
ANAEROBIC DIGESTION TECHNOLOGY FOR THE TREATMENT OF PETROLEUM SLUDGE

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ABSTRACT

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 regulations for sludge disposal. 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. This increases Nigerian gross domestic product and enhances sustainable development. The potential of anaerobic digestion for the treatment of Petroleum sludge was proved by a reduction in Biochemical Oxygen Demand (BOD) 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 Naphthalene; 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 in an anaerobic Jar gave 10,500 m³/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 shows 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 Oxygen Demand; Total Hydrocarbon Content; Spectrophotometry; Economic Viability.*

Introduction

Besides health related problems, disposal of untreated petroleum sludge onto land or onto water bodies causes land pollution, water pollution and destruction of ecosystem. In Nigeria, the treatment and disposal of sludge imposes a major challenge to the oil and gas industry. Winter (1984) stated that anaerobic biogas digesters have historically been used for sewage sludge stabilization in Waste Water Treatment Plants. Owabor & Owihiri (2011) gave 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 naphthalene, phenanthrene and anthracene which can be used as representative of the PAHs.

Besides destroying disease pathogens in the sludge, the treatment of sludge yields biogas and biosolids fertilizer, hence saving the fuel needed to manufacture petrochemical-based fertilizers (Appels *et al.*, 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 *et al.*, 2008). Besides enhancing sustainable development and increasing the Nigerian Gross Domestic Product (GDP), anaerobic digestion of petroleum sludge optimizes 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. 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, hence hampering food production. This technical paper describes anaerobic digestion technology 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.

Process Description

Microbial Digestion

The thickened sludge was pretreated to disrupt chemical bonds of cell walls and membranes, thus enhancing solubilisation of cell components and then fed into anaerobic digester where the sludge was degraded by microbial action in the absence of oxygen into biogas and NPK rich biosolids fertilizer. The supernatant from the digester and water from the thickener were recycled to the WWTP and the biosolids dried, pelletised and sent to bagging unit. Green & Perry (1997) gave Solid Retention Time of 15 – 30days, Hydraulic Retention Time of 10 – 30days, Mesophilic temperature 30 –38 °C, and Thermophilic temperature 50 –70 °C. Boe (2006) gave optimum pH for the *methanogenic* bacteria to be between 6.5 to 7.2.

Formation of Biogas

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

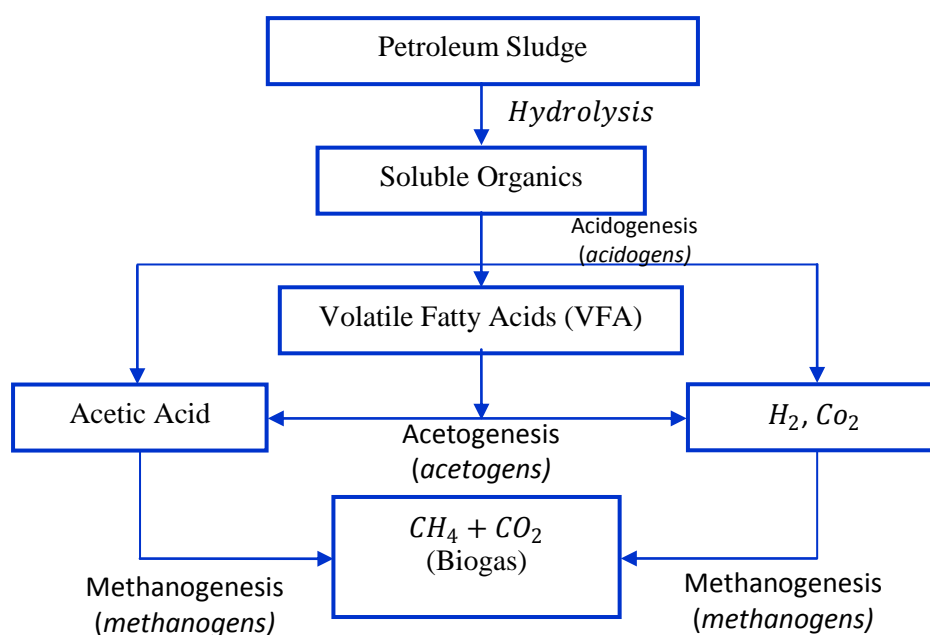


Fig. 1: Steps in Anaerobic Digestion Process of Petroleum Sludge
Source: Appels *et al.* (2008)

Biogas Upgradation

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.

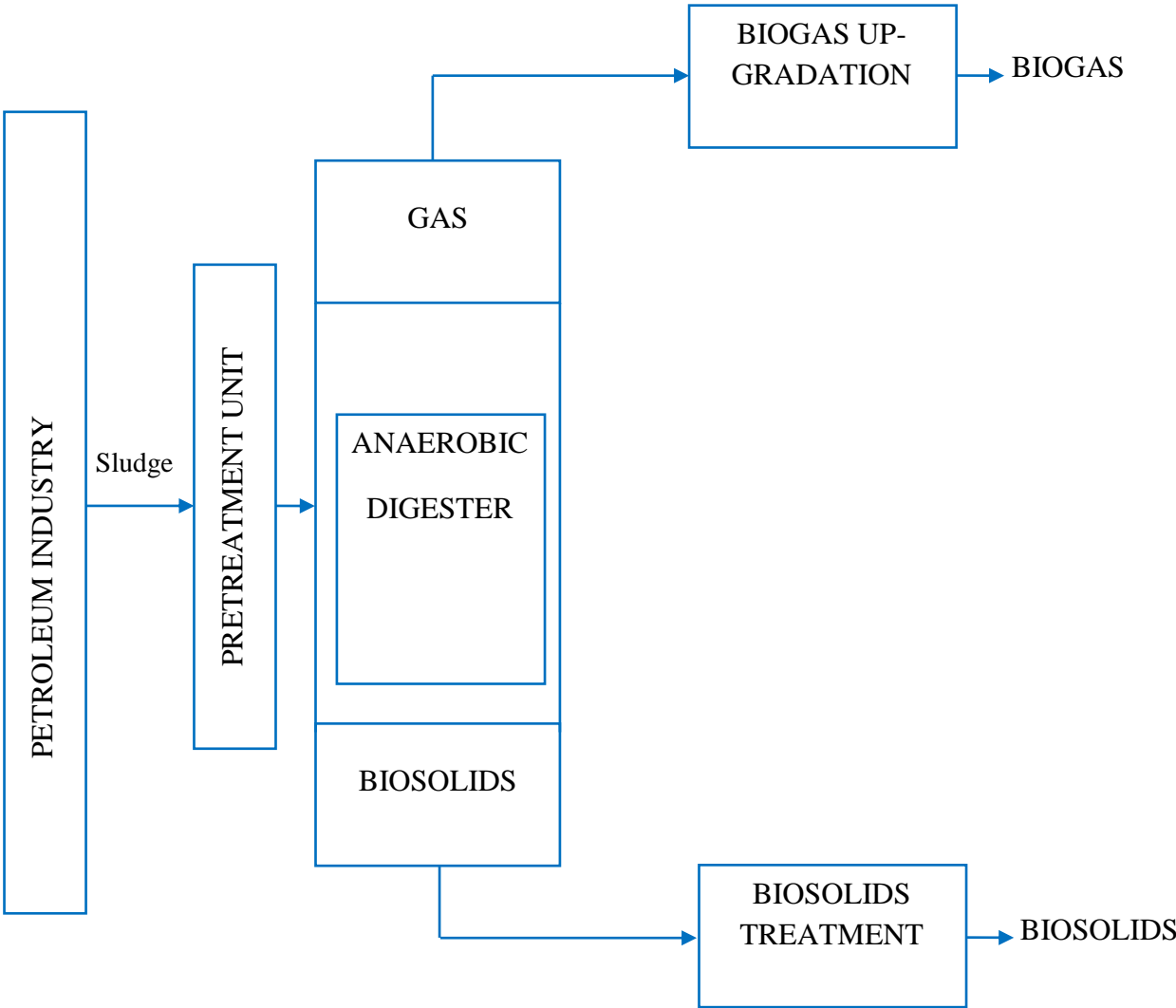


Fig. 2: Block Flow for Anaerobic Digestion Process

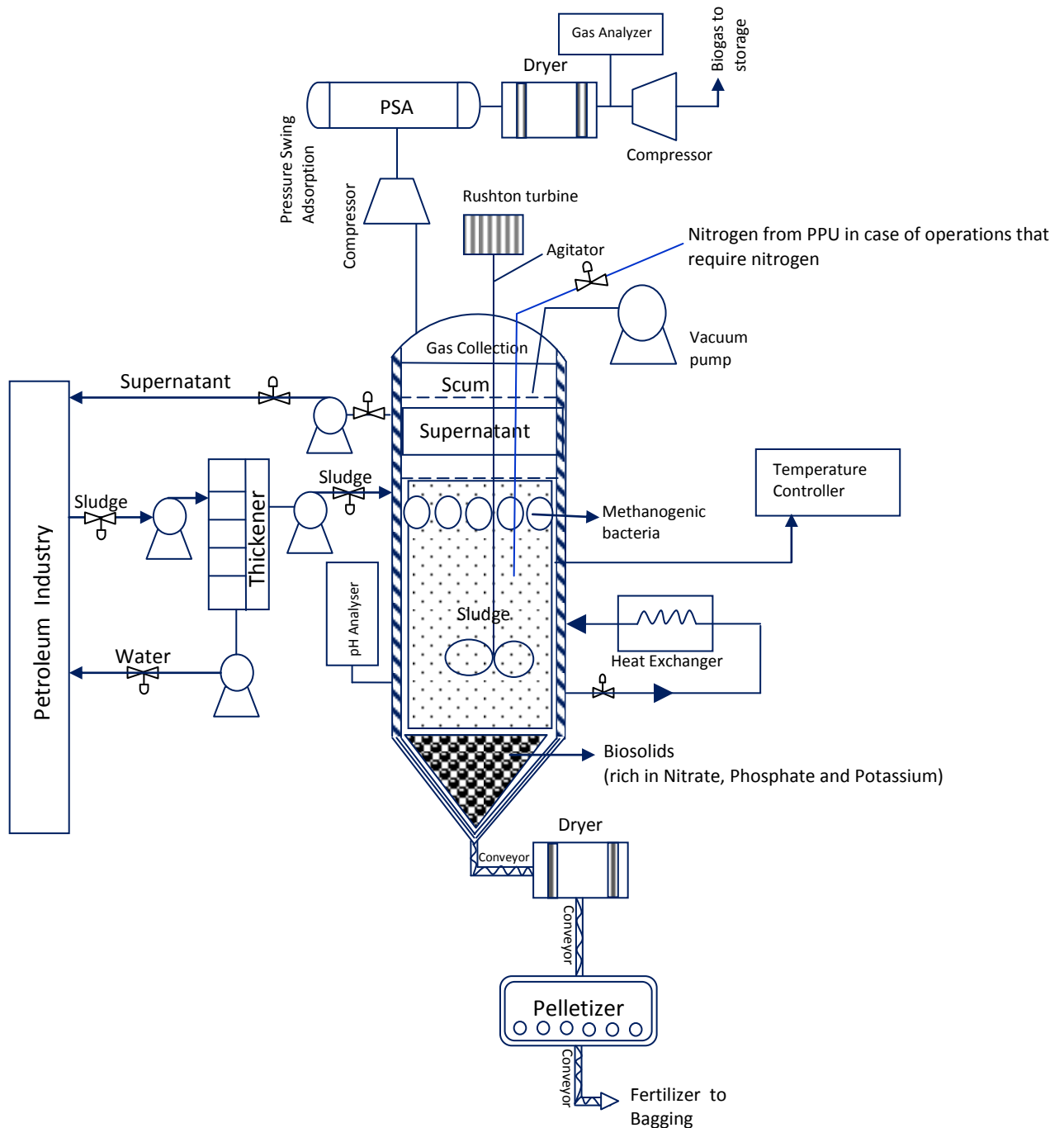


Fig.3: Process Flow for a typical Anaerobic Digestion Process.

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:

$$\begin{aligned} \text{Flow of materials in} + \text{microbial biodegradability of sludge} - \text{Flow of materials out} \\ = \text{Accumulation} \end{aligned} \quad (1)$$

For the Biomass

$$F x_{1,0} + \mu x_1 V - F x_1 = \frac{V dx_1}{dt} \quad (2)$$

Dividing through by V

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

Writing in the pattern of Monods equation: $\mu = \frac{\mu_m X_2}{K_m + X_2}$

Give

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

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.

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

For the Sludge

From materials balance:

Flow of materials in + microbial biodegradability of sludge – Flow of materials out
= Accumulation

$$\frac{V dX_2}{dt} = F X_{2,0} - \frac{\mu X_1 V}{Y} - F X_2 \quad (6)$$

$$\frac{V dX_2}{dt} = F(X_{2,0} - X_2) - \frac{\mu X_1 V}{Y} \quad (7)$$

Dividing through by V

$$\frac{dX_2}{dt} = \frac{F}{V} (X_{2,0} - X_2) - \frac{\mu X_1}{Y}$$

$$\frac{dX_2}{dt} = D(X_{2,0} - X_2) - \frac{\mu X_1}{Y} \quad (8)$$

Writing in the pattern of Monods equation: $\mu = \frac{\mu_m X_2}{K_m + X_2}$

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

Troubleshooting

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

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.

Materials and Methods

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.

Methods

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

The BOD was measured using the modified Winkler method. The THC was measured using spectrophotometric method and the VSS using gravimetric method. 200 grammes of the

sludge was measured using a chemical balance and put into a beaker. 2 grammes of *methanogenic methanobrevibacter* bacteria was pipetted and put into the sludge in the beaker after which the beaker was put into Labtech anaerobic jar with improvise for gas collection point. Anaerobic condition was maintained with the help of Oxoid Anaerobic Gen TM AN 0035A gas park and catalyst. The Anaerobic Jar was corked airtight and kept in a Gallenkamp incubator maintained at 37 °C (Mesophilic) for a solids retention time of sixteen days. One gramme of the mixture was taken daily for tenfold serial dilution to find the amount of microorganisms and a new gas park replaced each day. After three days, two grammes of the sludge mixture was taken for BOD and THC and replaced with 1 gramme of fresh sludge and 1 gramme of *Methanobrevibacter* bacteria. This is called recycling.

After fifteen days, two grammes of the sludge mixture was taken for BOD, THC and GC-MS analysis using Agilent 7890 GC-MS equipment. Nitrate, Phosphate and potassium test were carried out using spectrophotometric methods. 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 flowguage at the gas collection point read $0.122m^3s^{-1}$. This was found to be equivalent to $10,500m^3/d$.

Results

Total Anaerobic Bacterial Count (TABC)

$$TABC = \frac{1}{DF} \times \text{Average Plate Bacterial Count} \times \frac{1}{\text{volume correction factor}} \quad (10)$$

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

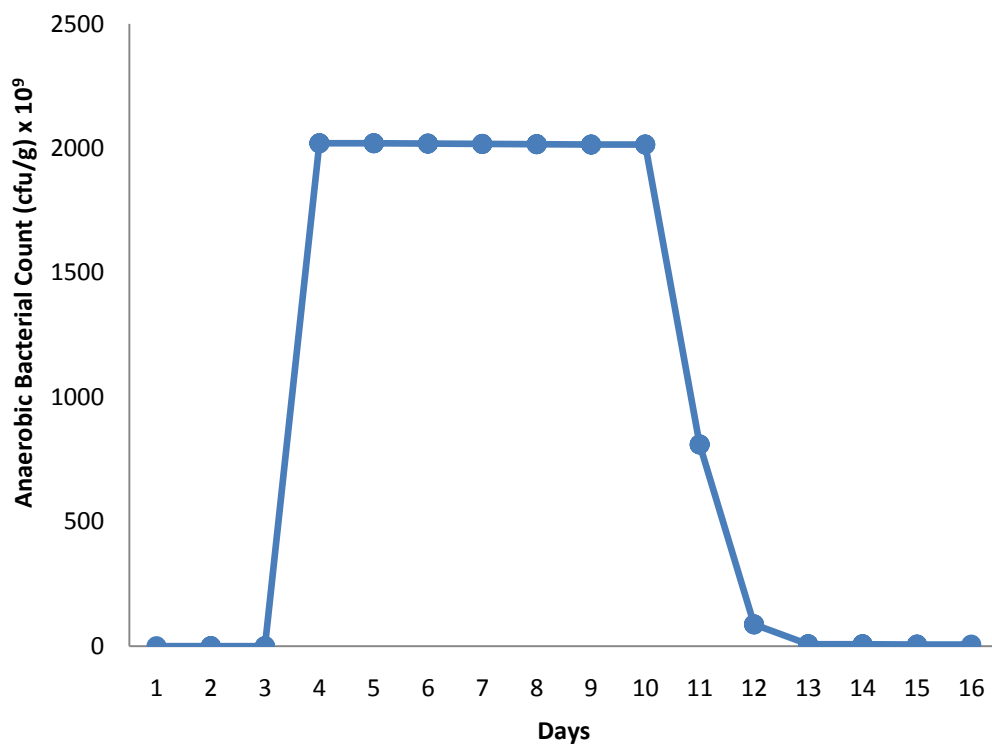


Fig. 4: Bacterial growth rate per day.

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

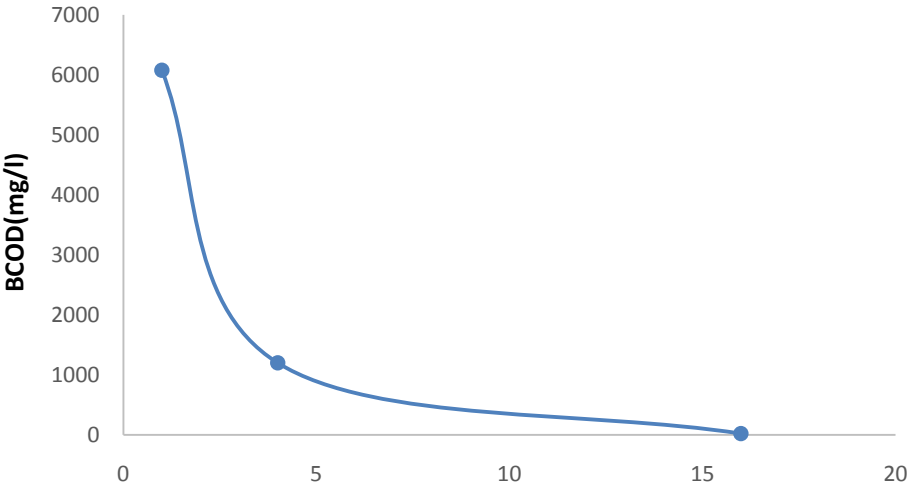


Fig. 5: Graph of change in BCOD with Time (days)

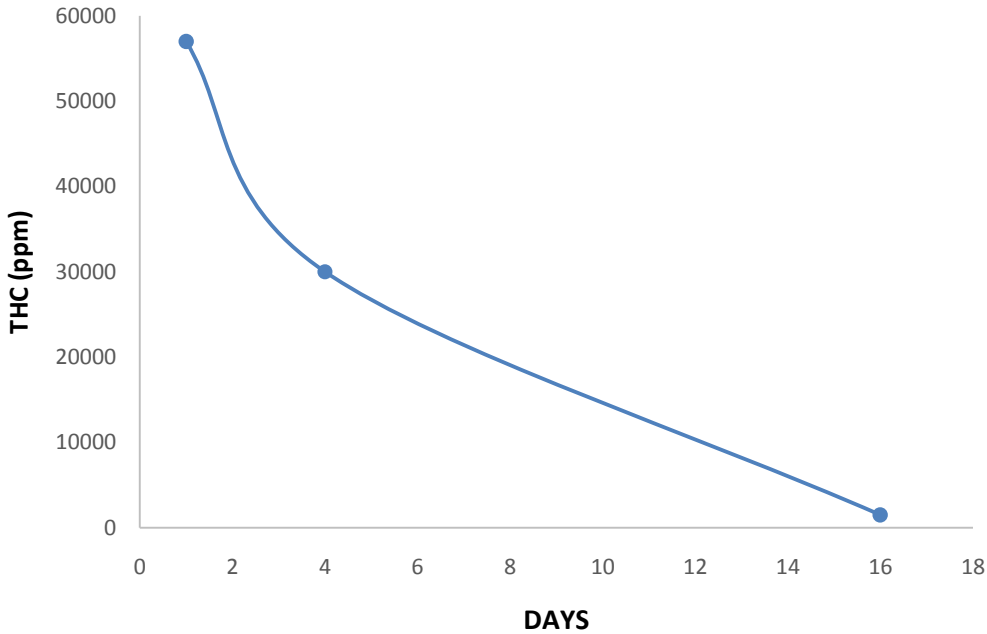


Fig. 6: Graph of Change in THC with Time

Polycyclic Aromatic Hydrocarbons (PAHs)

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

Abundance

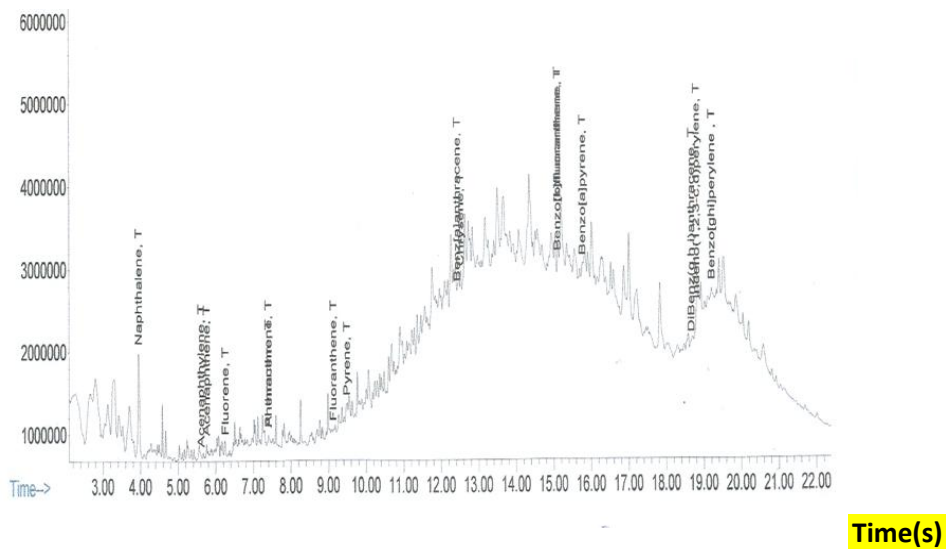


Fig. 7: Waveform of GC-MS Analysis of Petroleum Sludge

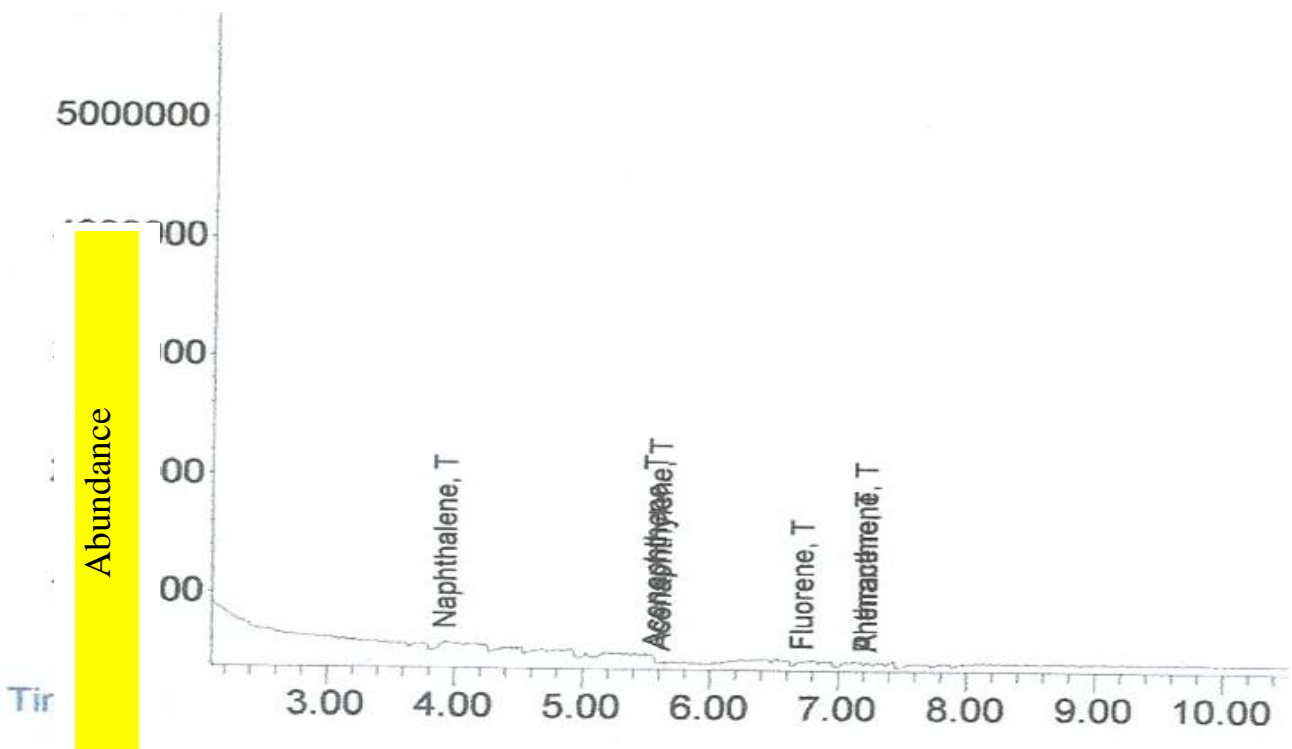


Fig. 8: Waveform of GC-MS Analysis of Biosolids

Fertilizer Value of Biosolids

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

Volume of Biogas Produced

$$V_{CH_4} = (0.35)(s_o - s)(Q)(10^3 g/kg)^{-1} - 1.42 P_x \quad (11)$$

(Tchobanoglous *et al.*, 2004)

$$P_x = \frac{YES_o}{1+k_d\theta_c} \quad (12)$$

(Appels *et al.*, 2008)

$$Y = \frac{V_{SS}}{BCOD} \quad (13)$$

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

From equation (12) $P_x = \frac{0.016 \times 0.9 \times 6080}{1 + 0.025 \times 16} = \frac{87.552}{1.40} = 62.54 \text{ kg/d}$

Volume of Methane

From equation (11) $V_{CH_4} = (0.35)(S_o - S)(Q)(10^3 g/kg)^{-1} - 1.42 P_x$

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

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

$$= 10,603.25 - 88.80683.25 - 88.8068 \text{ m}^3/\text{d}$$

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

Economic Evaluation

$$\text{Net Annual Profit (NAP)} = [\text{Product Sales}] - [\text{Operating Cost}] - [\text{Fixed Capital}] \quad (14)$$

$$\text{Total Investment (TI)} = \text{Fixed capital} + \text{Working capital} \quad (15)$$

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

$$\begin{aligned} \text{Rate of Return on Investment (ROI)} &= \frac{\text{Net annual profit}}{\text{Total investment}} \times \frac{100}{1} & (16) \\ &= \frac{£4,937,767.42}{£10,452,170.28} \times \frac{100}{1} \\ &= 47.2415516 \approx 47 \% \end{aligned}$$

$$\text{Pay Back Period} = \frac{\text{Total investment}}{\text{Net annual profit}} \quad (17)$$

$$\begin{aligned} \text{PBP} &= \frac{£10,452,170.28}{£4,937,767.42} \\ &= 2.1167806 \approx 2 \text{ years} \end{aligned}$$

$$\text{OR: } \frac{1}{\text{Rate of return on investment}} \quad (18)$$

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

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

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 BOD and THC decrease with sludge biodegradation. BCOD and THC can therefore be used as a measure of sludge biodegradation.

The potential of anaerobic digestion for the treatment of sludge is proved by GC-MS analysis for priority toxicants in the sludge. Table 3 shows that the concentration of naphthalene, anthracene and phenanthrene in the untreated sludge reduced from tens to units after the sludge treatment. Table 4 shows 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 (11). 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 pay back 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 shows that a

petroleum sludge anaerobic digestion plant if well managed could be economically viable in Nigeria.

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. 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 Federal Environmental Protection Agency (FEPA) standards and regulations will be solved.

Recommendations

It is recommended that:

- i. With the present call for the amendment of the Nigerian Petroleum Industry law, 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. Sludge incineration in Nigerian petroleum industries should be stopped with the adoption of the anaerobic digestion technology so as to enhance the realization of the Nigerian vision 2020 (now 2030) of zero gas flaring. Private investors and government are encouraged to invest in the anaerobic digestion plant considering its high economic viability and profitability.
- ii. With the present call for the promulgation of the Nigerian Water resources law, Nigerian Federal Environmental Protection Agency standards and regulations for the treatment and disposal of hazardous waste (Sludge) onto land and water bodies should be strictly enforced. This could curb the menace of land and water pollution and its consequent detriments on agricultural production, human health and aquatic life. Moreover, the chemical and microbiological properties of water should be strictly monitored by the relevant regulatory agencies so as to safeguard the health of downstream users as disease pathogens present in the improperly treated disposed sludge could be infiltrated into the water table and surface waters.
- iii. Biogas produced from anaerobic digestion of petroleum sludge be upgraded and its production maximised so that with rising natural gas exports, biogas could substitute natural gas as a domestic fuel source. Biogas is environmentally friendly and a renewable energy source, natural gas being exclusively for exports.
- iv. The use of biosolids as fertilizer be encouraged and farmers made aware of its advantages over the petrochemical based fertilizer.

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Appendix

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/mgBOD)	
k_d	Endogenous Respiration Coefficient or specific maintenance rate, per day (d ⁻¹) ranging from 0.02 to 0.04.	
S_0	Biochemical Oxygen Demand (BOD) in the influent sludge	(mg/L)
S	Biochemical Oxygen Demand (BOD) 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
BOD	Biochemical 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