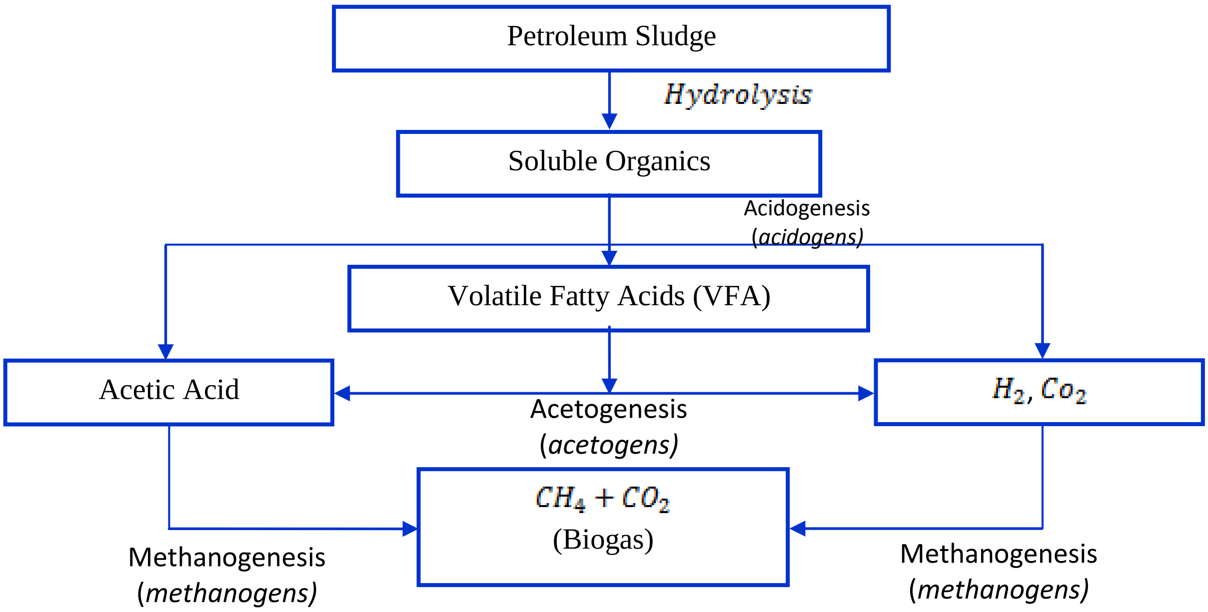


Figure 1: Steps in Anaerobic Digestion Process of Petroleum Sludge (Source: Appels *et al.*(2008))

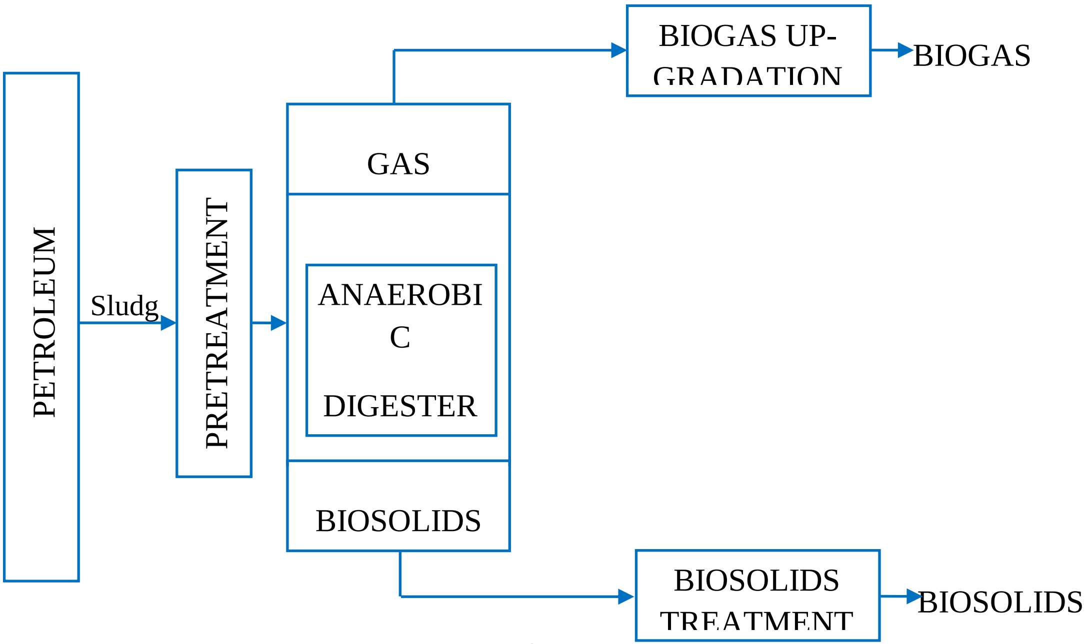


Figure 2: Block Flow for Anaerobic Digestion Process

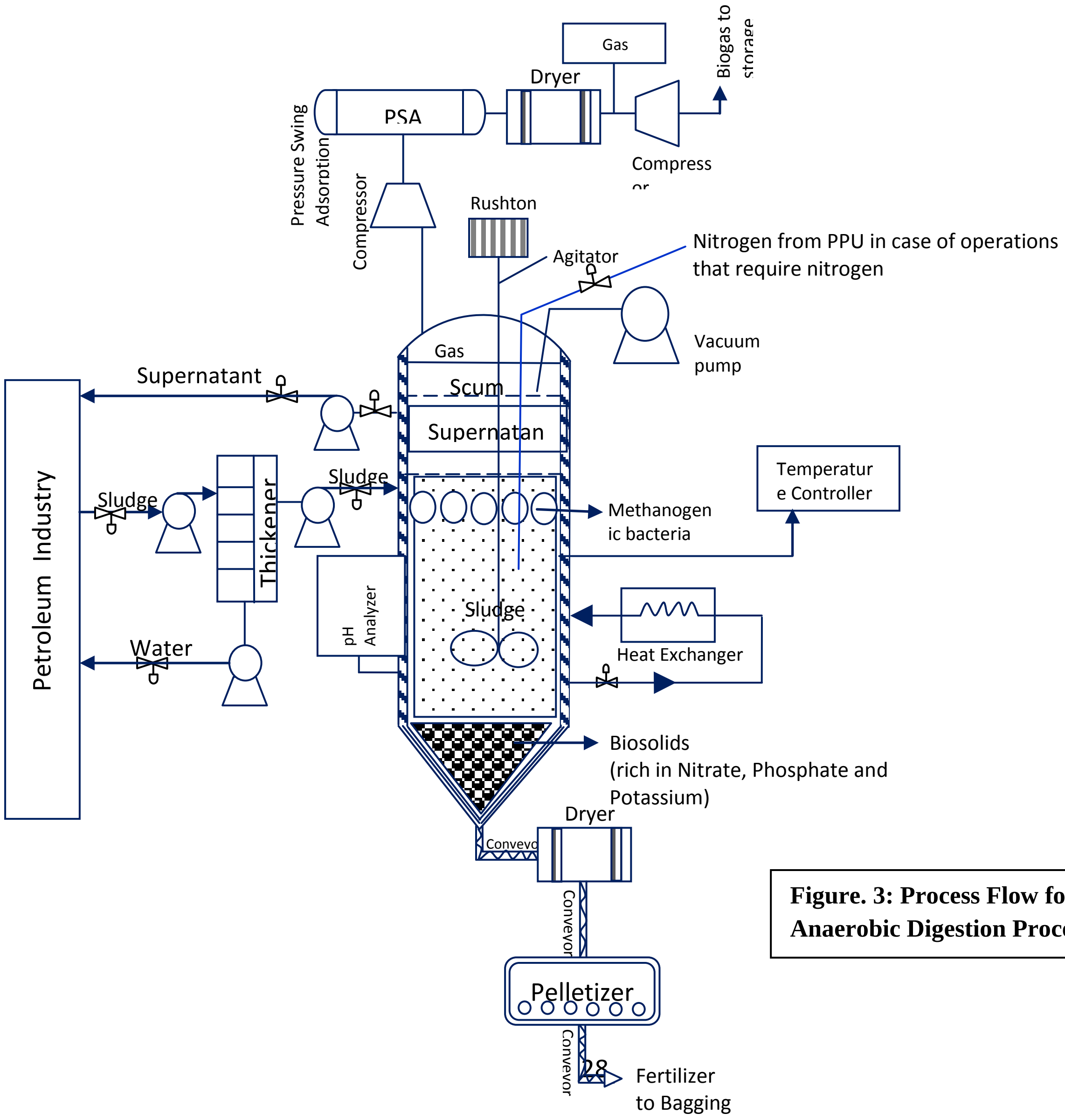


Figure. 3: Process Flow for a typical Anaerobic Digestion Process

1.1.4. Kinetic Models

Applying the Monods Kinetics for continuous stirred mode with substrate inhibition, the following Kinetic Models were obtained for the biomass and for the sludge.

From material balance equation:

Flow of materials In + Microbial Biodegradability of Sludge - Flow of Materials OUT = Accumulation (1)

For the Biomass

$$Fx_{1,0} + \mu x_1 V - Fx_1 = \frac{Vdx_1}{dt} \qquad (2)$$

Dividing through by V

$$\frac{dx_1}{dt} = \frac{F}{V}\left(X_{1,0} - X_1\right) + \mu X_1 \qquad (3)$$

From Monods equation: $\mu = \frac{\mu_m X_2}{K_m + X_2}$, we have

$$\frac{dX_1}{dt} = D\left(X_{1,0} - X_1\right) + \frac{\mu_m X_1 X_2}{K_m + X_2} \qquad (4)$$

Writing in the pattern of the modified form of monods equation: $\mu = \frac{\mu_m X_2}{K_m + X_2} - K_d$ to account for consumption of cellular material to produce maintenance energy.

$$\frac{dX_1}{dt} = D\left(X_{1,0} - X_1\right) + \frac{\mu_m X_1 X_2}{K_m + X_2} - k_d X_1 \qquad (5)$$

For the Sludge

From materials balance:

Flow of materials In + Microbial Biodegradability of Sludge - Flow of Materials OUT = Accumulation

$$\frac{VdX_2}{dt} = FX_{2,0} - \frac{\mu X_2 V}{Y} - FX_2 \qquad (6)$$

$$\frac{VdX_2}{dt} = F\left(X_{2,0} - X_2\right) - \frac{\mu X_2 V}{Y} \qquad (7)$$

Dividing through by V

$$\frac{dX_2}{dt} = D\left(X_{2,0} - X_2\right) - \frac{\mu X_2}{Y} \qquad (8)$$

From Monods equation: $\mu = \frac{\mu_m X_2}{K_m + X_2}$

$$\frac{dX_2}{dt} = D\left(X_{2,0} - X_2\right) - \frac{\mu_m X_1 X_2}{Y(k_m + X_2)} \qquad (9)$$

Where: X_1, is the concentration of Biomass (mg/L)
X_2, the concentration of Sludge (mg/L)
$X_{1,0}$, initial concentration of Biomass (mg/L)
$X_{2,0}$, initial concentration of Sludge (mg/L)
F, Volumetric flow rate of feed (m^3s^{-1})
V, Volume of reactor used (m^3)
D, Dilution rate or space velocity (hr^{-1})
µ, Specific growth rate (hr^{-1})
μ_m, Maximum specific growth rate or half minimal velocity concentration (hr^{-1})
K_m, Monods constant ($kmol/m^3$)
K_d, Coefficient of endogenous respiration or specific maintenance rate (d^{-1})
Y, Yield coefficient (mgVSS/mgBCOD)
VSS, Volatile Suspended Solids
BCOD, Biochemical Carbonaceous Oxygen Demand

1.1.5 Troubleshooting

Troubleshooting of anaerobic digester plant is in exhaustive. Readers are therefore referred to the operations manual by Zickefoose and Hayes (1976) (www.nepis.epa.gov)

1.1.6. Optimisation

The optimization of anaerobic digestion and the assessment of its operation as a function of varying feed or operating conditions can be achieved using appropriate digestion models provided in AQUASIM software to:

i. Estimate the optimum retention time, reactor volume, gas production and composition for a requested system performance and investigate the sensitivity of the system performance to various parameters.
ii. Predict on a time basis how the system will react to sudden or progressive changes in operating parameters of feedstock flow rate and composition, temperature, inhibition, pH, Etc and choose the optimum conditions.

2.0. MATERIALS AND METHODS

2.1. Materials

Petroleum sludge was collected from Akpada flow station, Shell Petroleum Development Company, Port Harcourt, Nigeria. *Methanogenic* bacteria (*Methanobrevibacter*) was isolated from the intestine of a cow and stored in glycerine. Oxoid Anaero Gen TM AN 0035A gas park was used in anaerobic Jar to create anaerobic condition.

2.2. Methods

2.2.1. Pretreatment of Petroleum Sludge

Petroleum sludge was heated on a hot plate and dried in an oven to remove water after which it was crushed. This helped break the cell walls and membranes.

2.2.2. Total Anaerobic Bacterial Count

To perform the each day tenfold serial dilution, the medium (nutrient agar) was prepared as directed by the manufacturers of nutrient agar (LAB M) and all the glassware, media and diluents such as physiological Saline were sterilized using autoclave.

After performing the tenfold serial dilution, 0.1ml of the desired dilution was transferred to the sterile dry agar plate and spread with a sterile hockey bent glass rod.
The inoculation was performed in duplicate plates of any of the desired diluents. The culture plates were all incubated at 37 ^{0}C for 24 hours using a Labtech anaerobic jar fitted with Gas Park and catalyst for anaerobic incubation. Once incubation was over, the plates average were counted in duplicates and average counts were calculated and further used for calculation of the colony forming units per gram (cfu/g) of the sample using the formula in equation (10). Where DF is the Dilution factor.

$$TABC = \frac{1}{DF} \times Average\ of\ plate\ bacteria\ count\ \times \frac{1}{Volume\ Correction\ factor} \qquad (10)$$

The bacterial count was carried out each day and a new gas park replaced each day.

2.2.3. Measurement of Biochemical Carbonaceous Oxygen Demand

0.1g sludge was weighed into a clean beaker and 200 *ml* of mineral water from the reagent dissolved oxygen bottle introduced into the sludge. This was stirred to disperse the sludge and obtain a homogenous mixture. The mixture was re-introduced into two dissolved oxygen reagent bottles filled to the brim which had previously been used to measure out the mineral water. The bottles were capped tightly with appropriate cork and the cork was removed and 0.5 ml Winkler A&B reagent pipetted into the reagent dissolved oxygen bottle respectively. The reagent bottle was re-corked and inverted gently for about three times and allowed to stand to sediment the precipitated components.

The reagent dissolved oxygen bottle was carefully opened and about 2 mls concentrated sulphuric acid was added, recapped and inverted gently and carefully thrice for the Precipitate to dissolve completely. 25 ml of this solution was titrated with 0.025 N Sodium thiosulphate using starch as indicator near the end point. The volume of the Sodium thiosulphate that was utilized to obtain colour change was recorded as the titre value.

The other reagent bottle containing the second batch of sludge and mineral salt water solution was placed in an incubator for 5 days and at the end dissolved oxygen analysis was carried out. The titre value of this batch was recorded and the titre at the fifth day. The BCOD value was calculated using equation (11)

$$BCOD_5 = \frac{DO_{initial} - DO_{Final}}{DilutionFactor} \qquad (11)$$

2.2.4. Measurement of Volatile Suspended Solids

An ashless filter paper was dried in an oven at 105 ^{0}C and cooled in the desiccator and weighed. The weight was recorded. The sample was filtered through the filter paper, dried in the oven and re-weighed.

The residue was burned in the Muffle furnace in the porcelain evaporating dish which was previously weighed. The remnant of the weighed residue was cooled to room temperature and weighed and % VSS calculated using equation (12)

$$\%\ Volatile\ Suspended\ solids = \frac{Weight.of\ Volatile\ residue}{Weight\ of residue} \times \frac{100}{1} \qquad (12)$$

2.2.5. Measurement of Total Hydrocarbon Content

0.01 gramme of sludge was weighed into a clean beaker and was diluted to 100 ml volume with chloroform and put into the sample compartment of the thermospectronic spectrophotometer.The absorbance was read at 420 nm wavelength using chloroform as blank.The absorbance obtained was recorded.The concentration of hydrocarbon in the sludge was calculated using the formular in equation (13)

$$THC = \frac{Absorbance\ of\ sludge \times Gradient\ of\ standard\ graph}{weight\ of\ sample\ diluted\ in\ 100ml \times \frac{1}{Dilution\ Factor}} \qquad (13)$$

2.2.6. Measurement of Concentration of Polycyclic Aromatic Hydrocarbons

The sludge or biosolids sample was extracted according to USEPA 3550 C using the ultrasonic extraction method. 10 g of the sample was extracted with dichloromethane. The extract was concentrated and 1µl of the sample extract was injected and analyzed using Agilent 7890 GC-MS according to USEPA 8270.

Five different calibration stocks were prepared in dichloromethane according to manufacturers Standard and peaks of size of different standards prepared used to plot a graph. The concentration of the analyzed sample was extrapolated from the graph of the standard sample.

2.2.7. Measurement of Fertilizer Value of Biosolids

2.2.7.1. Measurement of Phosphate (Phosphorus) Content in Biosolids

1 gramme of biosolids sample was extracted with 50 ml, 2.5 % glacial acetic acid. The extract was filtered into 250 ml capacity conical flask and 0.8 ml of combined reagent was added to the flask. A blank and standard phosphate ion concentration ranging from 0.001 - 0.007 was prepared and 0.8 ml combined reagent added respectively.

The bluish colour developed within 30 mins interval was read at 840 nm wavelength in thermospectronic spectrophotometer. Absorbance of the sample extracted was also read at the same wavelength and recorded. The concentration of the phosphate ion in the sample was calculated using equation (14).

$$\begin{aligned}&\textit{Concentration of ion} = \textit{Concentration of sample}\\ &\textit{extrapolated from}\\ &\textit{concentration versus}\\ &\textit{absorbance graph in } mg/l \times\\ &\textit{Conversion factor to } mg/kg \qquad (14)\end{aligned}$$

2.2.7.2. Measurement of Nitrate Content of Biosolids

0.5 ml Brucin reagent was added to 1mg of the biosolids sample in a beaker. 2 ml of concentrated sulphuric acid was then added and 1 ml of the mixture pipetted into a clean test tube. The yellowish colour formed was read at 400nm in a Thermospectronic Spectrophotometer. The concentration of nitrate in the biosolid sample was calculated using equation (14).

2.2.7.3. Measurement of Potassium ion Concentration in Biosolids

The biosolids sample was diluted and made up to 50 mls with distilled water. 766 nm wavelength was selected. Slit width, air and gas pressure was adjusted and settings programmed. Standard potassium ion concentrations were aspirated into the instrument "Bunsen Chamber" to calibrate the equipment and to plot a graph of standard ion. The aspirator tubing system was occasionally flushed with water before samples were aspirated. The absorbance and concentration of potassium ion in the sample was automatically displayed on the equipment screen and also printed out for documentation. The concentration of potassium ion in the biosolids was calculated using equation (14).

2.2.8. Detection of Biogas

After collecting some of the gas in a balloon, the gas evolved from the anaerobic jar was made to pass through a small metallic hose connected to a Bunsen burner. Methane gas was confirmed by the blue colour of the flame. The flow gauge at the gas collection point read $0.122m^3s^{-1}$. This was found to be equivalent to $10{,}500m^3/d$

3.0. RESULTS

3.1. Total Anaerobic Bacterial Count (TABC)

Table 1: Total Anaerobic Bacterial Count

Day	Anaerobic Bacterial Count $cfu/g \times 10^9$
1	0.129
2	1.020
3	1.021
4	2020
5	2020
6	2019
7	2018
8	2017
9	2016
10	2015
11	8010
12	87
13	8.50
14	8.45
15	7.20
16	7.199

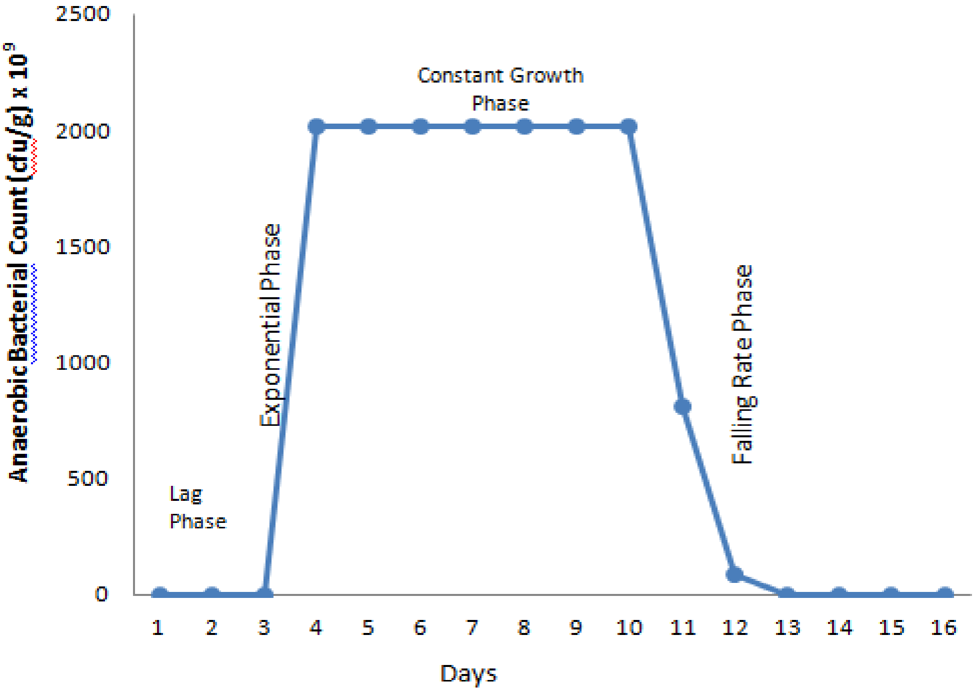


Fig. 4: Bacterial growth rate per day

3.2. Biochemical Carbonaceous Oxygen Demand and Total Hydrocarbon Content

Table 2: Biochemical Carbonaceous Oxygen Demand and Total Hydrocarbon Content

DAYS	1	4	16
BCOD (mg/L)	6080	1200	20.40
$THC(ppm)$	57000	30,000	1500

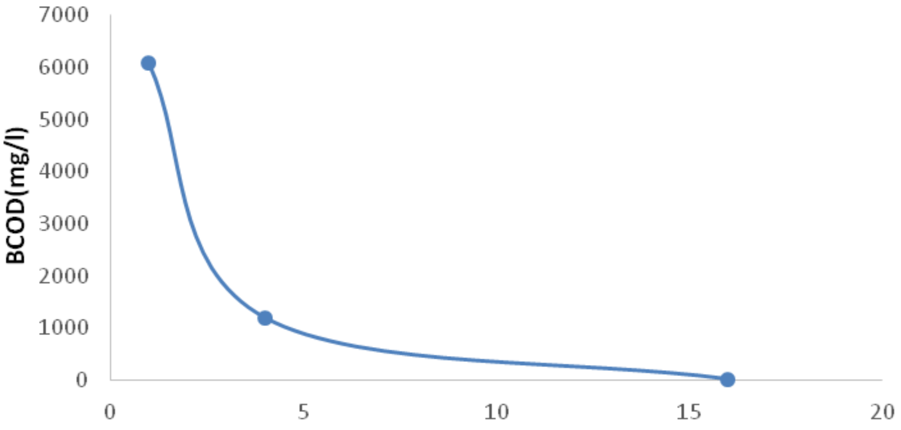


Fig. 5: Graph of change in BCOD with Time (days)

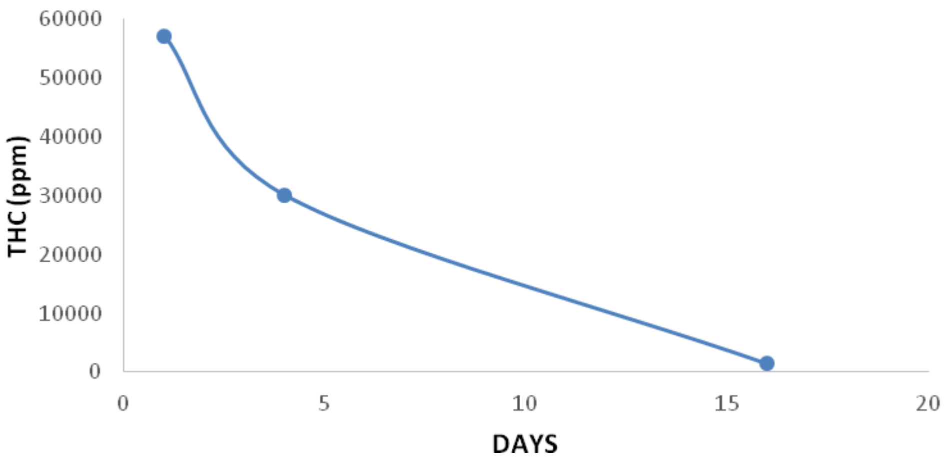


Fig. 6: Graph of Change in THC with Time

3.3. Polycyclic Aromatic Hydrocarbons (PAHs)

GC-MS Waveforms

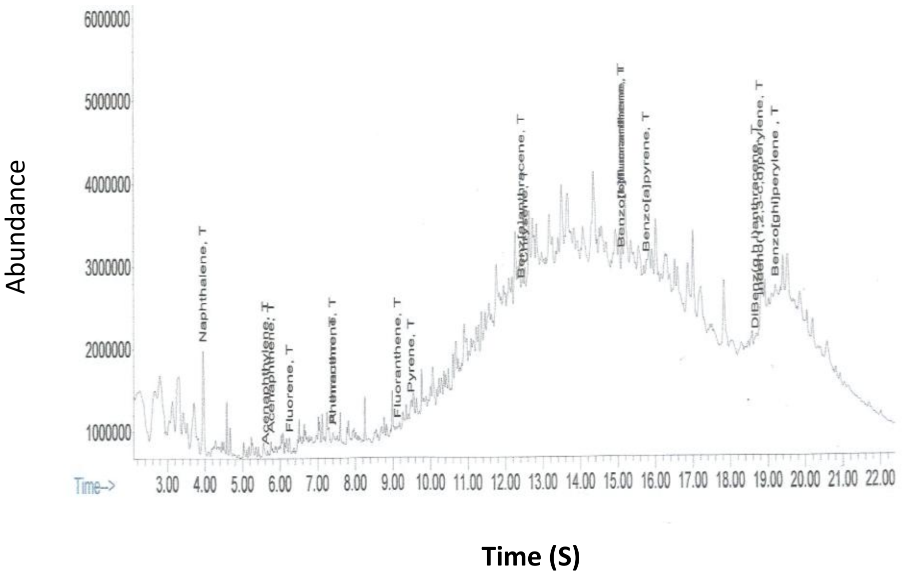
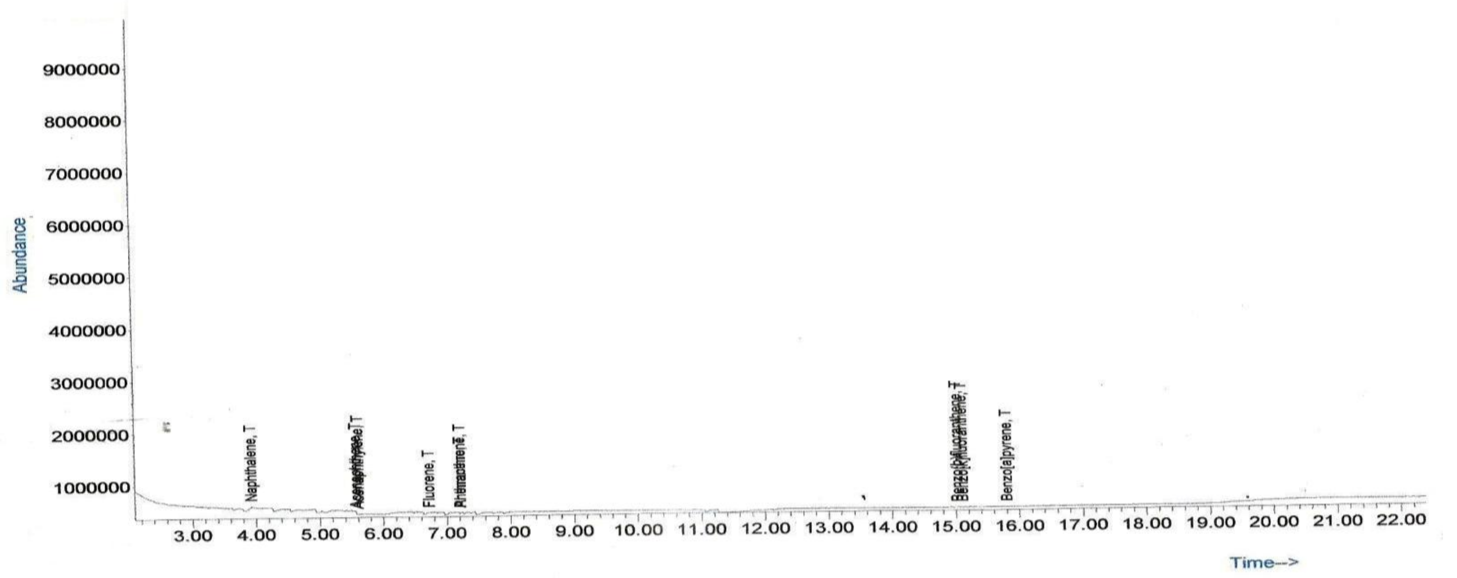


Fig. 7: Waveform of GC-MS Analysis of Petroleum Sludge

Figure 8: Waveform of GC-MS Analysis of Bio solids Produced from Anaerobic Digestion Treatment of



Petroleum Sludge

Table 3: GC – MS for the priority Toxicants in the Petroleum Sludge

Toxicant	**CONCENTRATION (mg/L)**	
	Untreated Sludge	**Biosolids**
Napthalene	37.1	0.32
Anthracene	33.43	8.24
Phenanthrene	33.97	9.86

3.4. Fertilizer Value of Bio solids

Table 4: Fertilizer Value of Bio solids

Component	**Absorbance**	**Concentration mg/L**	**Conversion Factor**	**Concentration mg/kg**
Nitrate	0.01	0.1	50	5
Phosphate	0.6	0.6	50	30
Potassium	1.3384	13.919	50	695.95

3.5. Volume of Biogas Produced

$$V_{CH_4} = (0.35)(s_o - s)(Q)(10^3\,g/kg)^{-1} - 1.42\,P_x \qquad (15)$$

(*Tchobanoglous etal*., 2004) (15)

$$P_x = \frac{YES_o}{1 + k_d\theta_c} \qquad (16)$$

(Appels *etal*., 2008)

$$Y = \frac{mg\ VSS}{mg\ BCOD} \qquad (17)$$

$$= \frac{99.6}{6080} = 0.016$$

From equation (16)

$$P_x = \frac{0.016 \times 0.9 \times 6080}{1 + 0.025 \times 16} = \frac{87.552}{1.40} = 62.54\ kg/d$$

Volume of Methane

From equation (15)

$$V_{CH_4} = (0.35)(So - S)(Q)\,(10^3\,g/kg)^{-1} - 1.42Px$$

$$(0.35)(6080 - 20.4)\,5000\ \times \frac{1}{1000} - 1.42\,(62.54)$$

$$= 0.35\ (6,059.6)(5)\ -\ 88.8068$$

$$= 10,603.25 - 88.8068$$

$$= 10,514.4432\ m^3/d$$

$\approx 10,500m^3/d$ biogas for 16 days.

3.6. Economic Evaluation

$$\text{Net Annual Profit (NAP)} = [\text{ Product Sales }] - [\text{Operating Cost} + \text{Fixed Capital}] \qquad (18)$$

$$\text{Total Investment (TI)} = \text{Fixed capital} + \text{Working capital} \qquad (19)$$

Calculations for Net Annual Profit , Total Investment , Etc could be obtained from appendix 1 of Sampson (2018).

$$\text{Rate of Return on Investment (ROI)} = \frac{\text{Net annual profit}}{\text{Total investment}} \times \frac{100}{1} \qquad (20)$$

$$= \frac{£4{,}937{,}767.42}{£10{,}452{,}170.28} \times \frac{100}{1}$$

$$= 47.2415516 \quad \approx 47\ \%$$

$$\text{Pay Back Period} = \frac{\text{Total investment}}{\text{Net annual profit}} \qquad (21)$$

$$\text{PBP} = \frac{£10{,}452{,}170.28}{£4{,}937{,}767.42}$$

$$= 2.1167806 \quad \approx \ 2 \text{ years}$$

$$\text{OR: } \frac{1}{\text{Rate of return on investment}} \qquad (22)$$

$$\frac{1}{\text{ROI}} = \frac{1}{\left(\frac{47}{100}\right)} = \frac{100}{47}$$

$$= 2.1276595756 \ \approx 2\ \mathit{years}$$

4.0. DISCUSSION

Recycle on day 4 resulted in exponential increase in micro-organisms. From Table 1 and Fig. 4 the Microbial digestion was terminated after sixteen days at the falling rate phase when most of the micro-organisms must have died. Table 2 and Figs 5 & 6 show that BCOD and THC decreases with sludge biodegradation. BCOD and THC can therefore be used as a measure of sludge biodegration. Figures 7 and 8 show that concentration of Polycyclic Aromatic Hydrocarbons (PAHs) are higher in the untreated sludge and negligible in the biosolids produced.

The potential of anaerobic digestion for the treatment of sludge is proved by GC-MS analysis for priority toxicants in the sludge. Table 3 show that the concentration of Napthalene, Anthracene and phenanthrene in the untreated sludge reduced from tens to units after the sludge treatment. Table 4 show that the treated sludge referred to as biosolids can be used as fertilizer as it is rich in Nitrate, Phosphate and Potassium. The gaseous effluent (biogas) can be obtained in substantial amount from anaerobic digestion of the sludge as shown in the analysis of equation (15). British Pounds is used for economic evaluation because of instability of the Nigerian Naira. However, conversion could be made based on the exchange rate at the time of conversion. It is worthy of note that the values of the rate of return on investment and payback period are not dependent on type of currency used because they are ratios. For 5 Tons per day of sludge plant capacity, economic analysis gave 2 years Pay Back Period (PBP) and 47 % Rate of Return on Investment (ROI). This show that a petroleum sludge anaerobic digestion plant if well managed could economically viable in Nigeria.

5.0. CONCLUSION

Anaerobic digestion helps transform the toxic Petroleum sludge to harmless biosolids useful as fertilizer of higher quality than petrochemical based fertilizers. Biogas, being a renewable energy source and environmentally friendly is a better substitute for natural gas. Besides enhancing sustainable development and increasing the Nigerian Gross Domestic Product (GDP) anaerobic digestion of Petroleum sludge could optimize petroleum oil and gas production in Nigeria as the Nigerian oil and gas reserve is being maximized and total reliance on petroleum and natural gas as the only energy sources minimized. With anaerobic digestion of Petroleum sludge, Nigerian oil and gas reserves and net petroleum exports will increase. With anaerobic digestion plant as a process unit in every Nigerian Petroleum industry and waste water treatment plant, the problem of sludge treatment and disposal according to Environmental Protection Agency (EPA) standards and regulations will be solved.

6.0. RECOMMENDATIONS

It is recommended that:

i. Every Nigerian oil and gas industry must have an anaerobic digestion plant as a process unit in its Process plant and Waste Water Treatment Plant. Private investors and government are encouraged to invest in the anaerobic digestion plant considering its high economic viability and profitability.

ii. Biogas produced from anaerobic digestion be upgraded and its production maximised so that with rising natural gas exports, biogas could substitute natural gas as a domestic fuel source, being environmentally friendly and a renewable energy source, natural gas being exclusively for exports.

iii. The use of biosolids as fertilizer be encouraged and farmers made aware of its advantages over the petrochemical based fertilizer.

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8.0. NOMENCLATURE

Symbol	Definition	Unit
X_1	**Concentration of Biomass**	mg/L
t	**Time**	hr
D	**Dilution Rate**	(hr^{-1})
μ_m	**Maximum Specific Growth Rate or Half Maximal Velocity Concentration**	(hr^{-1})
$X_{1,0}$	**Inlet Biomass Concentration**	mg/L
K_m	**Monods constant**	
X_2	**sludge concentration**	mg/L
$X_{2,0}$	**Inlet Sludge Concentration**	mg/L
Y	**Yield Coefficient given as mass of sludge or biomass produced per unit biosolids removed** $(mgvSS$ volatile suspended solids$/mgBCOD)$	
k_d	**Endogenous Respiration Coefficient or specific maintenance rate, per day** (d^{-1}) **ranging from 0.02 to 0.04.**	
S_0	**Biochemical Carbonaceous Oxygen Demand (BCOD) in the influent sludge**	(mg/L)
S	**Biochemical Carbonaceous Oxygen Demand (BCOD) in the effluent biosolids**	(mg/L)
V_{CH_4}	**Volume of Methane produced**	(m^3/d)
P_x	**Net Mass of Cell Tissue produced per day**	kg/d.
E	**Efficiency of Sludge Utilization** $(0.6 - 0.9)$	
θ_c	**Mean Cell Residence Time**	$(days)$

Abbreviations

Abbreviation	Meaning
BCOD	**Biochemical Carbonaceous Oxygen Demand**
CFU	**Colony Forming Unit**
DF	**Dilution Factor**
EPA	**Environmental Protection Agency**
EU	**European Union**
GC – MS	**Gas Chromatography and Mass Spectrophotometry**
GDP	**Gross Domestic Product**
HRT	**Hydraulic Retention Time**

NAP	**Net Annual Profit**
NPK	**Nitrate, Phosphate and Potassium**
PAHs	**Polycyclic Aromatic Hydrocarbons**
PBP	**Pay Back Period**
PPM	**Parts Per Million**
PPU	**Power Plant and Utilities**
PSA	**Pressure Swing Adsorption**
ROI	**Rate of Return on Investment**
SRT	**Solids Retention Time**
TABC	**Total Anaerobic Bacterial Count.**
TI	**Total Investment**
THC	**Total Hydrocarbon Content**
VSS	**Volatile Suspended Solids**
WWTP	**Waste Water Treatment Plant**

CHEMICAL ENGINEERING PROFESSION: A DRIVER OF MICRO, SMALL AND MEDIUM SCALE ENTERPRISES

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ABSTRACT

The world is saddled with disturbances due to worries of unemployment and under-utilization of labour. These conditions are either created by the individuals (who have refused to make themselves available for acquaintance of useful skills for increased productivity), or due to bad governance. Whatever may be the cause, the ever-remaining fact is that several skills abound that can always be harnessed to assuage the pitiable situation of idleness and laxity in our society. What is required is just the will and zeal, with little support, to convert a formerly idle man to a creator of jobs; this is achievable through Chemical Engineering. The technology of the discipline is so large diverse and versatile that it affects almost every aspect of human life. Thomas More once said: "what more could a man do for himself greater than doing his own things the way he desires them''. Many opportunities can be created and easily driven, with lean resources at hand, through chemical engineering. The present study, therefore, reviews a number of MSME driven skills obtainable in chemical engineering profession, such as Production of Paint (emulsion), Insecticide, Bleach, Soap (bar) and Liquid Disinfectant. With keenness and little capital, a little beginning can metamorphous into large enterprise.

Keywords: MSME Skills, Chemical Engineering, Empowerment, Human Development.

1. INTRODUCTION

Chemical Engineering, as a discipline, applies chemical / physical change and processing into various practical applications. The profession was developed by those who practiced industrial chemistry in the late 19th century (Collins and Sean, 2000). The industrial revolution led to an unprecedented escalation in demand, as regards to quality and quantity of pr oducts. Chemical engineering was first introduced (as a profession) in the United Kingdom, when the first chemical engineering course curriculum was invented by *George .E. Davis* in the form of industrial chemistry practice in 1887 (John, 1932). Since its introduction, the profession has continuously played its roles efficiently, especially in the development of humanity. Chemical Engineers offer many skills perfectly, in accordance to their professional ethics. One of their main tasks is to train and engage young talents who have the desire of being members of the family. They help in process definitions, improving already existing products and solving environmental, health and safety issues. A chemical engineer plays active roles in the main stages of products' life cycle, during which he/she fosters good communication skill and cooperation with other colleagues (from different fields) to maintain good product quality, management and technical services. Through a detailed modeling, relevant products needed in the society are produced. The boost on the empowerment capabilities of this noble profession is anchored on the fact that it can easily lay hands on any available resources (including the ones that are already tagged as being useless) to create an economically viable product at a very minimal production cost.

2. RELATIONSHIP BETWEEN CHEMICAL ENGINEERING AND HUMAN EMPOWERMENT

Chemical engineering is a field of engineering that deals with process design, modeling and operations, while human empowerment is expressed as the individual /organizational condition of gaining the ability to control and integrate changes in one's life (Perkins, 2003; UNDP, 2003; Radovic et al, 2012; Sutton and Pollock, 2000; UNRISD, 2010). It is all about self-modification and independent achievement the roles of chemical engineering lead to self-modification and individual achievements; it promotes human development through the development of efficient systems in wastes management and products generation. The synergy between chemical engineering and human empowerment has gotten to a height that cannot be reversed such that the activities of this unique discipline have streamlined it to tacking the needs of the society.

Chemical engineering offers great effects to human development through the provision of opportunities and structures for people to achieve success via employment and education. It is primarily a matter of providing people with the means of empowerment through detailed teaching of various production techniques, environmental studies and analysis. The society has, also, received numerous displays of empowerment from the profession in diverse ways through the inculcation of research findings, that are beneficial to interested individuals or groups, who wish to join the league of professionals. As a matter of fact, chemical engineering is now one of the leading courses in our higher institutions of learning, thereby helping to reduce the level of the illiteracy and empowering young talents with the opportunity of becoming experts in a few years.

3. SOME CHEMICAL ENGINEERING SKILLS IN MSMES

A hooping lot of micro, small and medium scale enterprises (MSME) skills abound in chemical engineering profession. Most of these skills require just little or no technicality to grab by any interested individual(s); it needs only attention/concentration by the individual, and upon continuous practice, there would be consolidation in expertise. Some of the production/manufacturing skills in chemical engineering include the Production of Paints, Insecticides, Disinfectants, Soap and Bleaching Agents.

3.1 Production of Paint (Emulsion)

Paint is any substance (in fluid or powdered form) which, when applied to a substrate, forms a firm decorative coating to it (Juner, 1967; Jordan, 1951; Martens, 1968; SON, 1989). Emulsion paints (as their name implies) consist of an emulsion of two phases, one of which is water. Their development is best understood by considering their relation to forms of coatings, in which water alone is the liquid medium. Wash resistance can be greatly improved by the introduction of casein paints, in which casein is used to form a continuous film. Here, alkaline solution of casein takes the place of the oil in an oil paint. The binding medium is made by dissolving casein in an aqueous solution of caustic soda, ammonia, sodium bicarbonate or borax. The pigment commonly used is titanium-dioxide or Lithopone. A small amount of an aqueous solution of resin, wax or soap in paints has the advantage of the fact that they can be made up as powders, mixed with pigments, and filled into packages. Casein paints are widely used for interior walls, ceilings, or other places, where a highly decorative flat finish (with excellent light reluctance, low odour, fast dry, and low cost of material and application) is desired. Their biggest draw-back is still lack of washability as compared with oil flat.

However, in the emulsion paints, the continuous phase is usually water. Thus, the paint can be readily diluted or timed with water. Emulsion may contain pigments and extenders, oils and resinous material, rubber-like materials, emulsifying agents, stabilizer, preservatives, antifoaming agents and driers. The water takes the place of the thinner, although in some formulations a certain amount of non-drying volatile oil may be used. In making emulsion paint, it is common practice to disperse the pigment in the emulsion immediately after the emulsion has been made. The ratio of binder to pigment (as in solution paints) depends upon the purpose for which the paint will be employed. For durable exterior white paints, it would usually contain approximately one part by weight of pigment to one part of binder. A good interior paint, on the other hand, would contain five or six parts by weight of pigment to one part of binder.

The production process involves the serial combination of the required reagents. With 20kg (One bucket) as ***Basis,*** the production of emulsion paint takes the following procedures:

STEP 1: 10kg of calcium carbonate is transferred into a reactor or mixer containing 10 Liters of water and stirred. If one is aiming at powdering white emulsion paint, the tether should be mixed in water before adding Calcium carbonate. About 30g of tether is okay.

STEP 2: Colours (pigments) are diluted, as required, in water, and added to the mixer. This is followed by continuous stirring until the desired mixture is obtained by the powder. If the colour is added in excess (such as in the case of yellow colour), it can be corrected by adding more calcium carbonate.

STEP 3: About 2.0kg of the polyvinyl acetate (P.V.A.) is added to the previous mixture in the reactor/mixer and stirred for three minutes.

STEP 4: About 0.04kg of nitrosol is added. It is important to note that nitrosol must be diluted in small quantity of water before adding to the mixture.

STEP 5: About 0.4kg of Biocide or Formalin is added, as well as 0.04 kg of ammonia solution and 1 litre of kerosene, and stirred very well.

FINAL STEP: When the above steps have been completed, the thickener (usually acrytext) is added to the mixture and stirring continued until the required thickness is obtained. This

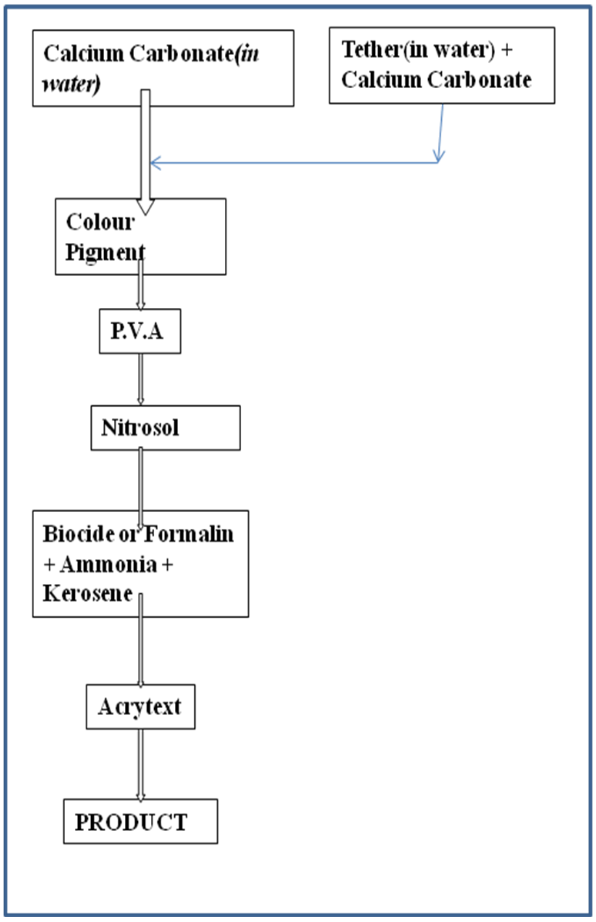

Figure 1: Flow Chart for the Production of Emulsion Paint

3.2 Production of Liquid Disinfectant

A disinfectant (otherwise called antiseptic) is any chemical combination or solution that helps or has the ability to prevent infection by preventing the growth of micro-organisms. Several reports have identified chloroxylenol (C_8H_9ClO) as the key ingredient of every disinfectant liquid, which gives it its antiseptic property (Class and Kintrup, 1991; Grainage and Ahmed, 1988; George, 1984). Other components include Pine Oil, Isopropanol, texapon, phenol and water. The product is formulated by direct mixture of the reagents. With 2litres as a reference point, the texapon (20g) is, first, turned into a reactor (a bowl). This is then followed by the addition of pine oil (200ml) and phenol (1litre). Then chloroxylenol (20ml) is added, followed by 500ml of isopropanol (isopropyl alcohol- IPA). In each case, the mixture is properly stirred at the addition of any reagent to ensure proper mixing. Finally, water is added slowly to test, before the addition of colourant (6ml). Colour is, also, added slowly and carefully until the desired colour is obtained.

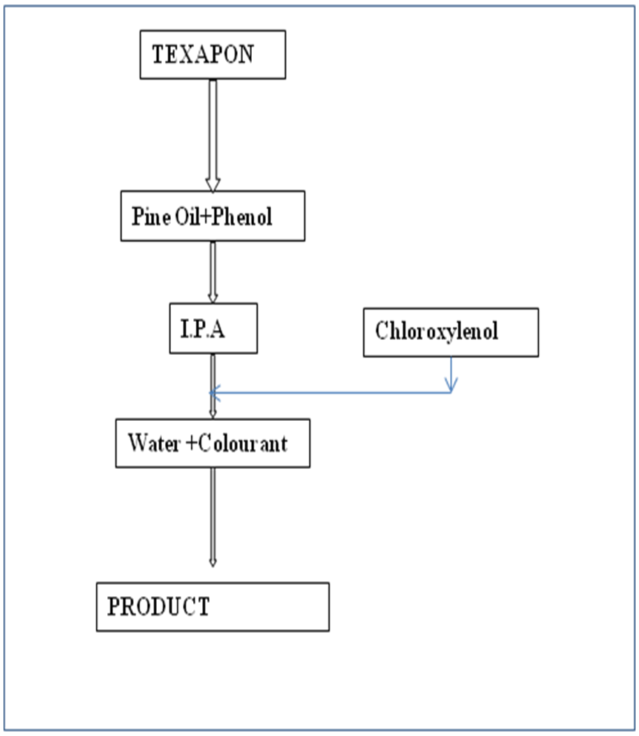

Figure 2: Flow Chart For the Production of Liquid Disinfectant

33.3 Production of Insecticide

An insecticide is any substance that has the ability to kill insects or drive them away. The killing action usually occurs when the insect comes in contact with the product, while the later condition comes up when the insect encounters the smell of the products. Current chemical engineering technology has converted insecticides from organophosphate products (OPPs) to pyrenoid products (PRPs), as ***OPPs*** are usually very hostile to air around the homes. ***OPPs*** can cause over-stimulation of nicotinic expression at the neuromuscular junctions, due to high presence of acetylcholine navigation. However, all insecticides work with the principle of “Over-powering”. This means that the smell and taste of the product must surpass the strength of the insect (Grainage and Ahmed, 1988; Smith et al, 1993). With the aim of producing 7litres, the process involves the use of kerosene (5litre), industrial camphor (2kg), DDVP-force (20ml), formalin (25ml) and Isopropylalcohol, that is I.P.A. (500ml). A given volume of kerosene is poured into a bowl (the reactor), after which industrial camphor is added to dissolve in the kerosene. The DDVP- force is then added, followed by formalin and, finally, I.P.A. The mixture is continuously stirred at each bit, to ensure proper mixing. The flow chart is given is follows:

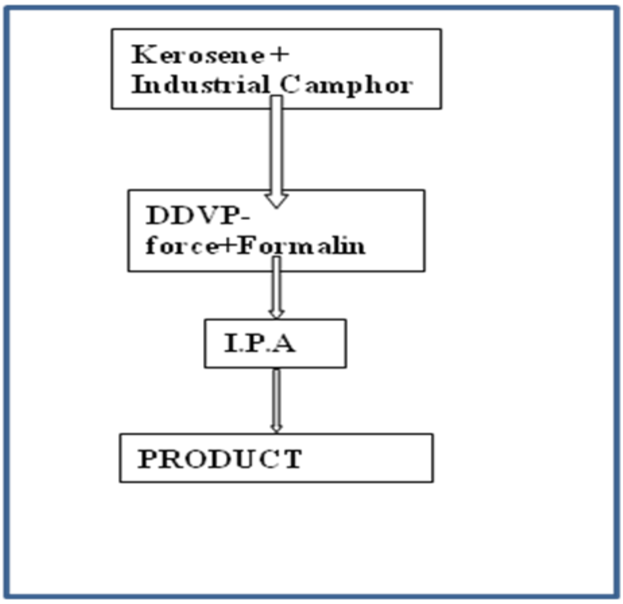

Figure 3: Flow Chart for the Production of Insecticide

3.4 Production of Bleach

Bleach is a household chemical used to whiten cloths and remove stains. Many forms of bleach have strong bactericidal properties, as reported by Odabasi (2008). These properties enable them to sanitize swimming pools of bacteria, Viruses and algae. Several reports have shown that chlorine is the basis for most of the commonly used bleaches (Field, 2006; Harrison and Schultz, 1976; Block, 1991; Trapp and Croteau, 2011). Calcium hypochlorite, for example, is a chlorine source, which when mixed with water forms hypochlorous acid and calcium hydroxide. The hypochlorous form is used for public health treatment, such as the sanitization of drinking water, sewage/wastewater, as well as swimming pools (Silra, 2003). The production of bleach is realizable by a simple combination of the three major components namely: Calcium hypochloride, Caustic soda and Soda ash. 7litres of bleach would require about 5litres of water for a moderate composition. 100ml beaker full of each of calcium hypochloride and sodium hydroxide (Caustic soda) are dissolved in the mixer (a large bowl or bucket), containing the water. The mixture is vigorously (but carefully) stirred to ensure appropriate homogeneity. After about five (5) minutes of continuous stirring, the mixture is then allowed to settle for twenty-four (24) hours, after which the mixture separates into two layers (*the denser and the less dense*). The denser layer (condensate) settles below, while the less dense layer (decant) settles at the top. The upper layer (which is the bleach) is then carefully decanted and stored in sterile containers. The flow chart for the production is represented as follows:

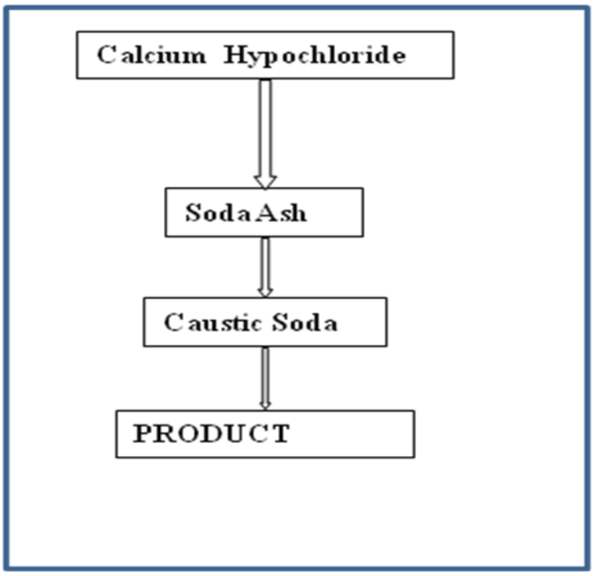

Figure 4: Flow Chart For the Production of Bleach

3.5 Production of Bar Soap

Soap, from the chemical point of view, is a salt (or a mixture of salts) of fatty acid. As with every salt, soap contains a positive ion (usually **Na^+** and **K^+**) and a negative ion (usually anions of carboxylic acid), obtained by the hydrolysis of animal or plant fats (Moulay and Zenimi, 2005; McCabe *et al*, 2005). There are different ways of explaining what soap really is and what it can be regarded as. For non-professionals (non-Chemical Engineers), it could regarded as any cleaning agent, manufactured in bars, granules, flakes or liquid form, from a mixture of mostly sodium or potassium salts of various fatty acids of natural oils and fats. But in addition to these basic raw materials, other substances of medicinal importance could be added as ingredients to produce medicated soaps. There are, also, other types of soap that are not used as cleaning agents, but serve other important purposes. Examples include soaps of calcium and magnesium origin that are used as lubricants and driers, soaps of aluminium and chromium origin that are used for sizing papers, Lithium sterrate soap that is used for thickening oils into greases, and so on.

For the production of bar soap, a given amount of oil/fat is measured into a bowl (which serves as the reactor), after warming it a little above its melting point. This is done to hasten the reaction between the lye (sodium hydroxide-*NaOH*) and the fat/oil. With 20kg weight of bar soap as basis, 1kg of lye is dissolved in a 10litres of water. The mixture is properly stirred to ensure good blending. Then a mixture 120g each of sodium carbonate (Na_2CO_3), Sodium Sulphate (Na_2SO_4) and Sodium Silicate (Na_2SiO_3) is added and stirred until proper blend is achieved. The fragrance (50g) is then added and stirred, after which the soap is poured into a mould and left for about 3 days for proper curing (solidification). The flow chart for the process is represented as follows:

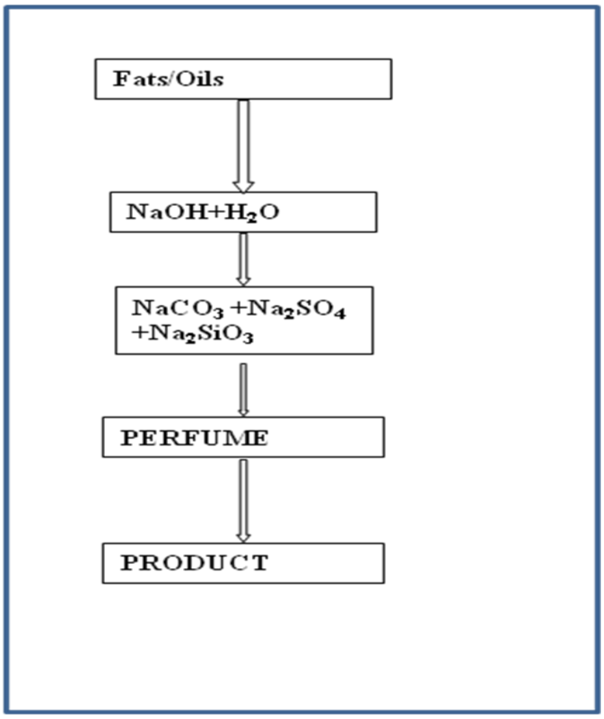

Figure 5: Flow Chart for the Production of Bar Soap

4. CONCLUSIONS

It is worthy to say that the society has been intertwined with the doctrines of chemical engineering, as the production of almost all products we use in furnishing our everyday life are linked , in one way or the other, to chemical engineering science/technology. However, unlike many professions that always require huge capital for business start-up, a lot of chemical engineering services can always offer low-key start-up alternatives, through *MSME* drives. This does not, however, limit their barriers of large scale developments within a limited time interval, with consistency and devotion. With little support by the government and the general public, this great family called chemical engineering has the ability to assuage the unemployment situation of underdeveloped nations, such as NIGERIA.

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IMPACT OF MAGNETIC NANOPARTICLES ON THE KINETICS OF BIODESULFURIZATION OF DIESEL

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ABSTRACT

The need to reduce sulfur content has become imperative. The sulfur content of hydrodesulfurized fuel are still high because of the presence of some sulfur compounds that are either recalcitrant or are refractory. The regulatory agencies are mounting pressure because the combustion of sulfur containing fuel produce substances that are harmful to the environment. Biodesulfurization readily comes handy as a complimentary method to hydrodesulfurization, however, biodesulfurization like other bioreactions is slow. For biodesulfurization to play the complimentary role effectively, deliberate attempt must be made to make it faster. This study in an attempt to do that has synthesized a magnetic nanoparticle, characterized it using Telescopic Electron Microscope, TEM and X-ray Electronic Microscope and then coat the synthesised particle with an isolated Pseudomonas stutzeri. The impact of the nanoparticle on the biodesulfurization activity of Pseudomonas stutzeri on diesel was investigated. The synthesized magnetic nanoparticles have a size range of predominantly between 9.75 and 10.25 nm. The results from this work showed a high level of desulfurization of 88% for coated bacteria as compare to 68% for uncoated bacteria. A kinetic model describing the desulfurization was also developed. In all cases, the coated organism desulfurise better than the uncoated one. The simulated data from the developed model were found to fit well to all the experimental data.

Keywords: *Biodesulfurization; Diesel; Magnetic; Nanoparticles; Kinetics*

1. INTRODUCTION

Researchers have shown that alkylated dibenzothiophenes are the major sulfur component in the conventional hydrodesulfurized treated oil fraction due to the fact that they are highly recalcitrant to chemical catalysts. According to Moheballi and Ball (2016), biodesulfurization technology should be viewed as complementary technology to remove recalcitrant molecules present in hydrodesulfurized-treated oils. In line with the above statement, more researches need to be carried out on desulfurization of petroleum fractions in order to meet up with the lower sulfur level (15-10ppm) as regulation proposed by United state environmental protection agency (Mayank *et al*, 2016).

Magnetic nanoparticles play a vital role in our industries and in the field of biosciences due to the fact that they have finite size effects such as high surface-to-volume ratio, different crystal structure and low toxicities. According to Ansari *et al*, (2009), the rate of biodesulfulrization activities shown by bacteria coated with nanoparticles increase as compared to uncoated bacteria. Karimi *et al*, (2016) investigated the application of magnetic nanoparticles on the rate of biodesulfurization of dibenzothiophene (DBT) using *rhodococcus erythropolis* IGTS8 and found that the coated cells had higher desulfurization activities as compared to uncoated cells. Likewise, Bardania *et al*, (2013), investigated the desulfurization activity and reusability of magnetite nanoparticle-coated *rhodococcus* bacteria and found that the coated cells had little impact on the rate of biodesulfurization of DBT.

In biotechnological processes, kinetic equations which describe the activity of microorganisms or an enzyme on a particular substrate are very important in understanding many phenomena. Description of a true behavior of a system can be done by obtaining an accurate estimate of the kinetic parameters in the models (Olsen, 2006). Kinetic studies of the four reactions of the 4S route have been reported in the literature, not as a reaction network but as single reactions. Several works have shown that desulfurization kinetics is only described as the DBT disappearance rate. Others researchers also used Michaelis–Menten equation as a model equation for biodesulfurization process (Mayank *et al*., 2016).

In this work, *Pseudomonas stutzeri* was isolated from the soil samples as a bacterium that feed on sulfur, this work also synthesized magnetic nanoparticles to coat the surface of the bacteria in order to investigate its impacts on the rate of biodesulfurization of diesel. This work further developed a kinetic model using Michaelis-Menten equation coupled with mass transfer factor in order to investigate the kinetic parameters of biodesulfurization of diesel.

2. MATERIALS AND METHODS

A microorganism was isolated by enrichment culture. The isolated microorganism was purified and transported to the Chevron Biotechnology Centre MAUTECH, Yola where some cultural, morphological and characteristic tests were carried out for the purpose of identification and confirmation of its identity. Further confirmation of the identity was carried out by Polymerize Chain Reaction (PCR)

To obtain the Fe_3O_4 nanoparticles, 25 mL of 0.2 mM ferrous chloride tetrahydrate ($FeCl_2\cdot 4H_2O$) was mixed with 100 mL of 0.1 mM ferric chloride hexahydrate ($FeCl_3\cdot 6H_2O$) solution in a flask. The testing begins at a temperature of 35 °C and after 90 minutes until the temperature reaches 80°C in refluxing condition under a nitrogen atmosphere while vigorously stirring the reaction mixture to prevent the development of particles larger than 25 nm. Then 1 g of glycine followed by 140 mL of NH_4OH (25% wt) was added to the reaction mixture under vigorous stirring until the pH was measured to be in the range of pH 10 – 13. The black precipitates were collected after cooling the reaction mixture to room temperature. Suspensions of the black precipitates were then washed several times with deionised water and were subsequently dried overnight at 50 °C. For complete coverage, the magnetite nanoparticles were synthesized by adding Polyethylene Glycol, PEG in two steps before synthesis (40 mL of solution containing 2 mg mL^{-1} PEG 1500MW) and after synthesis (60 mL of solution containing 2 mg mL^{-1} PEG 1500MW).

To coat the isolated microorganism with the synthesized magnetic nanoparticle, 15 mL of a magnetic suspension (15 g Fe_3O_4 nanoparticles per litre of saline water) was mixed with 100 mL of a cell suspension (25 g of cells/L of saline water). The microbial cells were coated by adsorbing the magnetic nanoparticles. The coated cells were concentrated on the side of the vessel containing the suspension and separated from the suspension medium with the aid of external magnet.

Biodesulfurization experiment was carried out by mixing 20 mL of diesel with 10 mL of sulfur-free phosphate buffer of pH 7 containing 0.5 mL of the cells suspension in sterile distilled water and 2%w/v glucose solution in a 250 mL flask. The flask was incubated on a Gallenkamp rotary shaker at 150 rpm for 5 hours in a temperature of 36 °C. The experiments were also conducted for 10, 15, 20, 25, 30, 35, 40, 45, and 50 hours in triplicates, the control experiment set up did not have the cell suspension. The experiments were done for both coated and uncoated cells of the isolate. The sulfur content was done with Gas Chromatograph Model 3800.

Model Development

The general mass balance equation of the substrate in the fuel over a batch reactor is given by

Input – Output – Reaction rate = Accumulation 1

But since the process is batch, input and output = 0

Therefore, Accumulation = – Reaction rate 2

There is no reaction in the fuel, so reaction rate is zero.

The material balance over the bacterium coated with nanoparticle, solid phase is given by

Accumulation = Rate of transfer of the substrate to the cell surface – Reaction rate 3

The rate of adsorption of DBT and BT into the reaction site (surface of the cells) from the bulk liquid is assumed to follow the Freundlich Isotherm. According to Muhammad et al., (2015), Freundlich isotherm is given by

$$Q = K(C - C_s)^n \tag{4}$$

Differentiating equation 4 gives

$$\frac{dQ}{dt} = nK\left(C - C_S\right)^{n-1}\frac{dC}{dt} \tag{5}$$

$nK = K'$ Therefore equation 5 becomes

$$\frac{dQ}{dt} = nK'\left(C - C_S\right)^{n-1}\frac{dC}{dt} \tag{6}$$

Where K' the Freundlich constant and the parameter n is the measure of heterogeneity of the surface of the adsorbent.

C is the concentration of DBT and BT in the liquid, C_s is the concentration of DBT and BT at the surface of the cell.

The external mass transfer is given by

$$r_{bf} = k_{La}(C - C_S) \tag{7}$$

From equation 7, r_{bf} is the mass flux in $Kg/m^3.s$; K_L is the mass transfer co-efficient and a is the surface area to volume ratio in m^2/m^3

The rate of substrate disappearance in the 4S pathway according to Kareem (2010) is given by

$$-\frac{dC}{dt} = \frac{2kC}{K_M + C} \qquad 8$$

On substituting equation 6, 7 and 8 into equation 3 gives

$$\frac{dC}{dt} = K'\left(C - C_S\right)^{n-1}\frac{dC}{dt} + k_L a\left(C - C_S\right) - \frac{2kC}{K_M + C} \qquad 9$$

On rearranging equation 9, we have

$$\frac{dC}{dt} = \frac{k_L a\left(C - C_S\right) - \dfrac{2kC}{K_M + C}}{\left[1 - K'\left(C - C_S\right)^{n-1}\right]} \qquad 10$$

Equation 10 is the model equation for mass transfer influenced kinetics of biodesulfurization process based on 4S pathway and would be solved numerically by the 4th order Runge-Kutta method using Microsoft Excel.

The mass transfer coefficient k_La was obtained from slope of the plot of the LHS of equation 11 against time t

$$\ln\frac{C - C_S}{C - C_0} = k_L at \qquad 11$$

K' and n were obtained by linearizing the Freundlich isotherm,

$$q_e = K'C_e^{\frac{1}{n}} \qquad 12$$

The linear form of equation 12 is

$$\ln q_e = \ln K' + \frac{1}{n}\ln C_e \qquad 13$$

Where $q_e = \dfrac{m\left(C - C_S\right)}{V}$

The V is the volume of the solution; m is the mass of the magnetite while Cs is the equilibrium concentration. k and K_M were obtained from the plots of Lineweaver-Burk equation.

3. RESULTS AND DISCUSSION

Biochemical and morphological tests carried out on the isolated microorganism showed that the isolate has rod shape and raised elevation on nutrient agar with cream colour. It was observed to be Gram-negative due to their inability to retain the purple colour of the basic stain and, therefore, appeared pink under the light microscope. The isolate was also positive to the hydrogen sulfide test due to the present of black coloration of the lead acetate test paper. The result of the PCR confirmed that the isolate was *Pseudomonas stutzeri*.

The synthesized magnetite nanostructure was viewed by JEOL 1010 Telescopic Electron Microscope. Figure 1 showed the image, the particle size was predominantly 10.0 nm. Further characterization of the synthesized magnetite nanoparticles was obtained using XRD. This is to enable us understand the chemical composition of synthesized nanoparticles as well as the size of the nanoparticle. The output from XRD analysis yields a plot of intensity versus diffraction angle which can be used to determine the crystallographic planes that are being diffracted. The peaks of XRD patterns were analyzed and indexed using ICDD data base, comparing with magnetite standards (Lopez *et. al.*, 2010). As it can be seen in Figure 2, the numbers in parenthesis are reference standard pattern of Fe_3O_4 and give the Miller indices of pure Fe_3O_4 assigned to the observed peaks (Ansari *et al*., 2009).

The XRD pattern indicates the presence of predominantly Fe_3O_4 crystals. The discernible peaks which can be clearly identified in Figure 2 can be matched to, the (111), (220), (311), (400), (422), (511) and (440) planes of a cubic Fe_3O_4 unit cell, and it reflected by the well matching of the diffraction peaks with the magnetic pattern and it corresponds to that of magnetite structure. An estimation of the magnetite nanoparticles size has been performed from the Scherrer formula

$$D = \frac{K\lambda}{L\cos\Theta}$$

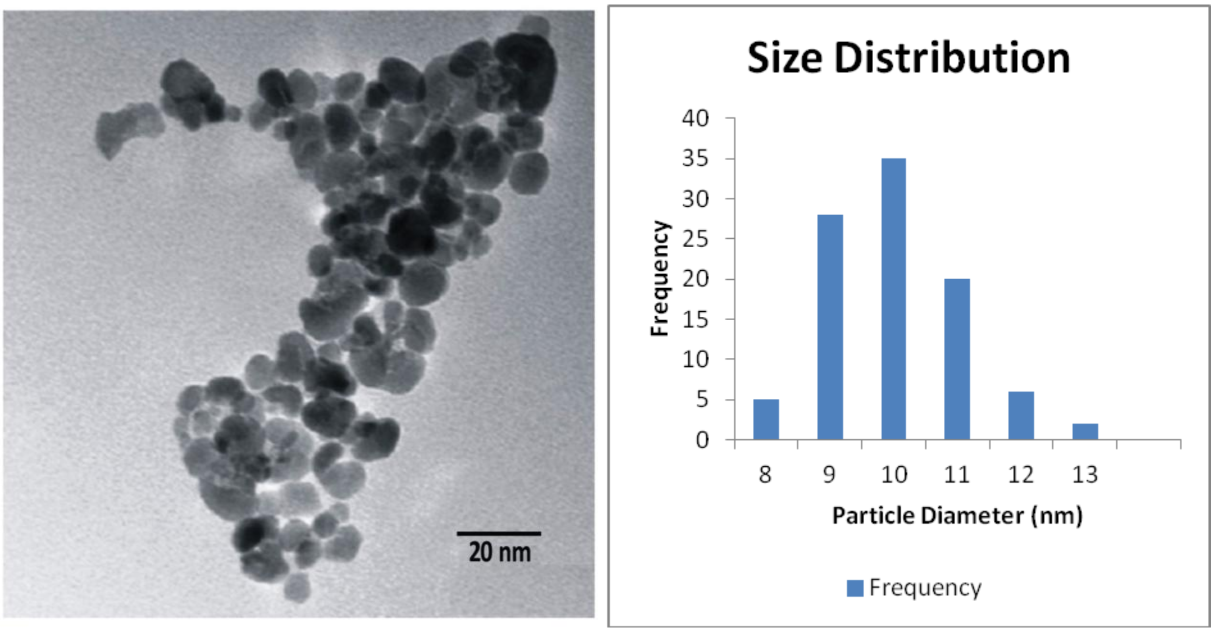

Figure 1 TEM Image and Particle Size Distribution of the Synthesized Magnetite

Where D is the crystallite mean size, λ is the X-ray wavelength (0.154 nm), L is the full width at half maximum (0.0142); θ is the corresponding Bragg angle; and K is the shape parameter, which is 0.89 for magnetite. Taking the highest intensity peak, namely the (311) plane, at $2\theta = 35.7°$, and the half maximum intensity width of the peak after accounting for instrument broadening, the calculated particle sizes was (10.15 ± 0.14) nm. The result is almost in agreement with the size as shown by TEM image which is 10.0 nm.

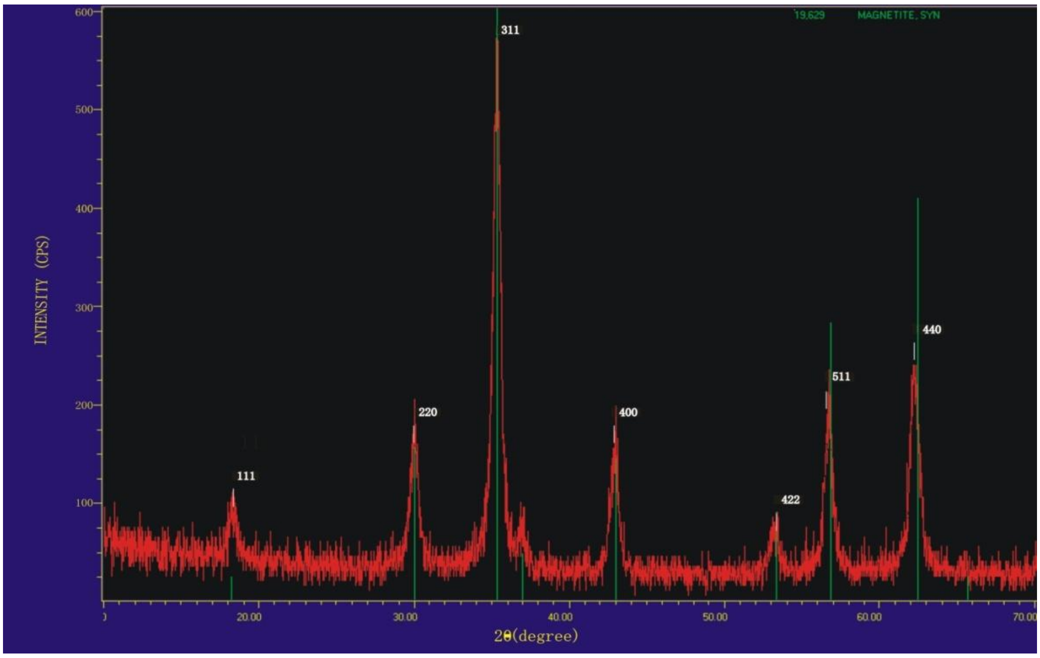

Figure 2: X-Ray Diffraction Patterns of the Synthesized Magnetite Nanoparticles

Analysis of the coated bacterium was done using Transmission electron micrographs. TEM image of the surfaces of cells coated with Fe_3O_4 nanoparticles is shown in Figure 3.

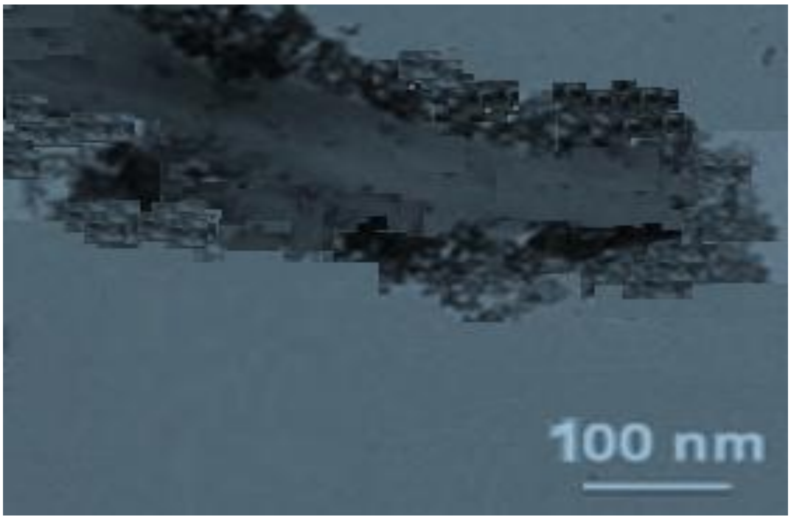

Figure 3: Magnetite-Coated Bacterium as Viewed by TEM

The Figure shows clearly that the magnetite nanoparticles were highly immobilized on the surface of the bacteria. This was due to magnetization effect of the nanoparticles (Ansari *et al*., 2009) and the size of the nanoparticles (Bardania, 2013). A more uniform coating of the nanoparticles on the surface of bacterium cells can be attributed to the larger specific surface area and the higher surface energy of the nanoparticles synthesized in the presence of glycine, which leads to a lesser tendency for nanoparticles to aggregate, the consequence of this is that additional surface area that would enhance adsorption has been created.

Figure 4 shows the concentration – time profile for the biodesulfurization of DBT in diesel. The plot for coated bacterium showed that the substrate was desulfurized steadily from its initial concentration of 127.61 mg/L to 15.31 mg/L in 50 hours of desulfurization. This translates to about 88% desulfurization. The plot for uncoated bacterium showed that the substrate was desulfurized steadily from its initial concentration of 127.61 mg/L to 40.84 mg/L in 50 hours of desulfurization. This translates to over 68% desulfurization.

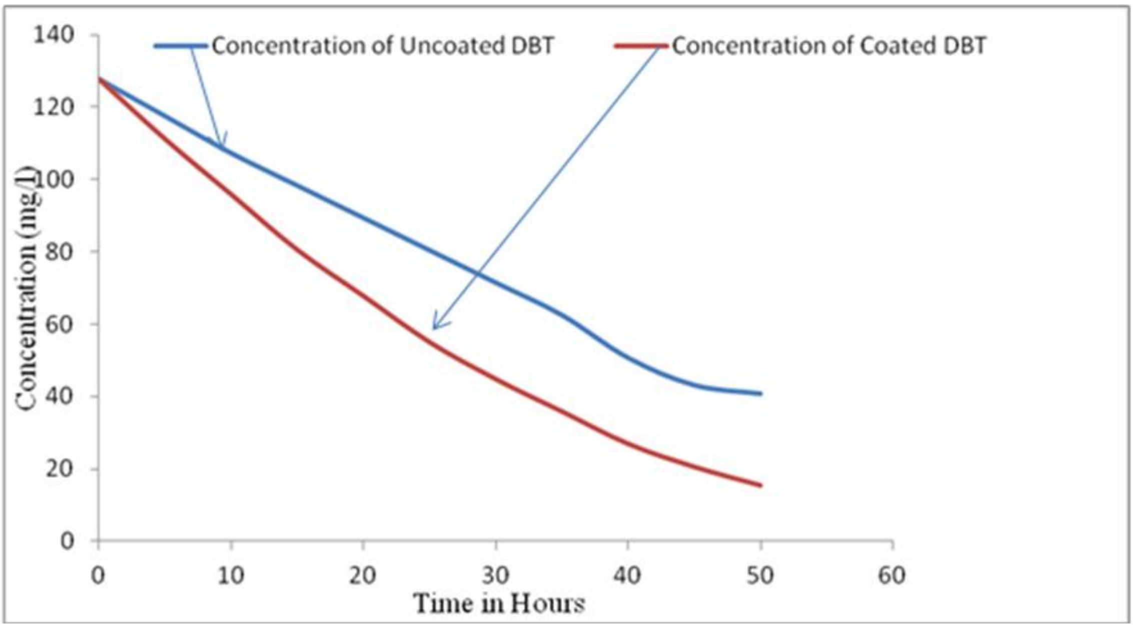

Figure 4: Plot of Experimental Data of DBT for Uncoated and Coated Bacterium

The augmented cellular permeability imparted by nanoparticle decoration of the cell surface, as employed in this study, had helped in improving the BDS kinetics (Karimi, 2016). In previous studies, Ansari *et al*. evaluated the coating of *R. erythropolis* IGTS8 by glycine-modified magnetite nanoparticles with a size range of 40–50 nm. It was shown that immobilization of magnetite nanoparticles on the surface of these bacteria cells enhances their desulfurization activity by 56%, (Ansari *et al.*, 2009). Although they determined the kinetic parameters using Optical waveguide lightmode spectroscopy (OWLS) which is an optical biosensor suitable for monitoring continuous adsorption processes. However, the results from this work have shown that coated bacterium (*Pseudomonas stutzeri*) increased biodesulfurization activity by 88% for DBT and 55% for BT. The increase in the rate of biodesulfulfurization of the coated bacterium is owing to the fact that biodesulfurization is extracellular, the microorganism secret enzymes which float at the surface of the nanoparticles thereby increasing the surface area of the reaction. The higher the surface area, the higher the rate of biodesulfurization. On the other hand, the increase may be attributed to the choice of the bacteria (Guobin *et al.*, 2006) and the size of the magnetic nanoparticle as observed by Ansari, *et al.*, (2009) and Bardania, (2013).

The kinetics of biodesulfurization of the uncoated bacteria followed the zero order kinetics while the coated one followed first order, this may be attributed to the likely increase adsorptive capacity created by the nanoparticle.

The measured kinetic parameters used in solving equation 8 are shown in Table 1, this equation was solved numerically using Runge-Kutta 4th order method with Microsoft Excel package.

The overall rate of substrate conversion is governed solely by the kinetics of the reaction. However, if mass transfer rate is lower than reaction rate, transport rate can be the step controlling the overall process rate and, moreover, the mass transfer rate may be influenced by the chemical rate of the bioprocess. Mass transfer limitations play an important role on the rate of reaction; the rate of conversion and product formation.

The kinetics data as presented in Table 1 shows that mass transfer is less in DBT when using coated bacterium. This therefore agrees with Bardania (2013) and Ansari (2009) that said mass transfer has little effect when magnetite nanoparticle is used to coat the bacteria strain capable of degrading sulfur. According to Felix (2009*)*, the volumetric mass transfer coefficient is often used in order to compare the efficiency of bioreactors and as an important scale-up factor. In view of that, volumetric mass transfer coefficient was determined for the substrate (DBT) in order to design a bioreactor that can be used to take the technology to a market place.

Table 1: Parameters used to Solve Model Equation

	k_La (m^3/L)	K_{M1} (mg/L)	k_1 (mg/L.h)	K' (mg/L.h)	C_s(mg/L.h)	N
DBT Coated Bacterium	2.15	5.83	3.53	3.98	9.35	1.61
DBT Uncoated Bacterium	2.86	12.90	14.11	2.49	14.50	1.85

Figure 5 shows the experimental and simulated data plot of concentration of DBT versus time for uncoated bacterium. The level of agreement between the experimental data and the simulated data was determined using the Root Mean Square Error, RMSE, Table 2 gives the summary of the RMSE for each of the possible scenario. The lower the sum the better the level of agreement, as can be seen from the Table, the model equation coated system is lower, consequently, one may draw a conclusion that the model equation described the kinetics of the coated microorganism better. Figure 6 showed the experimental and simulated concentration – time profile of the biodesulfurization of DBT in diesel by *Pseudomonas stutzeri* coated with magnetite nanoparticle.

Table 2 Root Mean Square Error for the Model

	DBT
RMSE UNCOATED	2.13
RMSE COATED	0.38

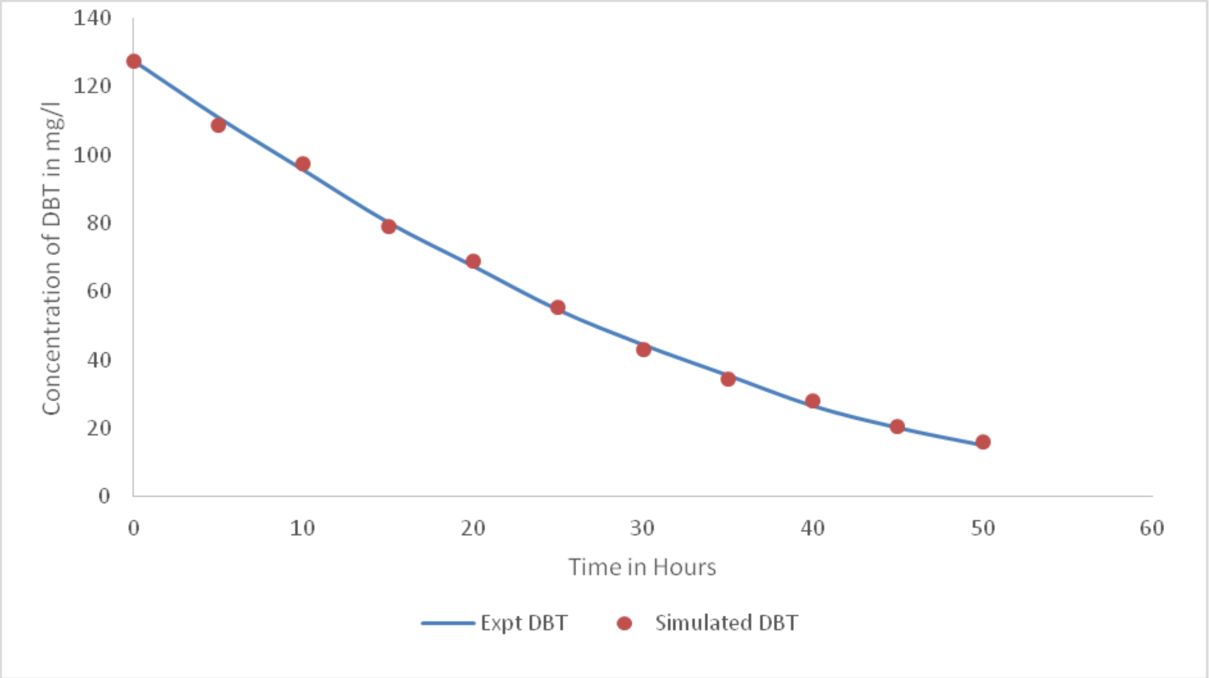

Figure 6 Experimental and Simulated Data Plot of Concentration of DBT versus Time using Coated Bacterium

It is worthy of mention that the biodesulfurization was carried out in diesel, a real petroleum feed.

4. CONCLUSION

In a nutshell, nanoparticles have the potential of enhancing microbial reaction. The coating of the isolated *Pseudomonas stutzeri* with the synthesized magnetic nanoparticle has shown great improvement in the biodesulfurization rate of diesel. The simulated data are also in good agreement with the experimental ones implying that all assumptions made in the development of the mathematical model are correct. Furthermore, the estimated and measured parameters would serve as useful tools for bioreactor design and analysis.

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PHYTOCHEMICAL AND THERMODYNAMIC STUDIES OF PAWPAW LEAF (*ASIMINA TRILOLA*) EXTRACT AS CORROSION INHIBITOR OF ZINC IN KOH MEDIUM

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ABSTRACT

This work presents a report of phytochemical and thermodynamic studies of pawpaw leaf extract as a corrosion inhibitor of zinc in 1M KOH. The extract was subjected to qualitative and quantitative phytochemical analyses. Applying the thermometric technique, reaction numbers for the zinc dissolution in free and inhibited KOH media were used to determine the inhibition efficiency of the extract. The gravimetric method was carried out using one-factor at a time coupled with response-surface methodology. Central Composite Design of Design Expert Software was employed in the optimization process. Analyses of the results revealed that the pawpaw extract is predominantly made up of flavonoids (365.0 mg/100g) and tannins (270.0 mg/g). The degree of surface coverage of the zinc increased with increase in inhibitor concentration, but decreased with increase in temperature. The adsorption of the extract on the zinc surface appears to obey the mechanism of physical adsorption, as it is best fitted by Langmuir adsorption isotherm. A quadratic model adequately described the relationship between the inhibition efficiency and the factors of concentration, temperature and time. The highest inhibition efficiency of 86.6% was obtained at inhibitor concentration of 1.0 g/l, temperature of 303 K and immersion time of 5 hours. The pawpaw leaf extract is therefore a suitable inhibitor for corrosion inhibition of zinc in KOH medium.

Keywords: Corrosion; Inhibitor; Pawpaw; Phytochemicals; Zinc.

INTRODUCTION

Zinc has a large negative standard electrode potential, which makes it highly reactive and acts as sacrificial anode in cathodic protection (Uppal and Bhatia, 2009). Its industrial usefulness is constrained by corrosion problem. Alkaline solutions of moderate strengths are much less corrosive than corresponding concentrations of acid, but are still corrosive enough to impair the usefulness of zinc. Corrosion is the deterioration of metal surfaces as a result of reaction with the surrounding environmental conditions. It can cause damage to metal and alloy structures with economic consequences in terms of repair, replacement, product losses, safety and environmental pollutions (Trethewey and Chamberlain, 1995). Application of inhibitors has been identified as a viable option for corrosion control of metals in corrosive media.

Corrosion inhibitor is a chemical substance which, when added in small concentrations to an environment, minimizes corrosion (Papavinasam, 2000; Nagm *et al*, 2012; Green and Perry, 2008). Anees et al (2009) investigated the effect of temperature and acid concentration on corrosion of low carbon steel in hydrochloric acid medium. Different methods, including chemical and electrochemical techniques, have been employed in the study of the effects of inhibitors on the corrosion of metals in various corrosive media. In the work of El Ouariachi *et al* (2010), *Rosmarinus officinalis* (Rosemary) essential oil obtained by hydro-distillation was tested as a corrosion inhibitor of steel in 0.5M H_2SO_4 using weight loss and electrochemical polarization methods. Singh and Mukherjee (2010) investigated the kinetics of mild steel corrosion in aqueous acetic solution using weight loss and polarization techniques. Nadia *et al* (2011) examined corrosion protection behaviour of zinc rich epoxy paint in 3% NaCl solution using electrochemical impedance spectroscopy (E1S). Experimental and quantum chemical studies on corrosion inhibition performance of inhibitors have been reported (Mistry et al, 2012; Udhayakala *et al*, 2012). Theoretical approach to corrosion inhibition study has also been considered (Udhayakala *et al*, 2012). It was reported that the basic relationship of the density functional theory (DFT) of chemical reactivity is precisely, the one that links the chemical potential of DFT with the first derivative of the energy with respect to the number of electrons, and with the negative of the electronegativity (χ) as given in Equation (1):

$$\mu = \left(\frac{\partial E}{\partial N}\right)_{v(r)} = -\chi \qquad 1$$

Where µ is the chemical potential, E is the total energy, N is the number of electrons, and ν(r) is the external potential of the system.

A review of pertinent literature shows the need for the study of corrosion inhibition of zinc. In the present work, pawpaw leaf extract as an inhibitor of the corrosion of zinc in 1M KOH medium was investigated. Pawpaw (*Asimina triloba* also commonly known as *Carica papaya*) is a tree-like herbaceous plant, and a member of the *Caricaceae* family. Economically, pawpaw is the most important species within the *Caricaceae* family. It has several industrial uses. Biochemically, pawpaw leaves are complex, producing several alkaloids and other phytochemicals with important pharmaceutical and industrial applications (Sikandar *et al*, 2013). The aim of this work is to study the phytochemical and thermodynamic properties of pawpaw leaf extract as corrosion inhibitor of zinc in KOH media.

MATERIALS AND METHODS

All the chemicals used in this study are of analytical grade. 1.0M KOH was used as the corrosive medium. Zinc with compositions of Si (0.35%), Fe (0.28%), Cu (0.04%), Al (0.27%), Cr (0.33%), Ti (0.13%), Sn (0.4%) and Zn (98.2%) was mechanically cut into coupons (length x breadth x thickness; 5 cm x 4 cm x 0.06 cm), and used for the corrosion inhibition study. The extraction method used by Omotioma and Onukwuli (2016) was adopted. The leaves were sun-dried for three days. The moisture content of the leaves was determined by placing the leaves in an oven at 105 ^{0}C. The leaves were withdrawn and weighed at regular interval until constant loss in weight was noticed. The dried leaves of 2.03% moisture content were ground to increase the surface area and stored in closed containers. 30g of the ground leaves (fineness; particle size of 0.85mm) was measured and soaked in 1000ml of ethanol (99.7% v/v) for 48 hours, and the mixture was filtered. The extract was concentrated by evaporating the ethanol from the mixture at 80 ^{0}C. The extract was weighed and stored for the corrosion inhibition study.

Characterization of the Extract

Methods used by previous authors (Marcano and Hasenawa, 1991; Mayuri, 2012; Mada et al, 2012; Joona et al, 2013) were adopted for the phytochemical analysis of the extract. For the alkaloids detection, 1g of solvent free pawpaw leaf extract was transferred into a test tube. Few drops of dilute hydrochloric acid were added, stirred and filtered. The filtrate was tested with alkaloid reagents; Mayer's reagent (Cream ppt) and Dragendorff's reagent (Orange-brown ppt). In the detection of cardiac glycosides, 1 ml of the extract, 5 ml water and 2ml glacial acetic acid were mixed in a vessel. A drop of $FeCl_3$ and 1 ml conc. H_2SO_4 were added. There was an appearance of brown ring. For the determination of flavonoids, 25 ml water was added to 1 g of the extract and oven heated at 100 ^{0}C for 15 minutes. 5 ml of NH_4OH was added to 2 ml of the extract. Then 1 ml conc. H_2SO_4 was added. There was an appearance of yellow colouration indicating the presence of flavonoids. The presence of phenols was determined by adding a few drops of 1% (w/v) solution of ferric chloride followed by 1% (w/v) gelatin in sodium chloride of the same concentration. The formation of a precipitate indicated the presence of phenols. For the determination of saponins, 1 g of sample was boiled in 40 ml of water, and then filtered. 10 ml of the filtrate was shaken vigorously. Formation of froth was noticed. 3 drops of oil were added, and the mixture was shaken. Emulsion of the oil was noticed. For the determination of tannins, 1 g of the sample was added to 25 ml of water. It was then put in oven at 100 ^{0}C for 15 minutes. To 1 ml of the extract, 10 ml water was added and then boiled. A few drops of 0.1% $FeCl_3$ were added. A green colouration appeared indicating the presence of tannins. Quantitative analysis of the leaf extract was carried out as follows:

a. Alkaloids

20 ml of 10% acetic acid in ethanol was added to the 1g of sample. The mixture was shaken and allowed to settle for 4 hours. It was then filtered. The filtrate was evaporated to about a quarter of its original volume. One drop of concentrated ammonium hydroxide was added. The precipitate formed was filtered through a weighed filter paper. The filter paper was left to dry in the oven at 100 ^{0}C. The filter paper was weighed after drying it to a constant weight.

$$Alkaloid = \left(\frac{w_r - w_f}{w_0}\right) \qquad 2$$

Where w_r is the weight of filter paper + residue, w_f is the weight of filter paper, and w_0 is the weight of the sample analyzed.

b. Cardiac glycosides

1g of the extract was placed in the oven at 100 ^{0}C for 15 minutes. 1 ml of the extract plus 5ml water was added to 2 ml glacial acetic acid plus one drop of $FeCl_3$. Also, 1ml conc. H_2S0_4 was added. The absorbance of the resulting solution was measured at 410nm.

Flavonoids

0.5ml of 2% $AlCl_3$ methanol solution was added to 0.05 ml sample solution. After 1hrs at room temperature, yellow colour appeared indicating the presence of flavonoids. Flavonoids content as mg/g quereetin was determined.

c. Phenols

0.2% formic acid was added to 2 g of the extract and left to settle for 2 minutes. It was then filtered. With the aid of pipette, 2 ml of the extract was put into a test tube and 0.5 ml folin-ciocalteau reagent was added. It was left for 20 minutes for colour development. The absorbance at 765 nm was read and the concentration for a standard graph was obtained. It is expressed as GAE/g (Gallic Acid Equivalent).

e. Phytate

Ferric ammonium sulphate was added to 0.5 ml of extract in a test tube. The test tube was heated in water bath for 30 minutes. It was cooled and centrifuged. To 1 ml of the supernatant, 1.5 ml of 2,2-bipyridine solution was added. Measurement was carried out at 519 nm, with distilled water as blank.

f. Saponins

Into 1 g of sample 15 ml ethanol was added and put in a water bath at 55 ^{0}C for 4 hours. It was filtered and the residue was washed twice with 20% ethanol twice. The extract was reduced to about 5 ml in the oven. 5 ml of petroleum ether was added to the concentrated extract inside a separating funnel. The petroleum ether layer was discarded and 3 ml of butanol was added to it. It was washed with 5 ml of 5% sodium chloride. The butanol was later poured onto a weighed petri dish. It was put in the oven to evaporate to dryness, and the residue was weighed.

g. Tannins

1 g of the sample was extracted with 25 ml of the solvent mixture of 80:20 acetone: 10% glacial acetic acid for 5 hours. It was filtered and the absorbance measured at 500 nm. The absorbance of the reagents blank was also measured. A standard graph with 10, 20, 30, 40, 50 mg/100 g of tannic acid was drawn. The concentration of tannin (taking into consideration any dilution factor) was obtained.

Thermometric Method of Study

In the thermometric method of study, the zinc samples were immersed in beakers containing inhibited and uninhibited KOH media. The beakers were placed in thermostat set at 303 K. The progress of the corrosion reaction was monitored and the temperatures of the system containing the zinc sample and the test solution were regularly recorded until a steady temperature value was obtained. Equations (3) and (4) were used for the determination of the reaction number and inhibition efficiency (Mabrouk *et al*, 2011; Eddy *et al*, 2012; Omotioma and Onukwuli, 2016).

$$RN = \frac{T_m - T_i}{t} \tag{3}$$

Where T_m and T_i are the maximum and initial temperatures (in ^{0}C) respectively, and t is the time in minutes taken to reach T_m.

$$IE\% = \left(1 - \frac{RN_{add}}{RN_{free}}\right) * 100 \tag{4}$$

Where RN_{free} and RN_{add} are the reaction numbers for the zinc dissolution in free and inhibited KOH media respectively.

Gravimetric Method of Study

Gravimetric method of study was carried out using one factor at a time and with response surface methodology (RSM). Thermodynamic parameters of activation energy, heat of adsorption and free Gibbs energy of the corrosion inhibition process were determined. Central composite design of Design Expert Software was used for the RSM. The weight loss (Δw), corrosion rate (CR), inhibition efficiency (IE) and degree of surface coverage were calculated using Equations (5), (6), (7) and (8); respectively (Omotioma and Onukwuli, 2016).

$$\Delta w = w_i - w_f \tag{5}$$

$$CR = \frac{w_i - w_f}{At} \tag{6}$$

$$IE\% = \frac{\omega_0 - \omega_1}{\omega_0} * 100 \tag{7}$$

$$\theta = \frac{\omega_0 - \omega_1}{\omega_0} \tag{8}$$

Where w_i and w_f are the initial and final weight of zinc samples respectively; ω_1 and ω_0 are the weight loss (g) in presence and absence of inhibitor respectively. A is the total area of the zinc sample and t is the immersion time (hr).

Linearized Arrhenius model given in Equation (9) was used to determine activation energy, E_a (kJmol^{-1}), while Equation (10) was employed to evaluate the heat of adsorption, Q_{ads} (kJmol^{-1}) (Octave, 2003; Orubite-

Okorosaye and Oforka, 2004; Nwabanne and Okafor, 2011; Nnanna *et al*, 2013).

$$\ln\left(^{CR_2}/_{CR_1}\right) = \left(^{E_a}/_{2.303R}\right)\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad 9$$

$$Q_{ads} = 2.303R\left[\log\left(\frac{\theta_2}{1-\theta_2}\right) - \log\left(\frac{\theta_1}{1-\theta_1}\right)\right] * \frac{T_2.T_1}{T_2-T_1} \quad 10$$

Where corrosion rates of the Zn at T_1 and T_2 are CR_1 and CR_2 respectively, R is the gas constant, θ_1 and θ_2 are the degree of surface coverage at temperatures T_1 and T_2 respectively.

The data obtained for the degree of surface coverage were fitted into adsorption isotherms of Langmuir, Frumkin, Temkin and Flory-Huggins isotherms expressed in Equations (11), (12), (13) and (14); respectively (Nwabanne and Okafor, 2011; Li and Deng, 2012; Alinnor and Ejikeme, 2012; Patel et al, 2013; Omotioma and Onukwuli, 2016). The free energy of adsorption (ΔG_{ads}) was calculated using Equation (15).

$$log\,\frac{C}{\theta} = \log C - logK \quad 11$$

$$\log\left((C) * \left(\frac{\theta}{1-\theta}\right)\right) = 2.303logK + 2\alpha\theta \quad 12$$

$$\theta = -\frac{2.303logK}{2a} - \frac{2.303logC}{2a} \quad 13$$

$$\log\left(\frac{\theta}{C}\right) = \log K + xlog(1-\theta) \quad 14$$

$$\Delta G_{ads} = -2.303RTlog\,(55.5K) \quad 15$$

Where K is the adsorption equilibrium constant, C is the concentration of the inhibitor, θ is the degree of surface coverage, α is the lateral interaction term describing the interaction in adsorbed layer, a is the attractive parameter, R is the gas constant and T is temperature.

RESULTS AND DISCUSSION

The Qualitative and Quantitative Results of the Extract

Table 1 shows the qualitative analysis of the extract, indicating the level of alkaloids, cardiac glycosides, flavonoids, phenolics, phytates, saponins and tannins present in the extract. The qualitative results of the extract phytochemicals are denoted with symbols; +++ (highly concentrated), ++ (concentrated), + (in traces), and – (absent or too little to be observed qualitatively). The quantitative analysis revealed that the extract is predominantly made up of flavonoids (365.0 mg/100g) and tannins (270.0 mg/g).

Table 1: Qualitative and Quantitative Analysis of the Pawpaw Extract.

Phytochemicals	Qualitative analysis	Quantitative analysis
Alkaloids (mg/100g)	+	83.3
Cardiac glycosides (mg/100g)	+	70.0
Flavonoids (mg/100g)	++	365.0
Phenolics (GAE/g)	++	24.9
Phytates (mg/100g)	+	70.0
Saponins (mg/100g)	-	11.7
Tannins (mg/100g)	++	270.0

The Thermometric Measurement Results

The results of the thermometric measurements are presented in Table 2. Increase in concentration increases with the inhibition efficiency of the extract. The inhibition efficiency appears to be a function of the reaction number in the absence and presence of the pawpaw extract. The highest inhibition efficiency of 85.78% was obtained, indicating that extract is a suitable inhibitor for corrosion control of zinc in KOH medium.

Table 2: Effects of concentration of the extract on the IE (%) of Zn in KOH medium.

Inh. conc., g/l	**RN**	**IE (%)**	**Degree of Surface Coverage, θ**
0.0	0.1476		
0.2	0.0751	49.11	0.4911
0.4	0.0563	61.87	0.6187
0.6	0.0300	79.67	0.7967
0.8	0.0245	83.41	0.8341

Inh. conc., g/l	**RN**	**IE (%)**	**Degree of Surface Coverage, θ**
1.0	0.0210	85.78	0.8578

Results of the Gravimetric Analyses

Table 3 presents the weight loss of the zinc, corrosion rate and inhibition efficiency as functions of concentration, temperature and time. Inhibition efficiency is observed to increase with increase in concentration of the extract (inhibitor), but decreased with increase in temperature. Figure 1 presents the degree of surface coverage versus inhibitor concentration at various temperatures. Increase in inhibitor concentration increases the degree of surface coverage. But the degree of surface coverage decreased with increase in temperature.

Table 3: Gravimetric Results of the Corrosion Inhibition Process

Parameter	**Time (hr)**	**Temperature of 303 K**					**Temperature of 333 K**				
Concentration		**0.2 g/l**	**0.4 g/l**	**0.6 g/l**	**0.8 g/l**	**1.0 g/l**	**0.2 g/l**	**0.4 g/l**	**0.6 g/l**	**0.8 g/l**	**1.0 g/l**
Weight loss (g)	1	0.023	0.020	0.017	0.013	0.010	0.037	0.030	0.027	0.023	0.020
	3	0.037	0.020	0.017	0.013	0.010	0.067	0.050	0.047	0.043	0.040
	5	0.043	0.037	0.020	0.017	0.013	0.090	0.070	0.050	0.047	0.043
CR (mg/cm^2hr)	1	1.150	1.000	0.850	0.650	0.500	1.850	1.500	1.350	1.150	1.000
	3	0.617	0.333	0.283	0.217	0.167	1.117	0.833	0.783	0.717	0.667
	5	0.430	0.370	0.200	0.170	0.130	0.900	0.700	0.500	0.470	0.430
IE (%)	1	37.84	45.95	54.05	64.86	72.97	30.19	43.40	49.06	56.60	62.26
	3	41.27	68.25	73.02	79.37	37.84	34.95	51.46	54.37	58.25	61.17
	5	55.67	61.86	79.38	82.47	86.60	40.00	53.33	66.67	68.67	71.33

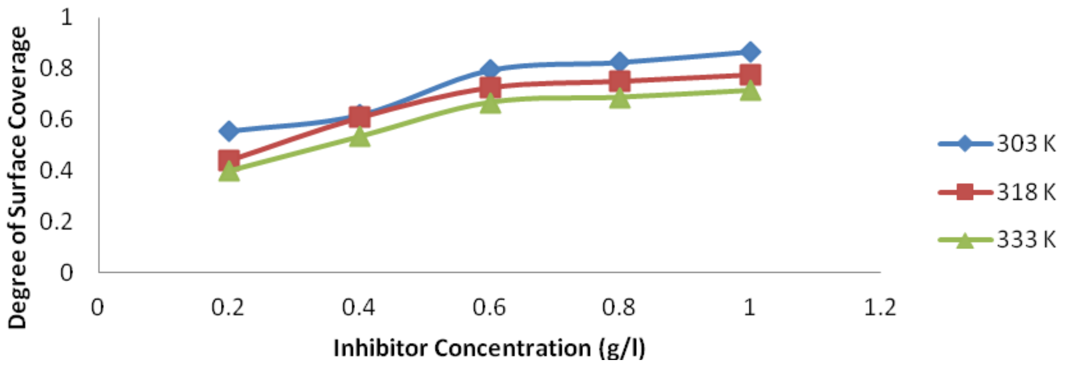


Figure 1. The Degree of Surface Coverage versus Inhibitor Concentration at Various Temperatures.

Linearized Arrhenius model of Equation (7) was used to determine the activation energy, E_a ($kJmol^{-1}$), while Equation (8) was employed to evaluate the heat of adsorption, Q_{ads} ($kJmol^{-1}$) (Octave, 2003; Orubite-Okorosaye and Oforka, 2004; Nwabanne and Okafor, 2011; Nnanna *et al*, 2013). The negative sign in the values of the heat of adsorption indicates an exothermic reaction process (Table 4).

Table 4: Activation Energy and heat of adsorption for the corrosion inhibition process

Conc. of pawpaw leaves extract (g/l)	Activation energy, E_a (kJ/mol)	Heat of adsorption, Q_{ads} (kJ/mol)
0.2	47.565	-17.710
0.4	41.058	-9.487

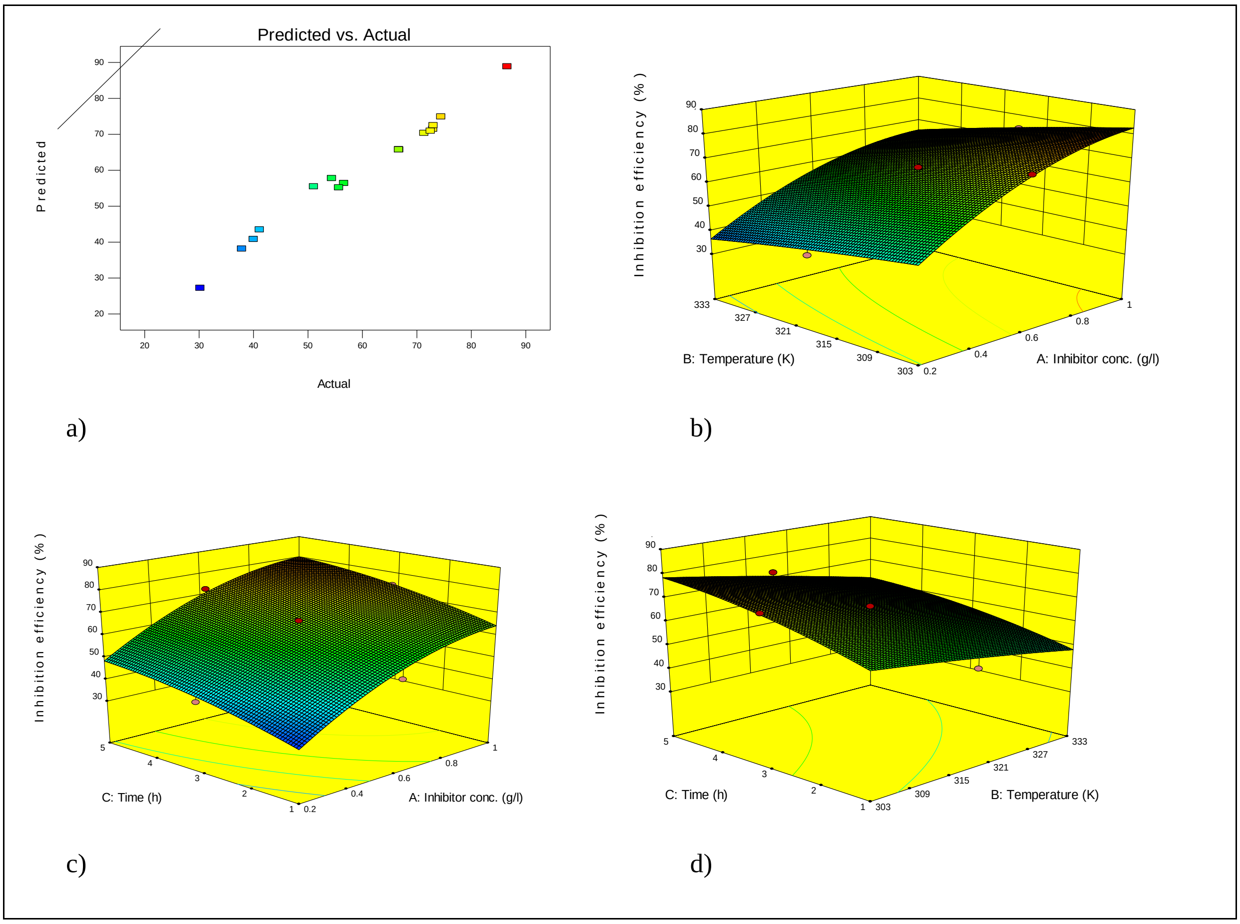
0.6	59.007	-18.323
0.8	65.488	-21.374
1.0	77.036	-26.697

The values of the correlation of determination (R^2) suggest that Langmuir isotherm (R^2 of 0.9876 and 0.9866 at 303K and 333K respectively) seems to best describe the process as shown in Table 5. From the Temkin isotherm, values of the attractive parameter (a) are negative, -2.455 and -2.419 for the temperatures of 303K and 333K respectively. This shows that there was no interaction between the layers of the extract. The free energy of adsorption is less than -40 kJ/mol, which is an indication that the adsorption of the pawpaw extract on the zinc surface obeyed physical adsorption mechanism. The findings are in agreement with a previous report (Omotioma and Onukwuli, 2016).

Table 5: Adsorption Parameters for the Corrosion Inhibition Process

Adsorption Isotherm	Temperature (K)	R^2	K	ΔG_{ads} (kJ/mol)	Isotherm property	
Langmuir Isotherm	303	0.9876	0.8358	-9.8		
	333	0.9866	0.7492	-10.3		
Frumkin Isotherm	303	0.9817	0.0565	-2.9	α	2.1
	333	0.9906	0.0881	-4.4		1.9
Temkin Isotherm	303	0.928	65.95	-20.7	a	-2.419
	333	0.971	36.36	-21.1		-2.455
Flory-Huggins Isotherm	303	0.847	4.3351	-13.8	x	0.804
	333	0.935	3.7154	-14.6		1.25

The analysis of inhibition efficiency of the pawpaw leaf extract (inhibitor) is presented in Figure (2). Plot of predicted versus actual inhibition efficiency was used to test the performance of the model. The predicted versus actual plot gave a linear graph. The graph (3-D surface plot) showed the relationship between the factors and response of the designed experiment. The inhibition efficiency increased with increase in concentration, but decreased with increase in temperature. A model describing the relationship between the inhibition efficiency and the factors of concentration, temperature and time is presented by Equation (16). The inhibition efficiency is a function of inhibitor concentration (C, g/l), temperature (T, K) and time (t, hr). The positive signs in the model signified synergistic effect, while the negative signs signified antagonistic effect. The highest power of at least one of the variables is 2, which showed that the mathematical model is a quadratic equation.



a) b) c) d)

Figure 2: IE (%) of the extract as corrosion inhibitor of Zn in KOH.
a) Predicted versus Actual IE (%), b) IE (%) versus concentration and temperature c) IE (%) versus concentration and time, d) IE (%) versus temperature and time.

The model for the corrosion inhibition of Zn in KOH by pawpaw leaves extract is;

$$IE = +65.73 + 15.71 * A - 7.36 * B + 7.74 * C - 1.04 * A * B + 0.090 * A * C - 0.86 * B * C - 6.53 * A^2 - 0.62 * B^2 - 2.53 * C^2 \qquad 16$$

Where A = inhibitor concentration, B = temperature and C = time.

CONCLUSIONS

The analyses of the results of this study showed that the pawpaw extract is predominantly made up of flavonoids (365.0 mg/100g) and tannins (270.0 mg/g). The degree of surface coverage of the zinc with pawpaw extract increased with increase in inhibitor concentration, but decreased with increase in temperature. The adsorption of the pawpaw extract on the zinc surface obeyed the mechanism of physical adsorption. A quadratic model adequately described the relationship between the inhibition efficiency and the factors of concentration, temperature and time. The highest inhibition efficiency of 86.6% was obtained at inhibitor concentration of 1.0 g/l, temperature of 303 K and immersion time of 5 hours. Based on the foregoing, the study has shown that pawpaw leaf extract has a strong inhibitive potential with respect to the corrosion of zinc in KOH medium.

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ELEMENTAL COMPOSITION OF PARTICULATES DEPOSITION IN SOME SELECTED INDUSTRIAL AREAS OF IKEJA, LAGOS, NIGERIA

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ABSTRACT

Particulate Matter (PM) samples were collected using deposition gauges (0.2m x 0,15m) at the selected industrial areas within Ikeja LGA during the period of May to June 2015 for the wet season and the period of December 2015 over January 2016 for the dry season respectively. The collected samples were filtered and dried for the wet season while that of the dry season was rinsed with distilled water and then subjected to the same process as of the wet season. The Deposition Flux (DF) of the measured PM ranged from 38.01 – 197.11 g/m^2.month in the wet season and ranged from 18.14 – 74.08 g/m^2.month in the dry season. The DFs for Lagos State University Epe (LSUE) ranged from 57.65-62.96 g/m^2.month and 42.39-51.06 g/m^2.month in the wet and dry seasons, respectively. The Iron elemental ratio ranged from 0.002-3.885 in the wet and dry seasons. The Enrichment Factor ranged from 0.00- 8940.93 on both seasons. PM samples collected exceeded the United States Environmental Protection Agency (USEPA), World Health Organization (WHO) and reveals anthropogenic sources

Keywords: PM; Deposition gauges; Elemental ratio; Enrichment Factor; Anthropogenic

1 INTRODUCTION

The urban atmosphere is subjected to large inputs of anthropogenic contaminants arising from both stationary (power plants, industries, incinerators, and residential heating) and mobile sources (road traffic) (Bilos *et al.*, 2001; Sulivan and Woods, 2000; Sweet and Vemette, 1993; Pacyna, 1984). PM contain heavy metals that are partitioned between particulate, liquid, and vapour phases and are subsequently transported to the Earth's surface through wet and dry deposition (Zufall and Davidson, 1997), according to their physical and chemical properties.

The mega city status of Lagos state has opened the state to more industrial revolutions. As industries increase, the emission released into the atmosphere also increases thereby putting the health of her citizen in danger (Abdul-wahab, 2012). Measurement of heavy metals in PM is, therefore, of immense importance for toxicological, environmental, and occupational health studies.

The aim of this study was to assess and characterized the atmospheric particulate deposited during wet and dry seasons in selected industrial areas within Ikeja, Lagos State. The objectivea of this study were to: 1) determine deposition flux of atmospheric particulates deposited during wet and dry seasons, 2) identify and characterize heavy metals composition of the particulates deposited in the selected industrial areas, 3) determine the elemental ratio of the characterized elements in the selected industrial areas and 4) identify the contributing source of particulate matter deposited using enrichment factor analysis

2 MATERIALS AND METHODS

2.1 Sampling site

The sampling was carried out in Lagos State, the former capital of Nigeria and one of the largest states in the country. Lagos State lies on the latitude 6^o 27' 55.5192" N and Longtitude 3^o 24' 23.2128" E respectively. Ikeja Local Government Area (LGA) was selected for this study (Fig.1). The four selected Industrial areas are Agidingbi Industrial Area (AGIA), Ojota Industrial Area (OJIA), Oregun Industrial Area (ORIA), and Ikeja Industrial Area (IKIA). Lagos State University, Epe (LSUE) was selected as the control experiment area. The study areas are characterized by high population, increased vehicular traffic and several other industrial activities. The choice of the selected industrial areas was borne out of their closeness to residential areas.

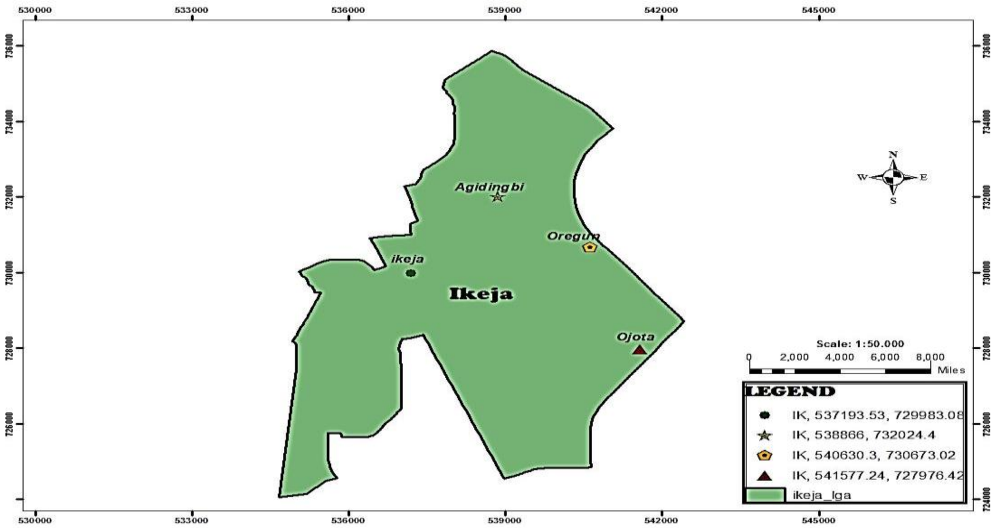


Figure 1: Location of Selected Industrial Area within Ikeja.

2.2 Sampling procedure

The sampling period covered wet and dry seasons that are typical of Lagos State climates. May to June 2015 was chosen as study period for the wet season while the study period for the dry the season was December 2015 to January 2016. It was assumed that the wet and dry seasons were at their peak at the chosen period. The deposition flux measurement was carried out using deposition gauges. Three deposition gauges (0.2m diameter by 0.15m depth) were deployed permanently to each sampling spot in the selected industrial area for a period of one month (Jimoda, *et al.,* 2010). Some sampling spot were located in residential areas, which are in close proximity to the industries to measure the particulates secondary source, in cases where access was denied to the industries.

Deposition gauges were planted at the industrial areas covering the selected Industrial Areas. The gauges were planted for a month; rain water and sediment in the deposition gauges during the wet season were collected and filtered through dry pre-weighed Whatman (125 mm diameter, Cat No 1001 – 125) filter paper on digital weighing balance (model PA2102). The filter papers were desiccated in a glass box to prevent further settlement of particles until they were completely dried. The filter paper and the particles were reweighed to determine the mass of the particles collected. In the same manner, the dried particles in the dry season were rinsed with distilled water and subjected through same process with wet season. The deposition flux was determined using Eqn. (1)

$$\text{Deposiion Flux} = \frac{Wp}{A.t} \qquad (1)$$

Where:

Wp = Weight of Particulate matter (g), A = Area of the deposition gauge (m^2) and

t = Duration of exposure (month)

2.3 Characterization of Heavy Metals in the Deposited Particulate Matter

The deposited particulate matter was characterized for heavy metals using Energy Dispersive X-ray Fluorescence Spectrometry (EDXRF) due to its high sensitivity and being a multi-elemental detector instrument. The elements detected are Silicon (Si), Sulphur (S), Chlorine (Cl), Potassium (K), Calcium (Ca), Titanium (Ti), Vanadium (V), Chromiumm (Cr), Manganese (Mn), Iron (Fe), Nickel (Ni), Copper (Cu), Zinc (Zn), Germanium (Ge), Strontium (Sr), Zirconium (Zr), Lead (Pb), Krypton (Kr), Tantalum (Ta), Rubidium (Rb), Molybdenum (Mo), Cadmium (Cd), Tungsten (W), Polonium (Po) and Actinium (Ac)

Equation (2) was used to determine the elemental ratio; where C_x and C_{ref} are the concentrations of the element x and the reference element from the characterized results.

$$ER = \left({}^{C_x}\!/\!_{C_{ref}}\right)_{\text{aerosol}} \qquad (2)$$

Equation (3) was used to determine the enrichment factor (EF). Where C_x and C_{ref} are the concentrations of the element x and the reference element, while $(C_x/C_{ref})_{aerosol}$ and $(C_x/C_{ref})_{crust}$ are the proportions of the element concentrations in the particulate matter and in the Earth's crust' respectively.

$EF_x = \frac{[C_x/C_{ref}]_{aerosol}}{[C_x/C_{ref}]_{crust}}$	(3)

The EFs were calculated by obtaining crustal elements data from literature (Taylor and McLennan, 1985). An element was chosen as indicator based on the type of industries located in these areas for enrichment factor to be used. Therefore, Fe was chosen because it is the conventional element for the main source of the Earth's crust (Dai, 2015; Yadav and Satang, 2013). Crustal element data were taken from Taylor *and McLennan*, (1985).

3 RESULTS AND DISCUSSION

3.1 Wet and dry deposition fluxes distribution at selected industrial areas

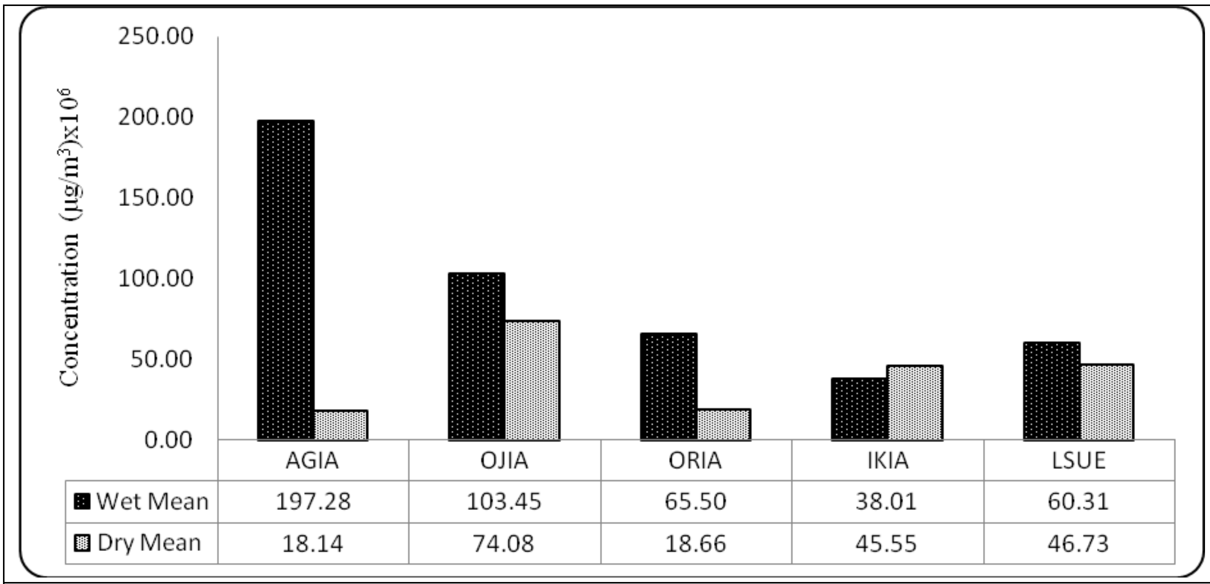
The deposition flux at Agidingbi industrial area ranges from 60.85 to 457.22 g/m^2.month in the wet season. The highest deposition flux was found at AGIA2 while the lowest was at AGIA1. The deposition flux ranges from 5.13 to 39.73 g/m^2.month in the dry season with the highest at AGIA2 and the lowest at AGIA1. Industrial activities here are food processing, bottling and casting. The highest deposition flux obtained in the wet season was higher than the highest deposition flux obtained in the dry season though positioned at the same sampling point.

The ranges of 28.31 to 234.534 g/m^2.month deposition flux were found at Ojota Industrial Area. The highest deposition flux of (234.54 g/m^2.month) was found at OJIA3 while OJIA2 has the lowest deposition flux of (28.31 g/m^2.month). The highest in the dry season whose deposition flux range from 57.19 to 96.37 g/m^2.month was found at OJIA3 with (96.37 g/m^2.month), while the lowest (57.19 g/m^2.month) was at OJIA2. The highest deposition flux obtained in the wet season was higher than the highest deposition flux obtained in the dry season they are at the same sampling point. The activities in the area include leather-processing, casting, food processing and packaging.

The deposition flux of the particulates collected at Oregun Industrial Area (ORIA) range from 42.4952 to 82.18 g/m^2.month. The highest deposition flux were found at ORIA2 being (82.18 g/m^2.month) while the ORIA3 has the lowest deposition flux (42.50 g/m^2.month). The deposition flux for the dry season ranges 15.27 to 24.83 g/m^2.month. The highest (24.83 g/m^2.month) was at ORIA2 while the lowest (15.27 g/m^2.month) was at ORIA3. The activities in and around this industrial area includes packaging, brewing, painting, dyeing, bottling and food processing. The highest deposition flux obtained in the wet season was higher than the highest deposition flux obtained in the dry season they are at the same sampling point.

The deposition flux of the particulates collected at Ikeja Industrial Area (IKIA) ranges from 27.40 to 58.03 g/m^2.month. Deposition flux of (58.03 g/m^2.month) was found to be the highest at IKIA3 while the lowest deposition flux of (27.37 g/m^2.month) was found at IKIA1. The ranges of deposition fluxes in the dry season were from 42.51 to 49.48 g/m^2.month. The highest (49.48 g/m^2.month) was at IKIA3 while the lowest (42.51 g/m^2.month) was found at IKIA1. The highest deposition flux obtained in the wet season was higher than the highest deposition flux obtained in the dry season they are at the same sampling point. Activities in this area include food processing, leather processing, packaging, paint production, purification and chemical processing.

The control experiment was carried out at the Lagos State University Epe (LSUE). The deposition flux collected was between 57.65 g/m^2.month and 62.96 g/m^2.month respectively. Only two gauges were planted. The highest being (62.96 g/m^2.month) was found at LSUE1 while the lowest was found at LSUE2 with a value of (57.65 g/m^2.month). The deposition flux in the dry season has the highest (51.06 g/m^2.month) at LSUE1 while the lowest (42.39 g/m^2.month) was at LSUE2. The highest deposition flux obtained in the wet season was higher than the highest deposition flux obtained in the dry season they are at the same sampling point and the activity around there are mainly academic. However, the average deposition fluxes (Fig. 2) of the selected industrial area of Ikeja revealed higher fluxes in the wet season except for IKIA. The reason for these higher fluxes could be due to washing down of the particles in the wet season compared to the dry season.

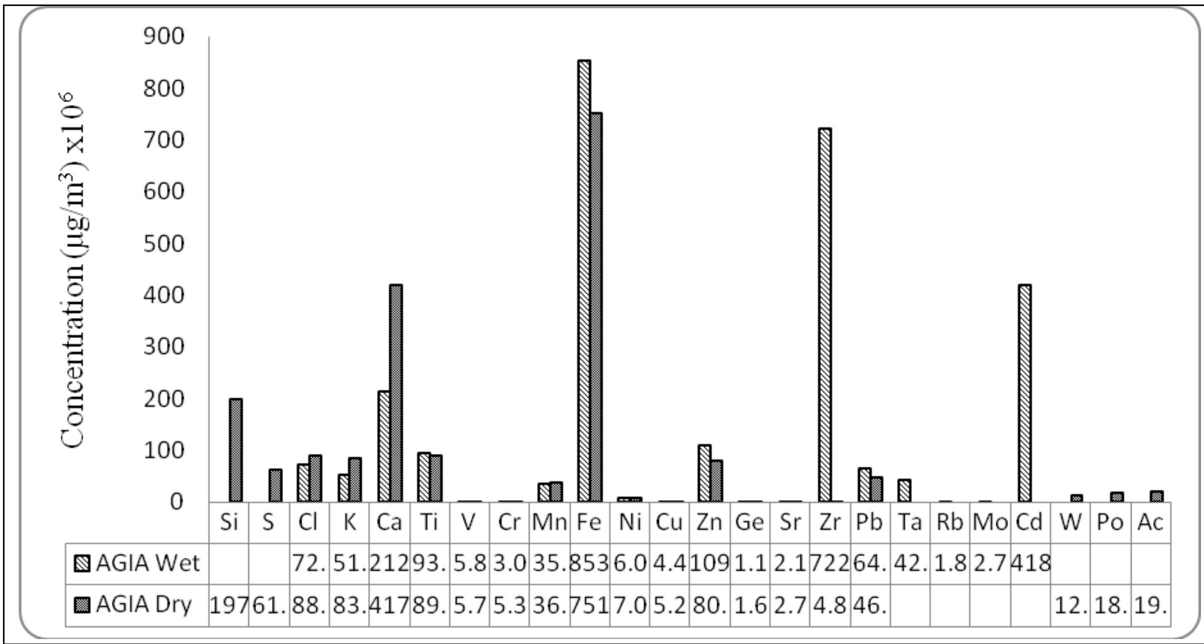


	AGIA	OJIA	ORIA	IKIA	LSUE
■ Wet Mean	197.28	103.45	65.50	38.01	60.31
▨ Dry Mean	18.14	74.08	18.66	45.55	46.73

Figure. 2: Average Deposition Fluxes of the Selected Industrial Area within Ikeja.

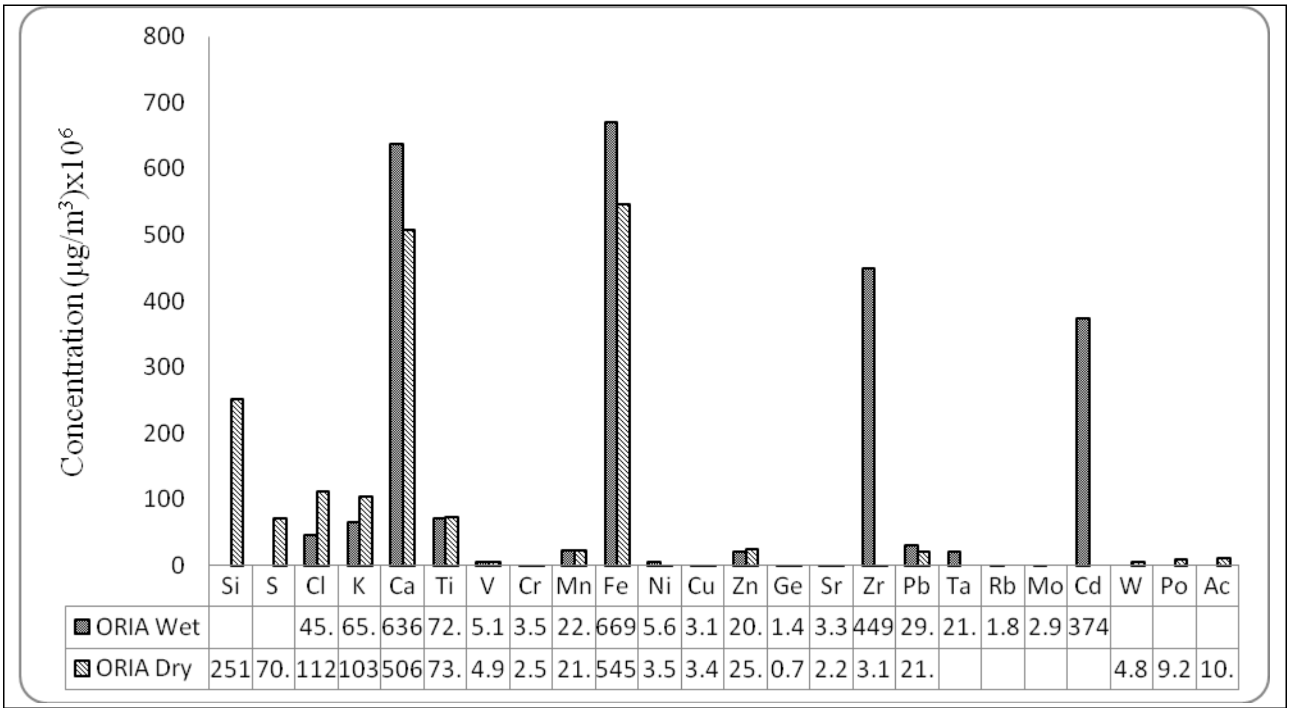
3.2 Characterization of the deposition samples for wet and dry season

The particulate matter obtained at the sampling spots were pooled together and then characterized, and elements such as Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Ge, As, Sr, Zr, Pb, Kr, Ta, Rb, Mo and Cd in the wet season were revealed. The first sixteen of these heavy metals were characterized again in the dry season with addition of Si, S, W, Po and Ac. The concentrations of the elements at the selected sampling industrial areas are discussed. Figures 3 to 6 showed that the concentrations of these elements in ambient air in the selected industrial area during the study periods. Among the analysed heavy metal concentrations, Fe showed the highest concentrations followed by Ca and Zr. Higher concentrations in Cd and Si could be due to the combine effects of industrial emission and vehicle exhaust from traffic areas. Since the units of the concentration were in µg/m^3, they were compared with The United State Environmental Protection Agency (USEPA) and the World Health Organization (WHO) who have respectively set the limit to 35 µg/m^3 and 25 µg/m^{3}as standards. Very high concentration of Si, Ca, Fe, Zn, Zr, and Cd were observed in all the locations. The high Cd concentration indicates the ubiquity of this toxic metal in the environment and shows that the areas are cadmium polluted. According to Federal Environmental Protection Agency (1988), World health Organization (2000), the recommended atmospheric limits for Cd are 0.003mg/l and 0.02mg/l respectively. Although, anthropogenic activities might be the reason for the result obtained in this study. All characterized values are higher than the standards and the study reported elsewhere (Gitari *et al.,* 2010; Kothai *et al.,* 2011; Fatma *et al.,* 2012)



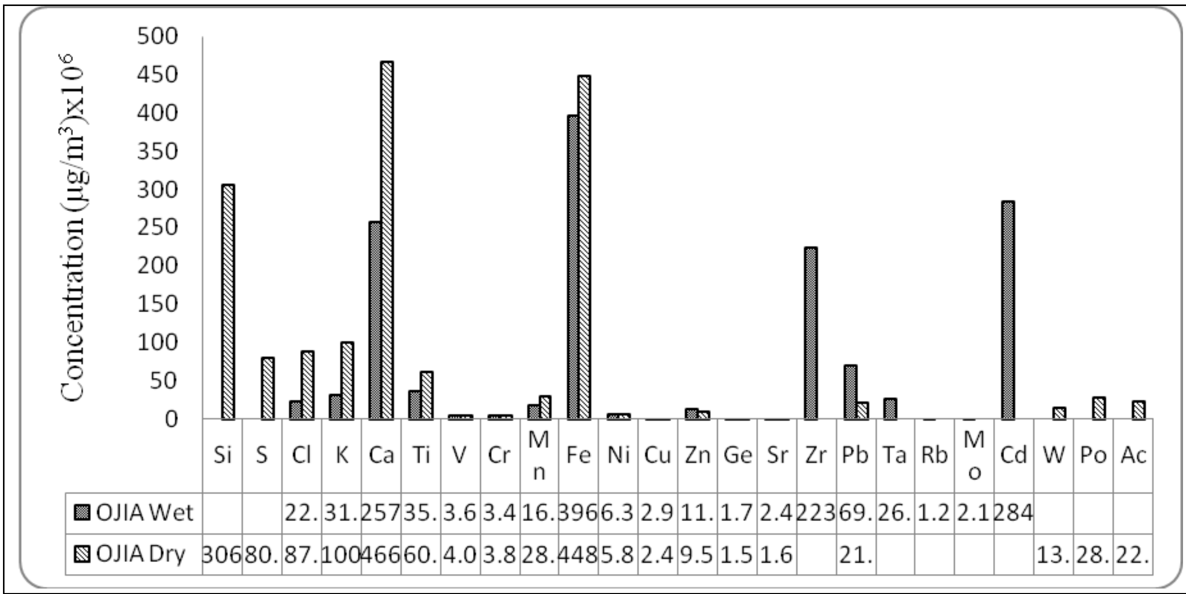
	Si	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Ge	Sr	Zr	Pb	Ta	Rb	Mo	Cd	W	Po	Ac
▧ AGIA Wet			72.	51.	212	93.	5.8	3.0	35.	853	6.0	4.4	109	1.1	2.1	722	64.	42.	1.8	2.7	418			
▩ AGIA Dry	197	61.	88.	83.	417	89.	5.7	5.3	36.	751	7.0	5.2	80.	1.6	2.7	4.8	46.					12.	18.	19.

Figure 3: Characterized elements at Agidingbi Industrial Area



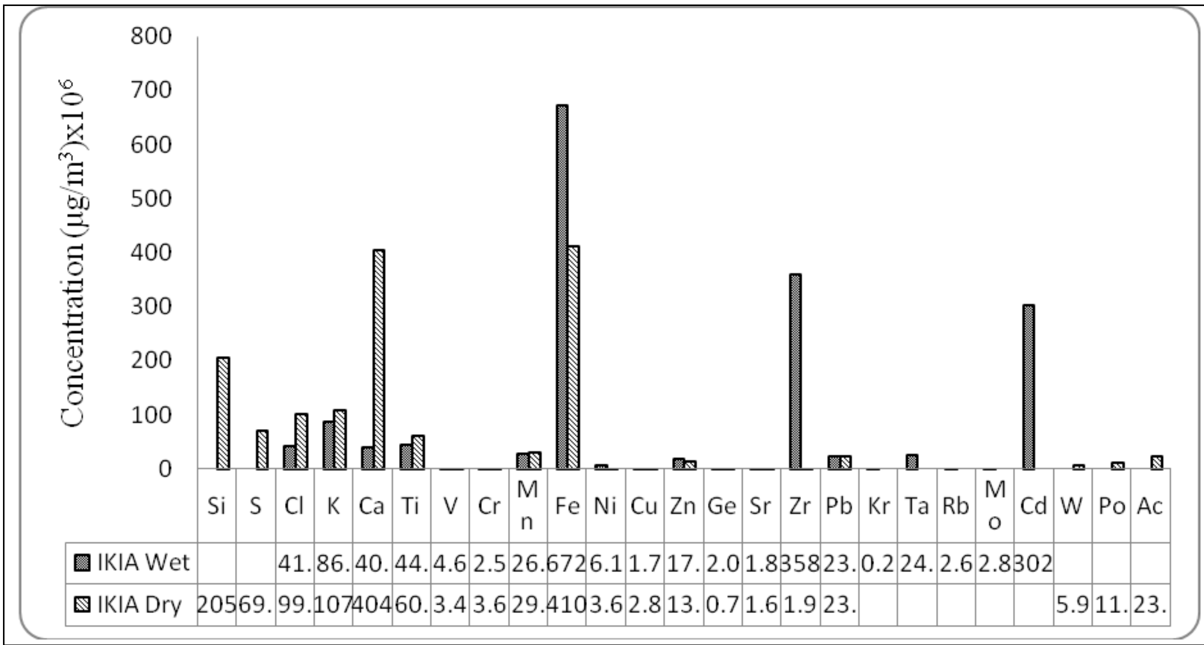
	Si	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Ge	Sr	Zr	Pb	Ta	Rb	Mo	Cd	W	Po	Ac
▩ ORIA Wet			45.	65.	636	72.	5.1	3.5	22.	669	5.6	3.1	20.	1.4	3.3	449	29.	21.	1.8	2.9	374			
▧ ORIA Dry	251	70.	112	103	506	73.	4.9	2.5	21.	545	3.5	3.4	25.	0.7	2.2	3.1	21.					4.8	9.2	10.

Figure 4: Characterized elements at Oregun Industrial Area



	Si	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Ge	Sr	Zr	Pb	Ta	Rb	Mo	Cd	W	Po	Ac
▩ OJIA Wet			22.	31.	257	35.	3.6	3.4	16.	396	6.3	2.9	11.	1.7	2.4	223	69.	26.	1.2	2.1	284			
▧ OJIA Dry	306	80.	87.	100	466	60.	4.0	3.8	28.	448	5.8	2.4	9.5	1.5	1.6		21.					13.	28.	22.

Figure 5: Characterized elements at Ojota Industrial Area



	Si	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Ge	Sr	Zr	Pb	Kr	Ta	Rb	Mo	Cd	W	Po	Ac
▩ IKIA Wet			41.	86.	40.	44.	4.6	2.5	26.	672	6.1	1.7	17.	2.0	1.8	358	23.	0.2	24.	2.6	2.8	302			
▧ IKIA Dry	205	69.	99.	107	404	60.	3.4	3.6	29.	410	3.6	2.8	13.	0.7	1.6	1.9	23.						5.9	11.	23.

Figure 6: Characterized elements at Ikeja Industrial Area

3.3 ELEMENTAL RATIO

The Iron elemental ratio was determined as shown in Table 1. Fe had the highest value across the selected industrial areas of Ikeja and it was used as the marker element to determine the elemental ratio. It was observed that only three (Si, S and Ca) elements have their ratio values above the 1.00 which suggest the emission of elements. Ca was suggested to be emitted in the dry season at OJIA and in the wet season at ORIA respectively. Also, Si, S and Ca were suggested to be emitted at IKIA in the dry season. The ratio values of all other elements apart from the three earlier reported were lower than 1.00 hence, suggesting the emission of Fe.

Table 1: Iron Elemental ratio for the Characterized Elements in the Wet and dry seasons

	Agidingbi		**Ojota**		**Oregun**		**Ikeja**	
Elements	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry
Si	Nil	0.362	Nil	0.770	Nil	0.466	Nil	2.235
S	Nil	0.093	Nil	0.191	Nil	0.145	Nil	1.501
Cl	0.086	0.129	0.063	0.206	0.068	0.208	0.064	0.814
K	0.060	0.131	0.081	0.233	0.105	0.191	0.129	0.937
Ca	0.251	0.667	0.568	1.268	1.359	0.935	0.060	3.885
Ti	0.109	0.121	0.095	0.131	0.106	0.137	0.064	0.448
V	0.007	0.007	0.009	0.009	0.008	0.009	0.007	0.023
Cr	0.004	0.008	0.008	0.010	0.006	0.005	0.004	0.037
Mn	0.041	0.046	0.044	0.060	0.034	0.040	0.039	0.275
Fe	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
Ni	0.007	0.010	0.019	0.014	0.008	0.007	0.009	0.031
Cu	0.005	0.007	0.008	0.005	0.005	0.006	0.002	0.027
Zn	0.129	0.101	0.033	0.020	0.029	0.045	0.026	0.116
Ge	0.001	0.002	0.005	0.004	0.002	0.002	0.003	0.005
Sr	0.003	0.004	0.006	0.003	0.006	0.004	0.003	0.015
Zr	0.855	0.005	0.620	Nil	0.623	0.006	0.554	0.003
Pb	0.076	0.059	0.172	0.048	0.040	0.039	0.036	0.210
Kr	Nil	Nil	Nil	Nil	Nil	Nil	0.0003	Nil
Ta	0.051	Nil	0.079	Nil	0.032	Nil	0.034	Nil
Rb	0.002	Nil	0.004	Nil	0.003	Nil	0.004	Nil
Mo	0.003	Nil	0.006	Nil	0.004	Nil	0.004	Nil
Cd	0.495	Nil	0.771	Nil	0.594	Nil	0.455	Nil
W	Nil	0.018	Nil	0.034	Nil	0.009	Nil	0.059
Po	Nil	0.034	Nil	0.060	Nil	0.018	Nil	0.086
Ac	Nil	0.023	Nil	0.056	Nil	0.020	Nil	0.216

3.4 ENRICHMENT FACTOR

The analyzed elements can be divided into two major groups: earth crust elements tracer and anthropogenic tracers. Therefore, the separation of natural and anthropogenic components is one of the basic tasks of aerosol measurements. The Enrichment Factor (EF) traditionally used for separating crustal derived from anthropogenic components (Yuanxun *et al.*, 2006). In this study, Fe was used as a reference element to determine the EF with respect to crustal elements and the elemental concentration of the particulates obtained (Wu *et al.*, 2007). It is customary that when EF <10, this indicate that a large fraction of the element can be attributed to crustal derived tracemetal sources in the atmosphere NEEs and when EF >10, it indicate that a large fraction of the element can be attributed to non crustal or anthropogenic sources trace metal in the atmosphere AEES (Cheng *etal.*, 2005). This study shows that sources of Cl, Zn, Zr, Si, S and W at AGIA are anthopogenic in both the wet and dry seasons. At OJIA, the sources of Cl, Ni, Zn, Zr, Cd, SI, S and W are anthropogenic also in the wet and dry seasons. The sources of Cl, Zn, Zr, Si, S, and W are also anthropogenic at ORIA while the sources of Cl, Zn, Zr, Si, S, V, Cr, Mn, Ni, Cu and W area anthropogenic as well in the wet and dry season respectively. The enriched elements in the particulates as reported were relatively volatile elements which could be transported from industrial to residential and urban areas. Other elements have their EF < 10 which indicates that they are crutal derive elements. The details of these are as shown in Table 2.

Table 2: Enrichment Factors for the Characterized Elements in the Wet and dry seasons

	Agidingbi		**Ojota**		**Oregun**		**Ikeja**	
Elements	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry
Si	Nil	1449.67	Nil	3079.52	Nil	1864.69	Nil	8940.93
S	Nil	35.23	Nil	72.34	Nil	54.84	Nil	568.65
Cl	58.83	87.96	42.90	140.73	46.49	141.76	43.55	556.24
K	0.23	0.51	0.31	0.90	0.41	0.74	0.50	3.62
Ca	0.48	1.27	1.08	2.41	2.58	1.77	0.11	7.38
Ti	1.26	1.40	1.10	1.51	1.22	1.58	0.74	5.18
V	3.12	3.40	4.32	4.11	3.55	4.20	3.12	10.73
Cr	2.16	4.93	4.76	5.79	3.64	2.89	2.25	22.36
Mn	2.49	2.80	2.64	3.60	2.04	2.42	2.34	16.60
Fe	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Ni	5.21	6.78	13.46	9.97	5.87	4.81	6.50	22.13
Cu	4.58	6.51	7.26	4.71	4.22	5.56	2.10	23.74
Zn	89.04	69.94	22.84	13.82	20.00	31.49	17.90	80.03
Ge	0.00	0.01	0.02	0.01	0.01	0.00	0.01	0.01
Sr	0.24	0.37	0.57	0.32	0.55	0.38	0.30	1.36
Zr	179.44	1.18	130.16	Nil	130.74	1.22	116.30	0.70
Pb	0.01	0.01	0.02	0.01	0.00	0.00	0.00	0.03
Ta	0.04	Nil	0.07	Nil	0.03	Nil	0.00	Nil
Rb	0.90	Nil	1.46	Nil	1.11	Nil	0.00	Nil
Mo	0.01	Nil	0.01	Nil	0.01	Nil	0.21	Nil
Cd	6.97	Nil	10.85	Nil	8.37	Nil	0.00	Nil
W	Nil	206.45	Nil	393.01	Nil	100.87	Nil	676.05

4 CONCLUSIONS

The measurement of the wet and dry deposition samples concentration elements were conducted at four selected industrial areas of Ikeja, lagos, Nigeria. The results showed that the concentrations of the studied heavy metals in both seasons deposition were high with higher anthropogenic activities. Particulate Matter was collected at selected industrial area of Ikeja to know the impact of their emissions in the ambient air. EDXRF technique has been used to determine the concentration of the elements in the filter samples containing only few hundred µg of total dust load.

In the wet season deposition, average metal concentrations were found to be higher in the selected industrial area except at IKIA. Elemental ratio of the characterized samples of the particulate matter revealed that only Ca, Si and S were emitted during the wet and dry seasons. Concentrations of crustal and sea salt derived elements found in high levels. The EF analysis showed very high enrichment for elements Si, S, Cl, V, Cr, Mn, Ni, Cu, Zn, Zr, Cd and W, and were found to be enriched in the samples which indicate their nature of origin could be from any anthropogenic sources; Industrial, Vehicular emission and Fuel and oil combustion.

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DESULPHURIZATION OF DIESEL USING ACTIVATED CARBON PRODUCED FROM COCONUT SHELL

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ABSTRACT

The presence of sulphur in fuels produces SO_x emissions after combustion. These emissions decrease the air quality with negative impact on the environment and public health. Unfortunately, relatively high levels of sulphur are present in both locally processed and imported diesel in Nigeria due to the natural presence of sulphur in crude oil. Efforts to reduce this content during processing is quite cost intensive. This necessitates the need for a cheaper but efficient method to reduce, if not totally eliminate the sulphur in the processed fuel prior to its use. In this study, Coconut shells were activated and used as adsorbents for sulphur removal from the fuel, via an adsorption process. Results obtained with coconut shell were compared with using imported activated carbon. The efficiency of both adsorbents were nearly at per. Adsorption isotherms were plotted and it was found that the Linear isotherm best described the adsorption of sulphur using activated coconut shell – with an R^2 value of 0.7118 as against that 0.6457 of Langmiur isotherm and 0.663 of Freundlich isotherms respectively. Using Coconut shell activated carbon will save our Nation some foreign currency in the importation of activated carbon for desulphurization and similar uses.

Keywords: desulphurization; oxides of sulphur; optimal conditions; activated; coconut shell,

1. INTRODUCTION

Diesel is a C_{11} – C_{18} fraction obtained from the distillation of crude oil. It has a boiling point of 200 - 300^0C. It is the world's second most widely used fuel and finds use as fuel for road vehicles, heavy machines and trains. The presence of sulphur in diesel is undesirable because during combustion, it gives off oxides of sulphur, SO_x (Adeyi and Aberuagba, 2012) which are injurious to plant and animal life. Asthma, respiratory diseases are some of the symptoms associated with sulphur oxides in the air and atmosphere.

During processing, compounds of sulphur in diesel cause corrosion in piping and equipment. It can also, poison the catalyst in the processing units. When sulphur dioxide combines with water and air, it forms sulfuric acid, which is the main component of acid rain (Adeyil et al, 2014). Acid rain can cause deforestation, acidify waterways to the detriment of aquatic life and corrode building materials and paints. Therefore, low sulphur fuels will both benefit health and climate.

Unfortunately, sulphur present in crude vary in amount and this presents itself in the different fractions. In Nigeria, the maximum allowable sulphur content is 500 ppm but efforts are underway to reduce it to less than 150 ppm by 2019. This is still quite high compared to other countries like the US of 10 ppm (Selvavathi et al, 2009)

Diesels of sulphur content that deviate from standard are quite common in countries where fuels are imported. Cost of refinery capacity, cost to consumers, lack of political prioritization of low sulphur fuels have been identified as barriers to low sulphur fuel adoption in countries like Nigeria, Ethiopia and Mozambique (CCAC-UNEP, 2016).

Different methods and procedures have been used to reduce the sulphur content of diesel during the refining process. These include desulphurization and desalting methods. However, high temperatures are required in these processes and therefore not cost effective. Therefore, it becomes necessary to desulphurize the fuels prior to its use. Neem leaves have been used to reduce sulphur content in diesel by more than 50% at optimal conditions of 3.5 hours, dosage of 2g in 10ml of diesel and at a temperature of 20^oC (Deware et al, 2015) different carbon materials have been shown to exhibit significantly different adsorption capacities and selectivities for sulphur removal (Selvavathi et al, 2009), in India, sulphur was also reduced by more than

50% using activated carbon from Coconut shell and optimal conditions were found to be a contact time of 4 hours and a dosage of 20g (Gawande and Kaware, 2017) the adsorption desulphurization of diesel was also studied using granular activated carbon and an efficiency of 20.94% at room temperature was obtained (Al Zubaidi et al 2015). Coconut shell was chosen because they are readily available and very cheap, if money is to be paid at all and have shown good adsorption properties. They are usually burnt in open pits to reduce their menace as waste, while a very small fraction is burnt as fuel for domestic use. This research, therefore, attempts to convert the coconut shell waste to a useful raw material in the desulphurization of diesel. In this work, activated carbon from locally obtained coconut shell was used to desulphurize diesel. Kinetic studies were also carried out in order to determine the optimal conditions for efficient desulphurization.

Activated carbon is known to be an effective adsorbent material due to its large number of cavernous pores. These pores provide a large surface area relative to the size of the actual carbon particle and its visible exterior surface. An approximate ratio is 1 gram = 100 m^2 of surface area (Hoehn, 2006).

Some carbons have a mesopore (20 Å to 50 Å, or 2 to 5 nm) structure which adsorbs medium size molecules, such as the Methylene blue dye, whose adsorption is reported in g/100g (range 11–28 g/100g).

This study converts coconut shell waste to activated carbon, characterizes the activated carbon obtained from the coconut shell, uses the activated coconut shell for sulphur removal in diesel, compare desulphurized fuels of activated coconut shell and the imported activated carbon.

The results of this research promises to impact on the importation of activated carbon as the process of activation is very cost effective.

2. MATERIALS AND METHODS

2.1 Materials

Diesel was purchased from the Fuel Station, (Total) in Epe (Lagos State, Nigeria).

Coconut shells were obtained from Eleko Coconut farm Epe (Lagos State, Nigeria)

Sulphur content in diesel was determined using ASTM D5453 method.

2.2 Methods:

2.2.1 Preparation of the activated carbon (carbonization stage)

The washed coconut shell waste was put in a tray and allowed to stand under the sun for 2 days until it became hard and dry. The shell was cracked into smaller sizes and further crushed with a crusher to yet smaller sizes between 1-4mm in size. 500g of the crushed shell was weighed out and placed in a metal pan. The metal pan was put in a furnace. The furnace was operated initially at 150°C for 1 hour. Gradually the temperature was increased to 200°C for 1hour. Further heating was done at 350°C for 30 mins. Finally, the furnace temperature was increased to 600°C for 30 mins. The hot charcoal obtained after heating was cooled using cold distilled water. Thereafter, it was dried in the oven at 105°C for 2 hours.

2.2.2 Activation stage

136.286g of zinc chloride ($ZnCl_2$) was dissolved in 1000cm^3 of distilled water to get 1M of zinc chloride ($ZnCl_2$) solution which was used to activate the crushed carbonized coconut shell. 250g of carbonized coconut shell was weighed and impregnated with 500ml of zinc chloride ($ZnCl_2$) activator (soak the 250g carbonized coconut shell inside 500ml of zinc chloride ($ZnCl_2$) solution).It was stirred and allowed to rest for 24 hours after which it was drained and dried in the oven at 105^oC for 3 hours. The result obtained was poured back into a metal pan and placed in a furnace. It was allowed to dry at a very high temperature of 1000°C for 2 hours. After 2 hours, the hot activated carbon was washed with distilled water to remove traces of the activating chemical. The wet activated carbon was dried in the oven at 105°C for another 2 hours. After drying, the activated carbon was weighed and milled to produce fine particles. The fine particles were packaged in glass jars and placed in a desiccators to prevent moisture absorption. The percentage yield was thereafter calculated or determined.

2.2.3 Characterization of the activated carbon

2.2.3.1 pH value

5g of the activated carbon was weighed out and dissolved in 50ml of distilled water. The resulted mixture was heated and stirred adequately for 1-3 mins for proper dilution of the activated carbon. The clear solution was filtered out and its pH is determined using a digital pH meter.

2.2.3.2 Percentage Yield

The percentage yield of activated carbon is determined by dividing the mass of activated carbon produced by the mass of the raw material used multiply by 100.

$$\%\,Yield = \frac{\text{mass of activated carbon produc}}{\text{mass of raw materials used}} \quad (1)$$

2.2.3.3 Ash Content

The ash content was measured by taking 5g of activated carbon produced from coconut shell waste and 5g of imported activated carbon was put alongside (each in different crucibles) were placed in the furnace at 650°C for 2 hours. The ash produced from each process was collected and weighed.

2.2.3.4 Adsorptive Property

The decolourizing capacity of the activated carbon produced from coconut shell waste and the reference activated carbon was determined by adding 2.5g of the activated carbon to 50ml of 100g/l brown sugar solution. The solution was observed for 30 mins for any colour change. Subsequently,0.5g of the activated carbon was added to the solution and observed for 30mins. This was repeated until there was decolourization. The cumulative quantity of activated carbon added to effect the decolourization was recorded as Wc for different colour presentation of the solution, that is, dark brown, light brown, pale brown, and colourless. The procedure was repeated 3 times for accuracy. The adsorptive capacity which is also the decolourization capacity (Qc) of the activated carbon and is determined using the formular:

$$Q_c = W_s \div W_c \qquad (2)$$

Where Ws=quantity of brown sugar decolorized (standard)

Wc=quantity of activated carbon required for the decolourization.

2.2.4 Desulphurization of the Diesel Fuel

This experiment was carried out by setting up 2 burettes with cotton wool loaded in the base of the $100cm^3$ high, 1.8cm wide column to give support to the imported activated carbon and the second column which is also loaded with cotton wool is filled with activated carbon produced from Coconut shell. Then, 100ml of the diesel fuel of the sample is filled into each burette respectively. The experiment proceeded till the entire diesel in the burette passed through under 16 hours.

3 RESULTS AND DISCUSSION

3.1 Tables

Table 1 Activated Carbon Characteristics

Parameters	activated carbon from coconut	reference activated carbon
pH	7.2	7.0
Percentage yield	21.06%	
Ash content	3.2	2.6%
Adsorptive properties	0.35	0.37
Average particulate size	15.58µm	5-50µm
Moisture content	10%	13.3%
Pore volume	2.35cm3	2.31 cm3
Porosity	0.027g/ cm3	0.022g/ cm3
Iodine number	546mg/g	600-1100mg/g

Table 2.Batch Adsorption Equilibrium by Coconut Shell Activated Carbon at Temp 26 °C								
S/N	**Activated Carbon Dosage g/100ml**	**Activated Carbon Dosage g/l M**	**Surphur mg/l Ce**	**X mg/l**	**qe x/M mg/g**	**log Ce**	**Log qe**	**Ce/qe**
1	0	0	356	0	-	2.551		
2	1	10	355	1	0.1	2.550	-1.000	3550.000
3	2	20	353	3	0.15	2.548	-0.824	2353.333
4	4	40	350	6	0.15	2.544	-0.824	2333.333
5	7	70	345	11	0.157	2.538	-0.804	2197.452
6	9	90	340	16	0.177	2.531	-0.752	1920.904
7	12	120	344	22	0.183	2.537	-0.738	1879.781

3.2 Figures

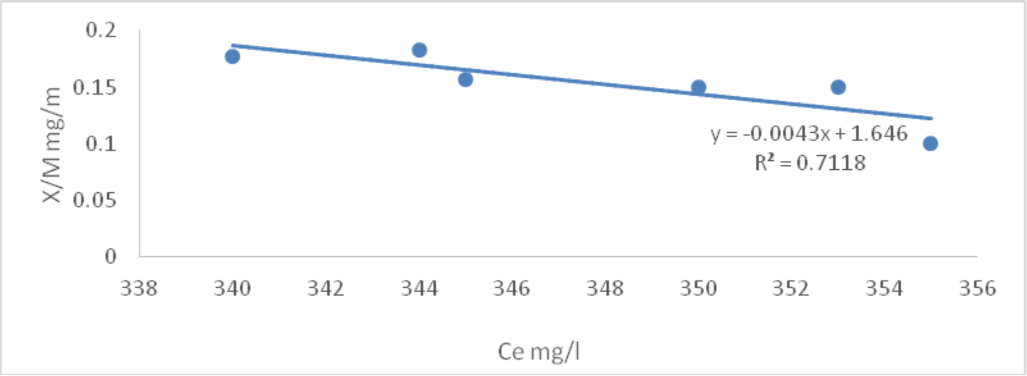

Figure 1: Linear Isotherm

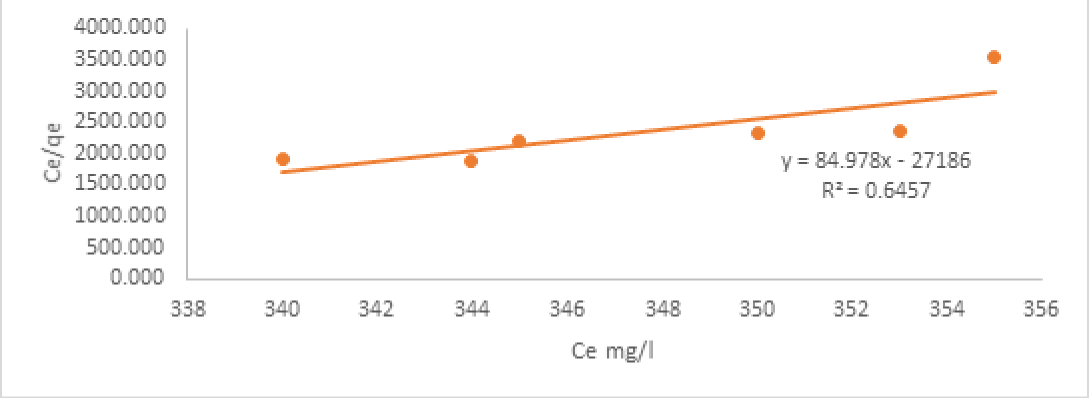

Figure2: Langmuir Isotherm

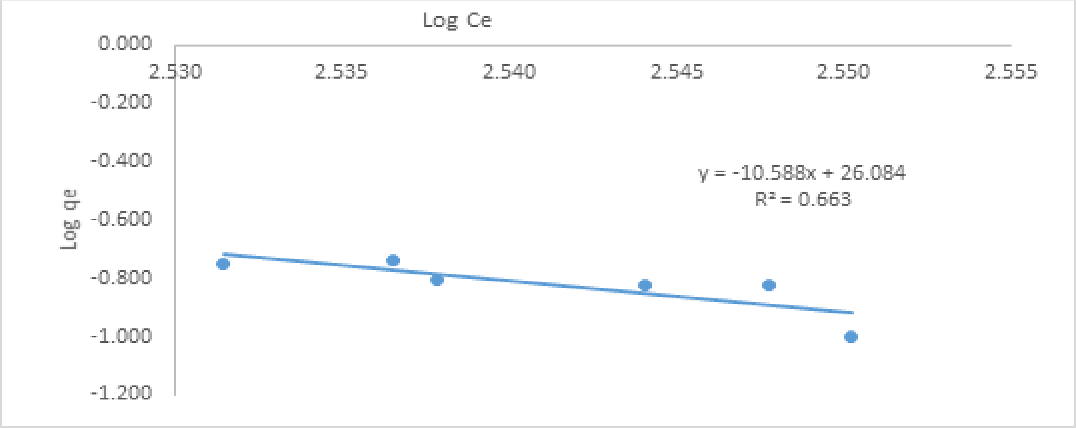

Figure 3: Freundlich Isotherm

The optimum condition for carbonization and activation was 600 °C and 1000 °C respectively. From the table of activated carbon characteristics, it is observed that there is only a 0.2 difference in the pH value of coconut activated carbon and the reference activated carbon and from literature; the pH value of activated carbon is 7 which is neutral.

From Table 1, it is observed that coconut shell gives a low yield of activated carbon. From literature, it is given that a low yield in the production of activated carbon corresponds to a higher degree of activation. Thus low yield record is equated to high degree of activated coconut shell yield abrasion resistance granules of carbon. Also, it is observed that the ash content obtained for coconut shell activated carbon is 3.2% and that of the imported activated carbon to be 2.6%. From text, the specified ash content for activated carbon 3.0%.

From Table 1and Figure 1, it was observed that coconut activated carbon decolorize brown sugar completely. The decolorization capacity of the imported activated carbon was 0.37 while that of coconut activated Carbon was 0.35. This means that coconut activated meet commercial requirement for the decolorization capacity of activated carbon. From Table 1, it is observed that coconut activated carbon has a very large pore volume of 2.35 cm^3. This is a very good value obtained because it makes adsorption easier. And the porosity obtained is 0.027g/ cm^3 which means that during adsorption, solids particles can’t pass easily.

From Table 1, it can be observed that the moisture content of the locally produced activated carbon is lesser than that of the imported activated carbon. Also, from Table1, it was observed that the coconut activated carbon has a large surface area. The value obtained for it was 546mg/g and from literature, the surface area of activated carbon is 600-1100mg/g.

The activated carbon produced was used for the desulphurization of diesel during which adsorption isotherm was used to describe the equilibrium relationship between adsorbent and adsorbate. This is usually the ratio between the quantity adsorbed and that remaining in solution at a fixed temperature at equilibrium.

The parameters in Table 2, values of Ce, the equilibrium concentration of sulphur, x/m, the amount of sulphur adsorbed per unit of adsorbent(mg/g) and other parameters required to plot the isotherms are shown. A curve of x/m vs Ce was plotted for the linear Isotherm as shown in Figure 1. Similarly, a graph of Ce/qe was plotted for Langmuir as shown in Figure 2 while values of log qe and log Ce was plotted for Freundlich isotherm as shown in Figure 3. The R^2 values were computed for the three types of isotherms. The results obtained showed that the three types of adsorption isotherm describes the desulphurization process but the Linear Isotherm best suits the adsorption, as used in this experiment.

4 CONCLUSIONS

This study shows that the activated carbon with developed pore structure and adsorption capacity obtained from coconut shell is effective in the desulphurization of diesel. Results show that the optimum condition for carbonization and activation were 600 and 1000 °C. The result also shows clearly that desulphurization of diesel can be done at room temperature and atmospheric pressure as against hydrodesulphurization which is carried out at elevated temperature and it is the common method used in the refineries.

The batch adsorption equilibrium data followed the Linear, Langmuir and Freundlich isotherms as shown by the value of R-squared for the three isotherms.

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7. APPENDIX

Table 3 Adsorptive Property of Coconut

Color	Run one	Run two	Run three	Average
Dark brown	3.5	3.5	3.4	3.5
Light brown	8.1	8.1	8.2	8.1
Pale brown	11.5	11.6	11.4	11.5
Colorless	14.2	14.3	14.4	14.3

Table 4 Adsorptive Property of Imported Activated Carbon

Color	Run one	Run two	Run three	Average
Dark brown	3.6	3.6	3.6	3.6
Light brown	7.5	7.6	7.6	7.6
Pale brown	11.2	11.0	11.1	11.1
Colorless	13.4	13.5	13.5	13.5

Table 5 Adsorptive Properties of Activated Carbon Samples

Activated carbon adsorbent	quantity of activated carbon required for decolorization of brown	Decolorization capacity of activated carbon adsorbent.
Coconut activated carbon	14.3	0.35
Reference activated carbon	13.5	0.37

A CHEMICAL ENGINEERING CURRICULUM - MEETING THE NIGERIAN NEED

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ABSTRACT

This paper is about the development of a Nigerian Chemical Engineering Curriculum of world class standards to train indigenous Chemical Engineers that will be instrumental to meeting the Chemical Engineering related needs of Nigeria. A brief history of the Nigerian Chemical Engineering undergraduate program is presented. The present state of the Curriculum was examined and compared with the Chemical Engineering Curricula of Universities with well-established Chemical Engineering Programs outside Nigeria. It was observed that about seventy-five (75) required courses are in the Nigerian Chemical Engineering Curriculum as against thirty-three (33) required courses in the foreign Curricula. Several needs of Nigeria that require the input of Chemical Engineers such as energy, job creation, agriculture etc. are discussed. Gaps in the Chemical Engineering Curriculum are succinctly presented and recommendations on how these gaps can be filled, such as; provision of options in Chemical Engineering, need for more focus on core areas, emphasis on entrepreneurship etc. are presented with a view of meeting the needs of Nigeria. The very needs for the Chemical Engineering Curriculum to not only be well developed but also well implemented is highlighted.

Keywords: *Curriculum, Chemical Engineering, entrepreneurship, Gaps, Needs*

1.0 INTRODUCTION

Chemical Engineering is a discipline that deals with the application of the basic sciences and technology in the design, operation and maintenance of equipment and processes for the large scale production, transformation and transportation of materials and energy to provide valuable goods and services. Such processes are the fundamental core of the Chemical, petroleum, iron and steel, pharmaceutical, and electronics industries. Along these lines, Chemical Engineering emphasizes fundamentals required to design, optimize, and operate Chemical processes as safely and efficiently as possible.

The role of Chemical Engineering in the development of any nation in this 21st century cannot be overemphasized. Chemical Engineering cuts across a wide spectrum of interconnected fields and disciplines needed for the industrialization and advancement of any 21st century civilization. These enormous responsibilities are within the capabilities of Chemical Engineers in meeting the Nigerian Needs if the Chemical Engineering Curriculum that seeks to expose the undergraduates of this noble discipline to the deep understanding of Engineering fundamentals, to enable them apply this knowledge to the management of complex systems with particular attention to the Chemical process and product industries, is updated to meet world-class standard. However, engineering education Curricula in Nigeria are not updated making them obsolete. The inadequacy in the Curriculum has made the nation to be weak in new technologies. Graduates of such obsolete Curricula can no longer handle new technologies and they often find it difficult to compete with their overseas counterparts.

Considering the present state of our beloved nation viz-a-viz the practice of the Chemical Engineering discipline for several decades in Nigeria, it is certainly not far-fetched to opine that the practice of Chemical Engineering in Nigeria is yet to deliver satisfactory dividends to the Nigerian state. Could this be, to an extent, attributable to gaps/defects in the present Chemical Engineering Curriculum in Nigeria as measured against world-class standards? If there are gaps, can they be filled and how do we go about remedying the situation? Thus this paper takes a look at the adequacy of the Nigerian Chemical Engineering Curriculum viz-a-viz the current and emerging expected needs of Nigeria.

2.0 THE NIGERIAN CHEMICAL ENGINEERING & ITS CURRICULUM

In order to have an accurate assessment of our present situation, we must understand where we are coming from, where we are going to and then we can attempt to assess our present location and possibly how to move onwards from our present location to the destination that we have envisioned.

2.1 Nigerian Chemical Engineering Undergraduate Program – An Historical Survey

In Nigeria, Chemical Engineering is a relatively young profession, dating back only to about the 1960s, when the first wave of Nigerian students graduated from Chemical Engineering schools in the United States and the United Kingdom. Even so, the profession was virtually unknown in Nigeria until the late 1960s, when several overseas-trained graduates returned to their home country (Dada et al 2013).

Nigeria started its domestic training of Chemical Engineers when the University of Ife (now Obafemi Awolowo University), introduced a course in Chemical technology in 1969. By 1972, the school had upgraded to a full Chemical Engineering program and consequently, graduated the first Nigeria - trained Chemical Engineers in 1973. Around that time, the University of Lagos and Ahmadu Bello University, in Zaria, also developed Chemical Engineering programs, producing their first graduates in 1976 and 1977, respectively (Dada et al, 2013).

The Student Industrial Work-Experience Scheme (SIWES) which started officially in 1974 was imbued in the Chemical Engineering Curriculum and now constitutes a requirement for the completion of the Chemical Engineering undergraduate program as specified by the National University Commission (NUC) and the Council for the Regulation of Engineering in Nigeria (COREN) (Mafe, 2018; NUC, 2014; COREN 2013).

2.2 The Present state of the Nigerian Chemical Engineering Curriculum

The Nigerian Chemical Engineering program has evolved over the years and presently is a five (5) years course at the University level comprising of nine (9) semesters of classroom learning and laboratory work. A period of six to nine months (6 - 9 months) distributed between the long sessional breaks and the entire 400L second semester is provided for Student Industrial Work-Experience Scheme (SIWES) as required by the NUC and COREN. (Mafe, 2018; NUC, 2014; COREN 2013; EUI, 2016; UNIBEN, 2015).

A semester in a typical Nigerian University comprises of 14 weeks of learning and 2 – 3 weeks of exams. The Chemical Engineering student is saddled with the task of learning and assimilating an average of about 8 - 9 usually voluminous courses in a semester and for the 400L first semester, they would need to offer about 10 to 12 courses comprising of about 9 heavy weight Chemical Engineering courses within 3 months in preparation for the SIWES programme.

The Curriculum comprises of about seventy-five (75) courses on the average comprising of about ten (10) practical courses.

The Curriculum covers the major core areas of Chemical Engineering such as Chemical reaction Engineering, Chemical Engineering design, transport phenomena, Biochemical Engineering, environmental Engineering, Engineering economics, software application in Chemical Engineering etc. (NUC, 2014; COREN 2013; EUI, 2016; UNIBEN, 2015) as well as the requisite foundational courses such General Chemistry, Mathematics, Physics etc. There are about twenty-five (25) general Engineering courses such as Engineer and society, Engineering mathematics I-IV, Engineering mechanics I & II, Engineering drawing I & II etc., in addition to seven (7) General studies courses (NUC, 2014).

The Chemical Engineering laboratory courses are available as from 300 Level and a total of 3 Chemical Engineering laboratory courses are provided for throughout the Chemical Engineering program and these laboratory courses are usually not linked with any specific area of Chemical Engineering but are designed to cut across all the various subject areas covered in each level.

As a requirement for obtaining a Bachelor’s degree in Chemical Engineering, the student is expected to undertake a Chemical Engineering research project and in some institutions, an additional Chemical Engineering design project.

2.3 A Comparison of Chemical Engineering Curricula

The Nigerian Chemical Engineering Curriculum as presented in the Benchmark Minimum Academic Standards (BMAS) of the National Universities Commission (NUC) is compared here with the Chemical Engineering Curriculum of YALE University, Manchester University and the University of Illinois; Universities in the United States of America (U.S.A) and the United Kingdom (U.K) with highly reputed Chemical Engineering programs.

2.3.1 Curricula of Foreign Universities

The Curricula of three foreign Universities namely; YALE University, Illinois University and Manchester University are compared with the Nigerian Chemical Engineering Curriculum.

The Chemical Engineering Curriculum of YALE University is presented contiguously with the Nigerian Chemical Engineering Curriculum in the Benchmark Minimum Academic Standards (BMAS) of the National Universities Commission (NUC) in Table 1 of the Appendix.

The Chemical Engineering program at YALE University requires 18 technical credits in addition to 9 prerequisite courses listed and 3 Engineering electives to a total of 30 courses for the undergraduate degree program (https://seas.yale.edu/departments/Chemical-and-environmental-Engineering/undergraduate-study-Chemical/undergraduate-curric 11/19/2018; http://catalog.yale.edu/ycps/subjects-of-instruction/Chemical-Engineering/Chemical-Engineering.pdf 2018). A typical schedule of required courses for the Chemical Engineering program of YALE University is presented in table 1 of the Appendix

The Chemical Engineering Curricula of Illinois University and Manchester University are also presented in Tables 2 and 3 of the Appendix.

2.3.2 Let Us Compare & Contrast

Comparing the Chemical Engineering Curricula of Yale University, Manchester University and the University of Illinois with the typical Nigerian Curriculum for Chemical Engineering as present in the NUC BMAS document, we find the following;

- The Nigerian Chemical Engineering Curriculum comprises about 75 courses which is more than double the number of courses, required (which is about 33 courses) in the foreign universities considered above. This may be clear indicators that there may be an assortment of borrowed and general courses that are not needed which have been infused into the Nigerian Chemical Engineering Curriculum. The effect of this large number of courses required to complete the Nigerian Chemical Engineering program is that there would be insufficient attention and emphasis paid on the specific course components of Chemical Engineering discipline.
- The courses taken in the foreign programs are core Chemical Engineering courses with necessary background courses in the physical sciences and only a few other general courses
- There is good emphasis on practical/laboratory work in both Curricula; however, the foreign Curricula have their laboratory courses tailor made to fit specific aspects of the various Chemical Engineering areas.

3.0 THE NIGERIAN NEEDS

The Refineries & Petrochemical Industry: There is need for functional refineries that are designed, built, operated and maintained by indigenous Chemical Engineers. It is indeed highly bewildering to find that a nation such as Nigeria exports her raw crude products in very large amounts only to import the refined products for use at relatively high costs. Our crude oil reserves are rapidly depleting with production at about 2 million bpd and our national purse is not growing commensurately with the amount of black gold that leaves our ground. This anomaly is one that needs urgent rectification and although, this problem is hydra-headed with the root being corruption at all levels of government and society, the Nigerian Chemical Engineers has a great role to play in remedying the situation.

Natural gas flaring has to be curbed and our natural gas reserves need to be harnessed to provide better economic value. About 30% of the total natural gas production of 6.5 billion scf/d is currently flared in the oilfields, primarily because there is insufficient manufacturing infrastructure to use it, as well as the sluggishness of the IOCs to comply with the Nigerian government's gas utilization and monetization policy. Of the 4.5 billion scf/d gainfully utilized, about 3.0 billion scf/d (67%) is liquefied for export in an integrated LNG plant. Another 0.5 billion scf/d is exported as pipeline gas to the neighboring countries of Benin, Togo, and Ghana. Only 1.0 billion scf/d (22%) is used domestically, out of which about 0.8 billion scf/d goes to power generation (Dada, 2013; Oniwon, 2010).

The Petrochemical industry also needs to be revitalized as it serves to provide feedstock to a large fraction of the manufacturing industry. If the manufacturing industry in Nigeria will receive a significant boost, the Petrochemical industry has to be up and running.

Energy: The poor level of energy generation and distribution has been a major problem and hindrance to the industrial development of Nigeria. Many international companies such as Michelin and Dunlop have packed out of Nigeria as a result of this (Ogedegbe, 2008). This again calls for the Nigerian Chemical Engineer to contribute his expertise in providing and helping to implement lasting solutions to this. Presently, the trend of power generation is shifting rapidly from use of fossil fuels in generating power to renewable energy sources such as biofuels.

Agriculture: In view of the collective attempts to diversify our economy and reduce our oil-dependency, we must of necessity look to develop other sectors of our economy. One of these key sectors of the economy that we must pay keen attention to is the agricultural sector. Chemical Engineering has a role to play in the provision of readily available and affordable locally manufactured fertilizers, pesticides, herbicides etc. as well as in the design and operation of equipment and processes for the long-term preservation of our perishable goods. Furthermore, our farm produce have to be further processed to produce value added products of high quality which can serve the local market and can also be exported to generate revenue.

Iron and Steel: Nigeria needs her iron and steel industry to come alive again if it is to experience the sort of industrialization that we desire. Also, there has to be much more emphasis on special steels and alloy steels so as to enable the Nigerian iron and steel products compete favourably with those from anywhere else in the world.

Unemployment: The establishment of small and medium enterprises (SME) is highly recommended to curb the menace of unemployment especially amongst the Nigerian youths. The Nigerian Chemical Engineering Curriculum has to be designed in such a way that the average graduate is armed with the requisite knowledge to set up an SME in his own area of interest in the Chemical Engineering discipline.

These challenges are indeed enormous, multi-faceted and intricately laden with below the surface dynamics and complexities, with corruption at all levels of government and societies being the bane of Nigeria, the solutions to these problems do not lie solely or even majorly with the Nigerian Chemical Engineer or the Chemical Engineering Curriculum.

However, we cannot deny that we have a great role to play in ameliorating these ailments. One sure way to play our part is to design a Chemical Engineering Curriculum that is discipline concentrate rather than Faculty based to produce graduates that can compete favourably with their counterparts from all over the world and at the same time, a Curriculum that is tailor-made to equip the average Chemical Engineer with the requisite skills and knowledge that will enable him contribute his quota towards addressing the Nigerian needs.

4.0 IDENTIFYING & BRIDGING THE GAPS – MEETING THE NEEDS

4.1 The gaps in the Chemical Engineering Curriculum

The Biology Deficiency

Chemical Engineering is a unique discipline amongst other Engineering disciplines for a number of reasons one of which is the way Chemical Engineering draws from a very wide spectrum of science subjects in a way that other Engineering disciplines do not. One of such very pivotal science subjects is Biology. Biology has however not been given the necessary attention in the Chemical Engineering Curriculum. Presently, Biology is not a compulsory entry requirement for admission into the Chemical Engineering Program in our Universities. Furthermore, there is no first year course on biology in the present Chemical Engineering Curriculum. How are our students expected to fair excellently in courses on Biochemical Engineering, Bio-molecular Engineering, Bio-technology, Chemical Reaction Engineering etc. without a sound and verified proficiency in biology?

Insufficient Industry Application Focused Courses: The Curriculum that guides Chemical Engineering programmes in Nigeria consists of the fundamental knowledge of mathematics, natural sciences, technology, a large assortment of general Engineering courses, core Chemical Engineering courses and only a few application courses. This fundamental knowledge, which forms the basis for understanding and solving Engineering problems, are good and very necessary, but we should not stop there. There appears to be too much focus on the fundamentals and generics. There should be provision in the Curriculum to accommodate some aspects of application of Chemical Engineering that are prevalent in today’s world.

Feedbacks received from employers of Chemical Engineering graduates (indicated by high rate of retraining) are evidence that the application part is either lacking in the Curriculum or inadequate. Since socio-economic and other factors that define an environment change with time, this aspect of the Engineering Curriculum should also vary to accommodate these changes. There are many examples of developed nations who still modify and continue to study and discover areas of modification in their Chemical Engineering Curriculum according to the changes and challenges of time. For instance, when the United States of America had the September 11th, 2001 problem in their country, one of the things they did in response was to adjust the school Curriculum to accommodate the study of homeland security.

Inadequate Attention & Depth of Coverage for Key Chemical Engineering Courses: It is opined that the overall amount of attention and depth of coverage given to some of the most vital aspects of Chemical Engineering such as Chemical reaction Engineering, unit operations, transport phenomena, Plant and process design etc. is less than commensurate because some other courses which are not so needed are given more than commensurate attention thereby greatly reducing the amount of resources (human resources and time) that are devoted to the most important and defining aspects of the Chemical Engineering Curriculum.

Too Many Irrelevant Courses: There appears to be excessive meddling of the Chemical Engineering Curriculum with several courses that are not so important in producing the crop of Chemical Engineers that we desire.

There are so many generalized courses infused into the present Chemical Engineering Curriculum leading to a situation whereby the average Chemical Engineering graduate is more like a jack-of-all-trade and a master of none.

In fact, most of our present day Chemical Engineering graduates do not find Chemical Engineering focused jobs, meanwhile, the few Chemical processing and manufacturing companies continually decry the inadequacy of highly trained, young indigenous Chemical Engineers needed to provide the Chemical Engineering expertise that they need.

The few ones who eventually manage to get employed have to be taken through the rigor of training and re-training in order to make them fit to handle the tasks required of them to perform as Chemical Engineers.

Too Much Focus On Producing Good Employees Rather Than Good Entrepreneurs: It is also opined that the focus of the Curriculum is geared towards making employees of our graduates rather than making employers of labor out of them. There is an insufficient emphasis on Chemical Engineering entrepreneurship in the present Chemical Engineering Curriculum adopted in most of our institutions adopted nationwide.

Deficient Training on Computer and ICT applications in Chemical Engineering: In addition to all of the above, there appears to be insufficient attention being paid to the use of computer & ICT tools and software in training of Chemical Engineers in our institutions of higher learning.
Engineering practice of yesteryears was man-machine relationship. However, in today's world, it is man-computer-machine relationship. In the history of Chemical Process Industries (CPI), no single development has affected in a more positive way the practice of Chemical Engineering than computers. The operation of plants has been transformed by distributed control systems. Perhaps even more profoundly, though, the personal computer and software like simulation and mathematical programs have changed the very way that Chemical Engineering is performed.

For a student to go through four/five years of a Chemical Engineering undergraduate program and not know and understand the workings of a process simulator is a tragedy. Now performing a multicomponent flash calculation or drawing a McCabe-Thiele diagram by hand definitely is not a good exercise. The application of computer-based methods in solving Chemical Engineering problems should be an integral part of the Chemical Engineering Curriculum.

Laboratory Courses Are Not Aptly Linked With the Theory Courses: It is also observed that practical courses are more or less generic and are not adequately tailor-made to match and provide practical understanding of the things taught by the lecturers in class. There seem to be a gap between what the students are taught in class and the practical work they are exposed to in the laboratories.

4.2 Bridging The Gaps – Meeting the needs

More Attention for Biology

Biology is an essential part of the study of modern day Chemical Engineering. Words like bio-sorption, bioreactors, bio-separation, Biochemical, bioremediation, bio-analysis, biomass, biotechnology, bio this bio that are no longer strange terms in the Chemical Engineers lexicon. The entry requirement for all Engineering courses is 5 credits, which must include credit passes, English, Mathematics, Physics, Chemistry and any other science or social science subject. It is worrisome therefore that today, a student who has not even done biology as a subject can be admitted to read

Chemical Engineering. This is an anomaly that must be addressed and corrected as soon as possible. Unlike other Engineering courses where this may be acceptable, the same cannot be said of Chemical Engineering. This should not be the case as biology ought to be a compulsory subject. It is therefore recommended that biology should be incorporated as a compulsory credit pass requirement for admission to Chemical Engineering programmes (Aluyor, 2016).

Biology should be part of the basic entry requirement for admission into the Chemical Engineering Program and there should be first and second semester first year courses in aspects of biology relevant to the Chemical Engineering Discipline.

Options in Chemical Engineering: Considering the very broad nature of Chemical Engineering and the need to produce Chemical Engineering graduates that have industry applicable knowledge in their various area(s) of interest, it is posited that it is high time that we make provision for options in the Chemical Engineering Curriculum at the undergraduate level. Taking a cue from sister departments, Electrical Engineering, with a Curriculum that provides for the electrical Engineering student to opt for either the power option or telecommunication option at the undergraduate level; Mechanical Engineering with options in Production and Manufacturing. Non-faculty based like Surveying with options in Land and Quantity Survey, Medicine with specialties in Gynaecology & Surgery, it is of necessity that there be about five options in the Chemical Engineering Curriculum at the undergraduate level namely Biochemical Engineering, Biotechnology, Polymer Engineering, Petrochemical Engineering and Refinery technology.

Focus on Core Areas: The Chemical Engineering Curriculum should be better stream-lined to give more focus to the core areas of the Chemical Engineering discipline so that the Chemical Engineering graduate has sufficient expertise in his field. The Pareto principle should be brought to bear on this matter in a sense. We should allocate a much greater fraction of the human resource requirement, course hours and course units in our Chemical Engineering Curriculum to the relatively small fraction of really important courses in our Chemical Engineering Curriculum. Also, courses that are not so relevant to the training of the crop of Chemical Engineers that we desire should be completely expunged from the Curriculum or at least presented as electives with zero credit units.

Entrepreneurship: Entrepreneurship should be thoroughly imbued into the Chemical Engineering Curriculum. The courses on entrepreneurship should also be further tailor-made to suit the Chemical Engineer who intends to use his training to start up an enterprise. It should not just be general entrepreneurship but entrepreneurship for Chemical Engineers. We may start with a general entrepreneurship course to be taken by the various Centre for Entrepreneurship Development (CED) Departments in our schools at the lower levels, we should go beyond this to provide a tailor-made course on entrepreneurship for Chemical Engineers at the higher levels.

More Strategic Laboratory Courses: Additional attention should be accorded to practical/laboratory work. Laboratory courses should be designed specifically for the various aspects of the Chemical Engineering discipline.

Industry relevant & local problem oriented research projects: There are a lot of problems in our environment that require Engineering solutions, yet, graduate students grope about in search of topics for research projects. Also, most of the research projects undertaken by our undergraduate and graduate students are neither relevant to the local industries that we have in the country nor do they really solve any local or national Chemical Engineering problem. A much greater emphasis should be laid on the need to carry out industry relevant/ local problem solving research projects. Industry and academia should partner to design research projects which will then be co-sponsored by both parties and the fruits of such work will be to the benefit of all. Part of the criteria for evaluating and scoring research projects should be the industrial relevance or ability of the work to solve a local or national Chemical Engineering problem, this should be well specified and highlighted in the Curriculum.

Industrial Visits/ Field Trips: The Student Industrial Work Experience Scheme (SIWES) is quite a good avenue for our students to gain relevant industrial experience, however, as a result of the considerably low number of functional manufacturing and processing companies/industries in Nigeria and also, the present state of our economy, most of our students are not able to secure placements in relevant companies and industries. It is therefore recommended that industrial visits /field trips be built into the Curriculum as a requirement for completing certain courses, reports of this industrial visit by the students should serve as a part of the continuous assessment for these courses. This will enable our students who are not so opportune to find relevant industrial placements, to have some form of vital industrial experience, also, other students who were able to secure placement in a relevant industry will also be able to visit other plants and industries thus providing them with a much more robust industrial experience.

Companies who are not willing to receive more than one or two students for the SIWES program lasting six months will likely not mind hosting a number of students for one or two days industrial visit.

A Course on Refinery Design and Operation: A course on refinery design and operation should be developed and included in the Curriculum. This would help to bolster the case for licenses to be given to Chemical Engineers or Chemical Engineering firms to run modular refineries with the long-term end effect of putting a stop to importation of refined crude products.

Introduction of Industry Specific/Applicable Courses: Certain Industry applicable courses should be built into the Chemical Engineering Curriculum to make it richer and also reduce the need and extent of retraining that our graduates have to go through when they finally get a job in an industry. Examples of such courses are: Process Safety in the Oil & Gas Industry, Process Safety in the Pharmaceutical, Food & Consumer Product Industries, Applied Hazard and Operability Studies (Applied HAZOP), Process Plant Reliability and Maintainability, Process Engineering for Control etc. These courses should be designed in collaboration with industry and possibly taught in partnership with industry.

Computer & Software Applications in Chemical Engineering:

Process simulation software such as ChemCAD HI, ASPEN PLUS, PRO II, HYSYS, PD Plus etc. should be given much more emphasis in the Chemical Engineering Curriculum. This will make the students to appreciate how it improves Engineering efficiency. Chemical process simulators are used by Chemical Engineers for a range of important applications such as mass and energy balances calculations, performance evaluation of process alternatives, equipment sizing, optimization and so on. A Chemical Engineer can now very quickly define a complex flow sheet and all the process conditions.

It is suggested that the computer & software application component of a course should be built into the course and taught together.

5.0 CONCLUSION

It is one thing to develop a Curriculum; it is another thing for it to be rightly implemented to achieve the desired results. In order to impart the right standard of training to the Chemical Engineering student, the academia must be equipped with adequate, up-to-date knowledge and skills and must have and demonstrate the right attitudes in the conduct of their duties.

Having a decent training is a pre-requisite for landing a fine Chemical Engineering job or establishing a company that will thrive in an equitable society. Having a decent training is hinged on the quality of the Curriculum with which one is trained and hence, the need for a wholesome Chemical Engineering Curriculum must not be down played.

Government, Industry and also the academia must be willing to demonstrate more commitment and synergy towards the actualization of our set targets of producing Chemical Engineers of world class standards that are fit in all respects to utilize the expertise and skills garnered in making significant contribution towards meeting the Nigerian needs for the collective good of us all.

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APPENDIX

Table 1: A comparison between a typical schedule of required courses in the Yale University Chemical Engineering Program and the schedule of required courses in the Nigerian Chemical Engineering Curriculum [3, 4, 7, 8]

NUC BMAS	YALE UNIVERSITY
YEAR 1	**YEAR 1**
1. GST 111: Communication in English I 2. GST 112: Logic, Philosophy and Human Existence 3. GST 113: Nigerian Peoples and Culture 4. GST 121: Use of Library, Study Skills and ICT 5. GST 122: Communication in English II 6. Communication 7. GST 123: Basic Communication in French 8. GST 124: Basic Communication in Arabic 9. GST 125: Contemporary Health Issues 10. GET 111: Basic Engineering Drawing 11. CHM 101: General Chemistry I 12. CHM 102: General Chemistry II 13. CHM 107: General Practical Chemistry I 14. CHM 108: General Practical Chemistry II 15. MTH 101: Elementary Mathematics I 16. MTH 102: Elementary Mathematics II 17. PHY 101: General Physics I 18. PHY 102: General Physics II 19. PHY 107: General Practical Physics I 20. PHY 108: General Practical Physics II	1. CHEM 161 General Chemistry I 2. CHEM 134L General Chemistry I 3. MATH 112 Differential Calculus I 4. CHEM 165 General Chemistry II 5. CHEM 136L General Chemistry II Lab 6. MATH 115 Integral Calculus 7. ENAS 130 Intro Computing for Engineers/Scientists
YEAR 2	**YEAR 2**
1. GST 211: Environment and Sustainable Development 2. GST 222: Peace and Conflict Resolution 3. GST 223: Introduction to Entrepreneurship 4. GST 224: Leadership Skills 5. GET 201: Applied Electricity I 6. GET 202: Applied Electricity II 7. GET 203: Engineering Drawing I 8. GET 222: Engineering Drawing II 9. GET 204: Students Workshop Experience 10. GET 205: Fundamentals of Fluid Mechanics 11. GET 206: Fundamentals of Thermodynamics 12. GET 207: Applied Mechanics 13. GET 208: Strength of Materials 14. GET 209: Engineering Mathematics I 15. GET 210: Engineering Mathematics II 16. GET 211: Computer Programming I 17. GET 212: Engineering Materials	1. CHEM 220 Organic Chemistry I 2. CHEM 222L Organic Chemistry I 3. PHYS 180 Physics I 4. ENAS 151 Multivariable Calculus 5. CENG 210 Principles of Chemical Engineering 6. CHEM 221 Organic Chemistry II 7. CHEM 223L Organic Chemistry II Lab 8. ENAS 194 Ordinary & Partial Differential Equations 9. PHYS 181 Physics II

NUC BMAS	YALE UNIVERSITY
18. GET 213: General Engineering Laboratory Course 19. GET 299: SIWES I	
YEAR 3	**YEAR 3**
1. GET 301: Engineering Mathematics III 2. GET 302: Engineering Mathematics IV 3. GET 303 Engineer-in-Society 4. GET 304 Engineering Communication 5. GET 399 SIWES II 6. GST 311 Entrepreneurship 7. STA 305 Statistics for Physical Science and Engineering 8. TCH 300 Chemical Engineering Laboratory I 9. TCH 301 Transport Phenomena I 10. TCH 302 Chemical Engineering Thermodynamics I 11. TCH 303 Separation Processes I 12. TCH 304 Chemical Kinetics 13. TCH 305 Biochemical Engineering 14. TCH 306 Science of Materials 15. TCH 307 Polymer Process Engineering 16. TCH 308 Process Instrumentation TCH 309 Process Simulation	1. CHEM 332 Physical Chemistry I 2. CENG Thermodynamics 3. MENG 361 Fluid Mechanics 4. CHEM 333 Physical Chemistry II 5. CENG 301 Kinetics and Reactors 6. CENG 315 Transport Processes 7. Engineering Elective
YEAR 4	**YEAR 4**
1. GET 499 SIWES III 2. TCH 400 Chemical Engineering Laboratory 3. TCH 401 Transport Phenomena II 4. TCH 402 Chemical Engineering Thermodynamics II 5. TCH 403 Separation Processes II 6. TCH 404 Plant Design I 7. TCH 405 Chemical Engineering Analysis 8. TCH 406 Particle Technology 9. TCH 407 Environmental Engineering 10. TIE 402 Economics for Engineers	1. CENG 411 Separation/Purification Processes 2. CENG 480 Process Control 3. Engineering Elective 4. CENG 412 Chemical Engineering Lab 5. CENG 416 Chemical Engineering Process Design 6. Engineering Elective
YEAR 5	**YEAR 5**
1. GET 501 Engineering Management 2. GET 502 Engineering Law 3. GET 500 Chemical Engineering Laboratory 4. TCH 501 Separation Processes III 5. TCH 502 Plant Design II 6. TCH 503 Process Control 7. TCH 504 Process Optimization 8. TCH 505 Reservoir Engineering 9. TCH 506 Loss Prevention in Process Industries 10. TCH 507 Chemical Reaction Engineering 11. TCH 508 Coal Processing Technology	

NUC BMAS	YALE UNIVERSITY
12. TCH 509 Sugar Technology 13. TCH 510 Detergent Technology 14. TCH 511 Fermentation Technology 15. TCH 512 Pulp and Paper Technology 16. TCH 513 Polymer Science and Technology 17. TCH 514 Technology of Fossil Fuel Processing 18. TCH 515 Biochemical Engineering 19. TCH 555 Chemical Engineering Research Project	

Table 2: A comparison between a typical schedule of required courses in the University of Illinois Chemical Engineering Program and the schedule of required courses in the Nigerian Chemical Engineering Curriculum [3, 4, 9]

NUC BMAS	UNIVERSITY OF ILLINOIS
YEAR 1	**YEAR 1**
1. GST 111: Communication in English I 2. GST 112: Logic, Philosophy and Human Existence 3. GST 113: Nigerian Peoples and Culture 4. GST 121: Use of Library, Study Skills and ICT 5. GST 122: Communication in English II 6. Communication 7. GST 123: Basic Communication in French 8. GST 124: Basic Communication in Arabic 9. GST 125: Contemporary Health Issues 10. GET 111: Basic Engineering Drawing 11. CHM 101: General Chemistry I 12. CHM 102: General Chemistry II 13. CHM 107: General Practical Chemistry I 14. CHM 108: General Practical Chemistry II 15. MTH 101: Elementary Mathematics I 16. MTH 102: Elementary Mathematics II 17. PHY 101: General Physics I 18. PHY 102: General Physics II 19. PHY 107: General Practical Physics I 20. PHY 108: General Practical Physics II	1. CHEM 202: Accelerated Chemistry I 2. CHEM 203: Accelerated Chemistry Lab I 3. ENG 100: Engineering Orientation 4. MATH 221: Calculus I 5. RHET 105: Writing and Research 6. Elective in Social Sciences or Humanities 7. CHBE 121 CHBE Profession 8. CHEM 204: Accelerated Chemistry II 9. CHEM 205: Accelerated Chemistry Lab II 10. CS 101: Introduction to computing Engineering Science 11. MTH 231: Calculus II 12. PHY 211: University Physics: Electromagnetism
YEAR 2	**YEAR 2**
1. GST 211: Environment and Sustainable Development 2. GST 222: Peace and Conflict Resolution 3. GST 223: Introduction to Entrepreneurship	1. CHBE 221 Principles of Chemical Engineering 2. CHEM 236 Fundamental Organic Chemistry I

NUC BMAS	UNIVERSITY OF ILLINOIS
4. GST 224: Leadership Skills 5. GET 201: Applied Electricity I 6. GET 202: Applied Electricity II 7. GET 203: Engineering Drawing I 8. GET 222: Engineering Drawing II 9. GET 204: Students Workshop Experience 10. GET 205: Fundamentals of Fluid Mechanics 11. GET 206: Fundamentals of Thermodynamics 12. GET 207: Applied Mechanics 13. GET 208: Strength of Materials 14. GET 209: Engineering Mathematics I 15. GET 210: Engineering Mathematics II 16. GET 211: Computer Programming I 17. GET 212: Engineering Materials 18. GET 213: General Engineering Laboratory Course 19. GET 299: SIWES I	3. CHEM 237 Structure and Synthesis 4. MATH 241 Calculus III 5. PHYS 212 University Physics: Electromagnetism 6. CHBE 321 Thermodynamics 7. CHEM 436 Fundamental Organic Chemistry II 8. MATH 285 Intro Differential Equations 9. MATH 415 Applied Linear Algebra 10. PHYS 214 University Physics: Quantum Physics Technical Elective**
YEAR 3	**YEAR 3**
1. GET 301: Engineering Mathematics III 2. GET 302: Engineering Mathematics IV 3. GET 303 Engineer-in-Society 4. GET 304 Engineering Communication 5. GET 399 SIWES II 6. GST 311 Entrepreneurship 7. STA 305 Statistics for Physical Science and Engineering 8. TCH 300 Chemical Engineering Laboratory I 9. TCH 301 Transport Phenomena I 10. TCH 302 Chemical Engineering Thermodynamics I 11. TCH 303 Separation Processes I 12. TCH 304 Chemical Kinetics 13. TCH 305 Biochemical Engineering 14. TCH 306 Science of Materials 15. TCH 307 Polymer Process Engineering 16. TCH 308 Process Instrumentation 17. TCH 309 Process Simulation	1. CHBE 421 Momentum and Heat Transfer 2. CHEM 315 Instrumental Chemical Systems Lab 3. CHEM 420 Instrumental Characterization 4. CHEM 442 Physical Chemistry I 5. Elective in Social Sciences or Humanities or Technical Elective
YEAR 4	**YEAR 4**
1. GET 499 SIWES III 2. TCH 400 Chemical Engineering Laboratory 3. TCH 401 Transport Phenomena II 4. TCH 402 Chemical Engineering Thermodynamics II 5. TCH 403 Separation Processes II 6. TCH 404 Plant Design I	1. CHBE 430 Unit Operations 2. Laboratory 3. CHBE 440 Process control and dynamics 4. Technical Electives** 5. CHBE 431 Process design 6. Technical Electives**

NUC BMAS	UNIVERSITY OF ILLINOIS
7. TCH 405 Chemical Engineering Analysis 8. TCH 406 Particle Technology 9. TCH 407 Environmental Engineering 10. TIE 402 Economics for Engineers	
YEAR 5	**YEAR 5**
1. GET 501 Engineering Management 2. GET 502 Engineering Law 3. GET 500 Chemical Engineering Laboratory 4. TCH 501 Separation Processes III 5. TCH 502 Plant Design II 6. TCH 503 Process Control 7. TCH 504 Process Optimization 8. TCH 505 Reservoir Engineering 9. TCH 506 Loss Prevention in Process Industries 10. TCH 507 Chemical Reaction Engineering 11. TCH 508 Coal Processing Technology 12. TCH 509 Sugar Technology 13. TCH 510 Detergent Technology 14. TCH 511 Fermentation Technology 15. TCH 512 Pulp and Paper Technology 16. TCH 513 Polymer Science and Technology 17. TCH 514 Technology of Fossil Fuel Processing 18. TCH 515 Biochemical Engineering 19. TCH 555 Chemical Engineering Research Project	

Table 3: A comparison between a typical schedule of required courses in the Manchester University Chemical Engineering Program and the schedule of required courses in the Nigerian Chemical Engineering Curriculum [3, 4, 10]

NUC BMAS	MANCHESTER UNIVERSITY
YEAR 1	**YEAR 1**
1. GST 111: Communication in English I 2. GST 112: Logic, Philosophy and Human Existence 3. GST 113: Nigerian Peoples and Culture 4. GST 121: Use of Library, Study Skills and ICT 5. GST 122: Communication in English II 6. GST 123: Basic Communication in French 7. GST 124: Basic Communication in Arabic 8. GST 125: Contemporary Health Issues 9. GET 111: Basic Engineering Drawing 10. CHM 101: General Chemistry I 11. CHM 102: General Chemistry II 12. CHM 107: General Practical Chemistry I 13. CHM 108: General Practical Chemistry II 14. MTH 101: Elementary Mathematics I 15. MTH 102: Elementary Mathematics II 16. PHY 101: General Physics I 17. PHY 102: General Physics II 18. PHY 107: General Practical Physics I 19. PHY 108: General Practical Physics II	1. Engineering Mathematics I 2. Engineering Chemistry 3. Process Flow 4. Process Engineering Fundamentals 5. Computational Methods for Chemical Engineering 6. Laboratory Project I 7. Engineering Mathematics 2 8. Fundamentals of Thermodynamics 9. Process Heat Transfer 10. Chemical Engineering Design 2 11. Introduction to Chemical Reaction Engineering 12. Chemical Engineering Design Project 13. Engineering Biotechnology 14. Chemical Thermodynamics
YEAR 2	**YEAR 2**
1. GST 211: Environment and Sustainable Development 2. GST 222: Peace and Conflict Resolution 3. GST 223: Introduction to Entrepreneurship 4. GST 224: Leadership Skills 5. GET 201: Applied Electricity I 6. GET 202: Applied Electricity II 7. GET 203: Engineering Drawing I 8. GET 222: Engineering Drawing II 9. GET 204: Students Workshop Experience 10. GET 205: Fundamentals of Fluid Mechanics 11. GET 206: Fundamentals of Thermodynamics 12. GET 207: Applied Mechanics 13. GET 208: Strength of Materials 14. GET 209: Engineering Mathematics I 15. GET 210: Engineering Mathematics II 16. GET 211: Computer Programming I 17. GET 212: Engineering Materials 18. GET 213: General Engineering Laboratory Course	1. Laboratory Projects 2 2. Managing My Future 3. Mathematical Methods 2 4. Solid-Fluid Systems 5. Distillation & Absorption 6. Heat Transfer & Process Integration 7. Chemical Thermodynamics 8. Momentum, Heat & Mass Transfer 9. Chemical Reaction Engineering 10. Safety & Reliability Engineering 11. Process Design & Simulation Biotechnology & Environmental Engineering

19. GET 299: SIWES I	
YEAR 3	**YEAR 3**
1. GET 301: Engineering Mathematics III 2. GET 302: Engineering Mathematics IV 3. GET 303 Engineer-in-Society 4. GET 304 Engineering Communication 5. GET 399 SIWES II 6. GST 311 Entrepreneurship 7. STA 305 Statistics for Physical Science and Engineering 8. TCH 300 Chemical Engineering Laboratory I 9. TCH 301 Transport Phenomena I 10. TCH 302 Chemical Engineering Thermodynamics I 11. TCH 303 Separation Processes I 12. TCH 304 Chemical Kinetics 13. TCH 305 Biochemical Engineering 14. TCH 306 Science of Materials 15. TCH 307 Polymer Process Engineering 16. TCH 308 Process Instrumentation TCH 309 Process Simulation	1. Design Project 3 - Part 1 2. Design Project 3 - Part 2 3. Process Synthesis 4. Design Project 3 - Part 3 5. Catalytic Reaction Engineering 6. Process Fluid Dynamics 7. Advanced Engineering Separations 8. Process Control
YEAR 4	**YEAR 4**
1. GET 499 SIWES III 2. TCH 400 Chemical Engineering Laboratory 3. TCH 401 Transport Phenomena II 4. TCH 402 Chemical Engineering Thermodynamics II 5. TCH 403 Separation Processes II 6. TCH 404 Plant Design I 7. TCH 405 Chemical Engineering Analysis 8. TCH 406 Particle Technology 9. TCH 407 Environmental Engineering 10. TIE 402 Economics for Engineers	
YEAR 5	**YEAR 5**
1. GET 501 Engineering Management 2. GET 502 Engineering Law 3. GET 500 Chemical Engineering Laboratory 4. TCH 501 Separation Processes III 5. TCH 502 Plant Design II 6. TCH 503 Process Control 7. TCH 504 Process Optimization 8. TCH 505 Reservoir Engineering 9. TCH 506 Loss Prevention in Process Industries 10. TCH 507 Chemical Reaction Engineering 11. TCH 508 Coal Processing Technology 12. TCH 509 Sugar Technology 13. TCH 510 Detergent Technology	

14. TCH 511 Fermentation Technology 15. TCH 512 Pulp and Paper Technology 16. TCH 513 Polymer Science and Technology 17. TCH 514 Technology of Fossil Fuel Processing 18. TCH 515 Biochemical Engineering 19. TCH 555 Chemical Engineering Research Project	

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