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Anaerobic Digestion Process for the Treatment of Industrial Waste Water sludge

IDONGESIT EFFIONG SAMSON
Rivers State University of Science & Technology, Nigeria

ABSTRACT The disposal of untreated industrial waste water 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 enhance sustainable development. The potential of anaerobic digestion for the treatment of industrial waste water sludge was proved by a reduction in Biological Carbonaceous Oxygen Demand (BCOD) of the sludge from 6080mg/l to 20.40 mg/l and Total Hydrocarbon Content (THC) from 57000 ppm to 1500 ppm. Gas Chromatography and Mass Spectrometry (GC-MS) result showed a decrease in concentration of Polycyclic Aromatic Hydrocarbons (PAHs) from tens to units. Anaerobic digestion of 200garmmes of the sludge in an anaerobic Jar gave 10,50 $\frac{m^3}{d}$ biogas $\frac{m^3}{d}$ and 190g biosolids with NPK value of 4.412mg/kg Nitrate, 37.95 mg/kg Phosphorus and 695.95 mg/kg Potassium. For 5 tonnes per day of sludge plant capacity, economic analysis gave 3years Pay Back Period (PBP) and 33% Rate of Return on Investment (ROI). This shows that an anaerobic digestion plant if well managed could be very viable in Nigeria. The plant should be sited as process unit in every Nigerian waste water treatment plant.

Keywords: Anaerobic digestion, treatment, waster water

Introduction

In the Nigerian Oil and Gas industry, spillages and unwanted products are flushed into underground drainages flowing to the waste water treatment plant (WWTP) where the waste water is treated and a solid sludge recovered.

This solid effluent from waste water treatment (the sludge) constitutes health hazard to personnel on exposure and environmental hazard on disposal if not properly treated before disposal. Besides health related problems, disposal of untreated 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) States that anaerobic biogas digesters have historically been used for sewage sludge stabilization in Waste Water Treatment Plants. Owabor & Owihiri, (2011) gives 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, the 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 waste water treatment plant (Appels *etal.,* 2008). Besides enhancing sustainable development and increasing the Nigerian gross domestic product (GDP), anaerobic digestion of industrial water 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 process for industrial waste water 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 is 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 is 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 are recycled to the WWTP and the biosolids dried, pelletised and sent to bagging unit.
Perry & Green, (1997) gives Solid Retention Time 15 - 30days, Hydraulic Retention Time 10 – 30days, Temperature 30 -, $38^{\circ}C$ Mesoph $38^{\circ}C$ illic 50 -, $70^{\circ}C$ Thermo $70^{\circ}C$ phillic
Boe, (2006) gives optimum pH for the *methanogenic* bacteria to be between 6.5 to 7.2.

Formation of Biogas

Appels *et al.,* (2008) states that the formation of biogas from anaerobic digestion of industrial waste water sludge involves four basic steps:
H_2 H_2 Co_2 Co_2 $CH_4 + CO_2$ $CH_4 + CO_2$ $Hydrolysis$ Hydrolysis, acidogenesis, acetogenesis and methanogenesis. Among these, hydrolysis is the rate, limiting step. These steps are illustrated on a block-flow diagram.

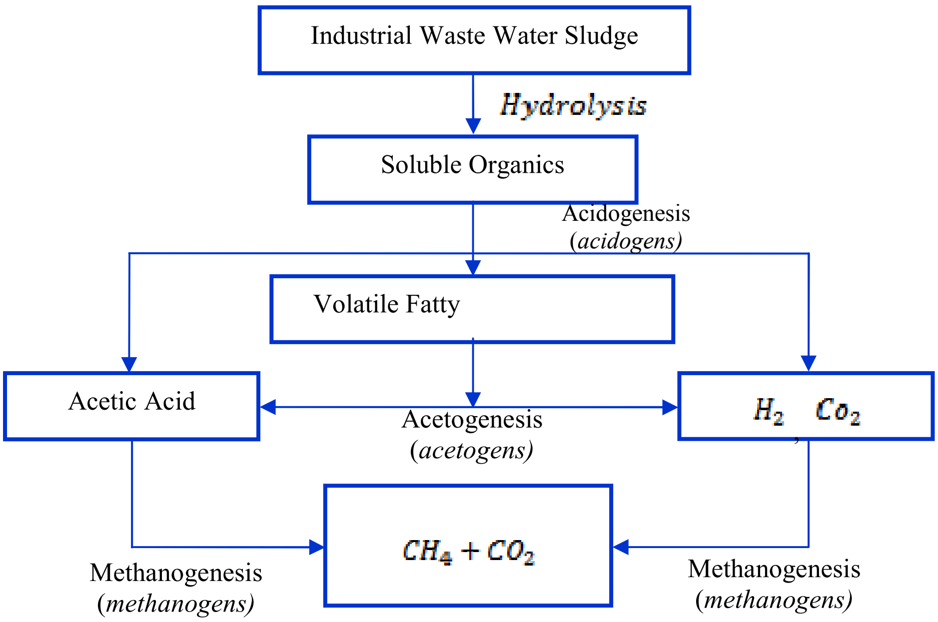

Fig 1: Steps in anaerobic digestion process of industrial waste water sludge. Source: Appels et al., (2008)

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.

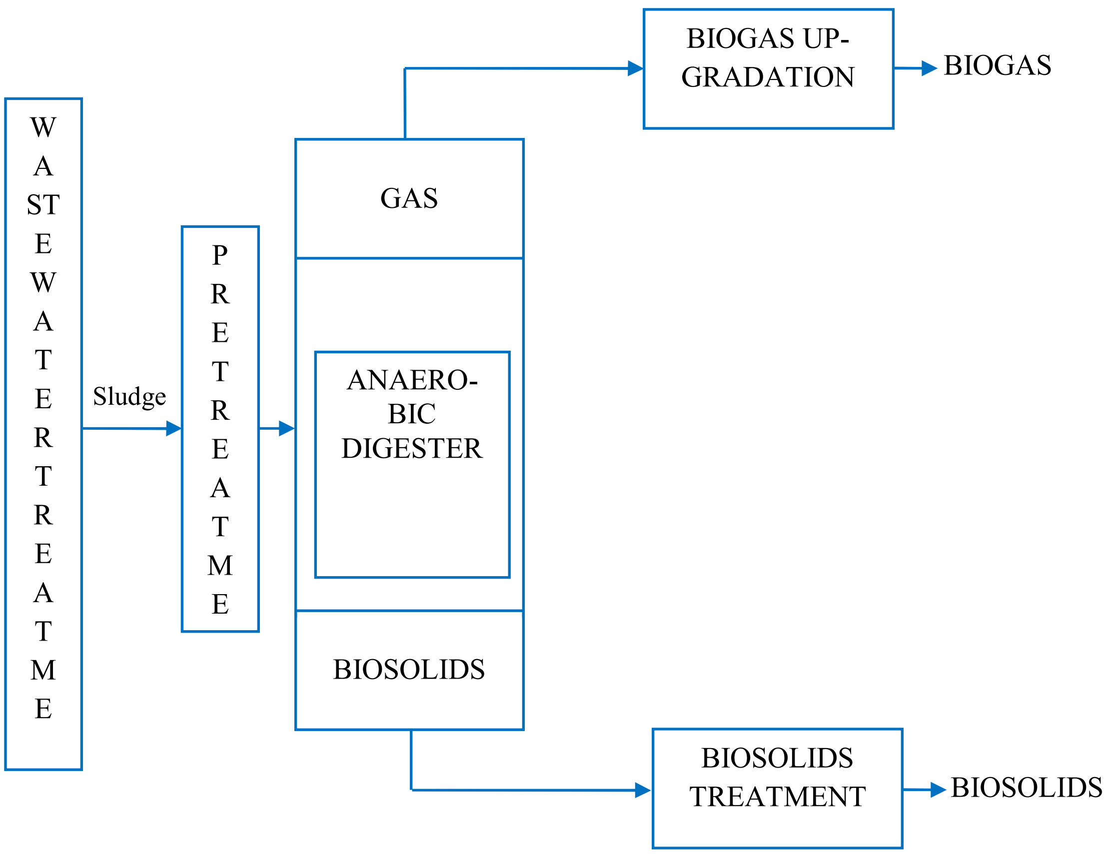

Fig 2: Block flow diagram for anaerobic digestion process

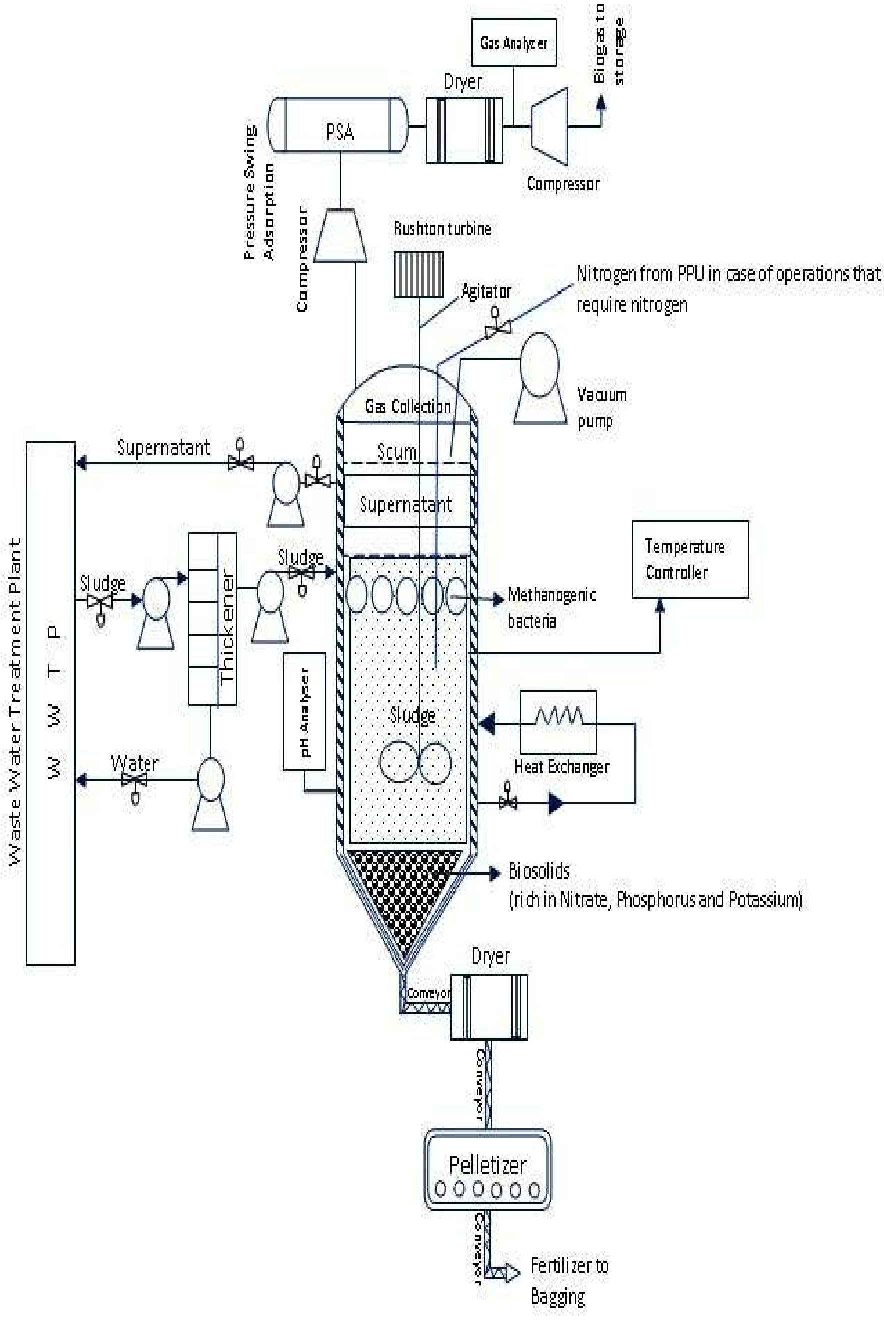

Fig 3: Process flow for a typical anaerobic digestion process

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:

$$\text{Flow of materials in} + \text{microbial biodegradability of sludge} - \text{Flow of materials out} = \text{Accumulation}$$

FOR THE BIOMASS:

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

Dividing through by V

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

Writin V g in the pattern of Monods equation

$$\mu = \frac{\mu_m X_2}{K_m + X_2}$$

Give $\mu = \frac{\mu_m X_2}{K_m + X_2}$ s

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

Writing $\frac{dX_1}{dt} = D(X_{1,0} - X_1) + \frac{\mu_m X_1 X_2}{K_m + X_2}$ in the pattern of the modified form of monods equation $\mu = \frac{\mu_m X_2}{K_m + X_2} - K_d$ to acco $\mu = \frac{\mu_m X_2}{K_m + X_2} - K_d$ unt for consumption of cellular material to produce maintenance energy.

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

FOR THE SLUDGE

From materials balance:

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

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

$$\frac{VdX_2}{dt} = F(X_{2,0} - X_2) - \frac{\mu X_1 V}{Y}$$

Dividing through by V

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

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

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

Troubleshooting

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

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:

1. 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.
2. Predict on a time basis how the system will react to sudden or progressive changes in operating parameters of feedstock flowrate and composition, temperature, inhibition, pH, etc and choose the optimum conditions.

Materials and Methods

Materials

Industrial waste water 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

The industrial waste water 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 BCOD was measured using the modified Winkler method. The THC was measured using spectrophotometric method and the VSS using gravimetric method. 200grammes of the sludge was measured using a chemical balance and put into a beaker. 2grammes of *methanogenic methanobrevibacter* bacteria was pippetted 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 $37℃$ (Mesoph $37℃$ illic) 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 BCOD 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 BCOD, THC and GC-MS analysis using agilent 7890 GC-MS equipment. Nitrate, Phosphorus and potassium test was 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 $0.122m^3s^{-1}$ found t $0.122m^3s^{-1}$ o be equivalent to. $10{,}500m^{\frac{3}{d}}$

Results and Discussion

Total Anaerobic Bacterial Count (TABC)

$$TABC = \frac{1}{DF} \times Y\ colonies \times \frac{1}{volume\ correction\ factor} \qquad (3)$$

Table 1: Total Anaerobic Bacterial Count

DAYS	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Anaerobic Bacterial Count	0.120	1.020	1.021	2020	2020	2019	2018	2017	2016	2015	810	87	8.50	8.45	7.20	7.190

Anaerobic Bacterial Count is calculated as: $^{cfu}/_{g} \times 10^9$

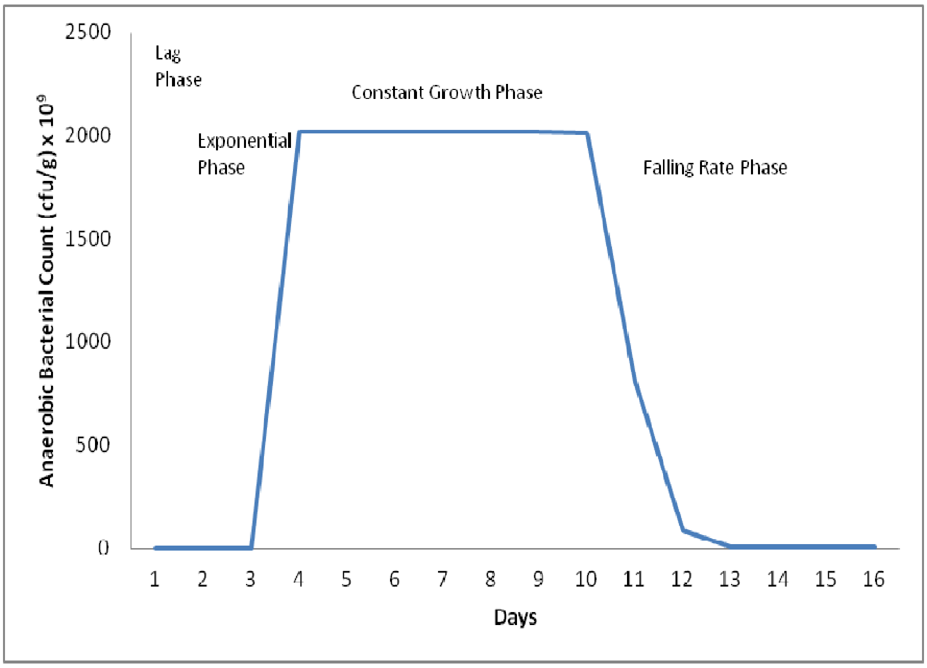

Fig 4: Bacterial growth rate per day

Table 2: Biochemical carbonaceous oxygen demand and total hydrocarbon content

DAYS	0	4	16
$BCOD/(mg/l)$	6080	1200	20.40
$THC(ppm)$	57000	30,000	1500

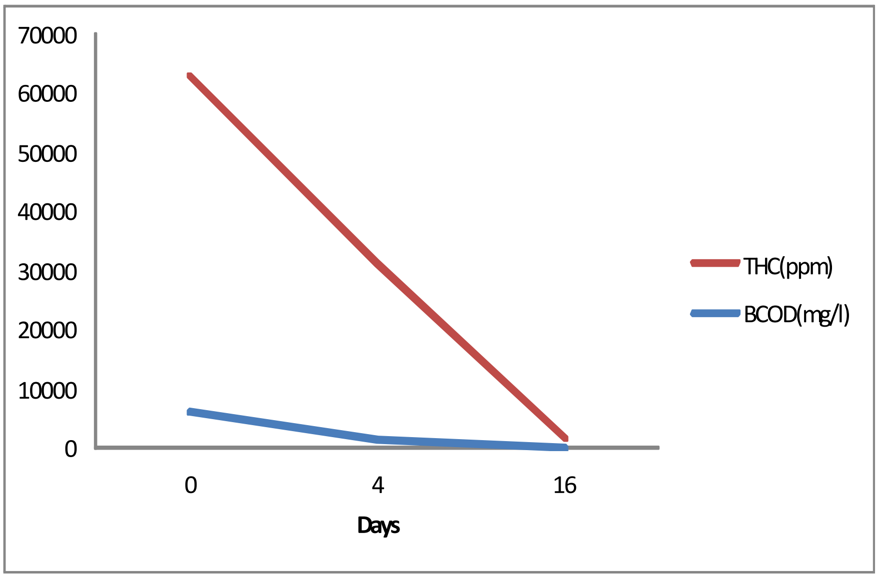

Fig 5: Graph of change in THC and BCOD with time

Polycyclic Ardramatic Hydrocarbons (PAHs)

Table 3: GC – MS for the priority toxicants in the industrial waste water sludge

Toxicant	CONCENTRATION (mg/L)	
	Untreated Sludge	**Biosolids**
Napthalene	37.1	6.32
Anthracene	33.43	8.24
Phenanthrene	33.97	9.86

GC-MS Waveforms

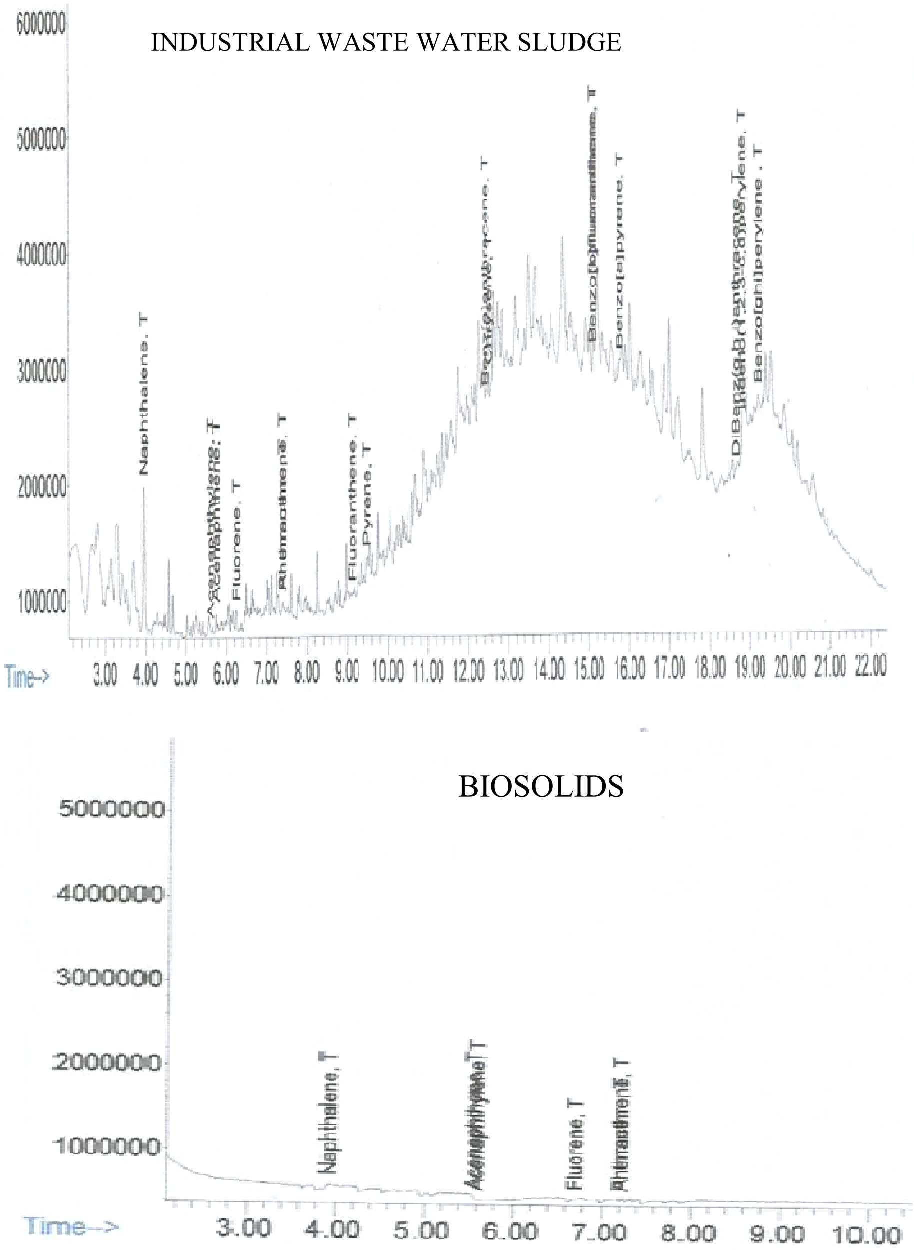

Fig 5: Waveforms GC-MS Analysis of Industrial Waste Water Sludge and Biosolids

Fertilizer Value of Biosolids

Tables 4: Fertilizer Value of biosolids

Component	Concentration (mg/L)
Nitrate	4.412
Phosphorus	37.95
Potassium	695.95

Volume of Biogas Produced

$$V_{CH_4} = (0.35)(s_o - s)(Q)(10^3 g/kg)^{-1} - 1.42\, P_x \quad (4)$$

(Tchobanoglous etal., 2004)

$$P_x = \frac{YES_o}{1+k_d\theta_c} \quad (5)$$

(Appels *etal.,* 2008)

$$Y = \frac{Vss}{BCOD} \quad (6)$$

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

From eqn (5)

$$P_x = \frac{0.016\times 0.9\times 6080}{1+0.03\times 16} = \frac{87.552}{1.48} = 59.16 kg/d$$

Volume Methane

From equation (4)

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

$$(0.35)(6080 - 20.4)\, 5000 \times \frac{1}{1000} - 1.42\ (59.16)$$

$$= 0.35\ (6,059.6)(5) - 84.0072$$

$$= 10,603.25 - 84.0072$$

$$= 10,519.2428$$

$$\approx 10,500 m^3/d$$

Discussion

Recycle on day 4 resulted in exponential increases 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 fig 5 shows that BCOD and THC decreases with sludge biodegradation. BCOD and THC can therefore be used as a measure of sludge biodegration. 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 Napthalene, 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, Phosphorus 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 (4).

Conclusion

Anaerobic digestion helps transform the toxic industrial waste water 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, anaerobic digestion of industrial waste water sludge could optimize petroleum oil and gas production in Nigeria. With anaerobic digestion of industrial waste water sludge, Nigerian oil and gas reserves and net petroleum exports will increase. With anaerobic digestion plant as a process unit in every Nigerian waste water treatment plant, the problem of sludge treatment and disposal according to environmental protection agency (EPA) standards and regulations will be solved.

Recommendations

The author recommends that:

- Every Nigerian oil and gas industry must have an anaerobic digestion plant as a process unit in its Waste Water Treatment Plant.
- 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.
- The use of biosolids as fertilizer be encouraged and farmers made aware of its advantages over the petrochemical based fertilizer.

Correspondence
Idongesit Effiong Samson
Department of Chemical Engineering
Rivers State University of Science & Technology
Port Harcourt, Nigeria
Email: idongesit.sampson@ust.edu.ng

Notes
Nomenclature

X_1, concentration of biomass (mg/l).
t, time (hr).

D, dilution rate (hr^{-1}).

$X_{1,0}$, inlet biomass concentration, (mg/l).

μ_m, maximum specific growth rate or half maximal velocity concentration, (hr^{-1}).

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, $(mgvSS \text{ volatile suspended solids}/mgBCOD)$.

Q, flowrate of methane, (m^3/d).

k_d, endogenous respiration coefficient or specific maintenance rate, per day (d^{-1}) ranging from 0.02 to 0.04.

S_0, biological carbonaceous oxygen demand (BCOD) in the influent sludge, (mg/l).

S, biological carbonaceous oxygen demand (BCOD) in the effluent biosolids,

(mg/l).

V_{CH_4} is volume of methane produced , (m^3/d).

0.35 is the theoretical conversion factor for the amount of methane produced in m^3 from the conversion of 1kg of BCOD. At $35°C$, the conversion factor is 0.40. 1.42 is the conversion factor for cellular material into the BCOD.

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

PSA, Pressure Swing Adsorption.
WWTP, Waste Water Treatment Plant.
EPA, Environmental Protection Agency.
EU, European Union.
GDP, Gross Domestic Product.
SRT, Solids Retention Time.
VSS, Volatile Suspended Solids.
HRT, Hydraulic Retention Time.
BCOD, Biological Carbonaceous Oxygen Demand.
CFU, Colony Forming Unit.
DF, Dilution Factor.
NPK, Nitrate Phosphorus & Potassium.
PPU, Power Plant and Utilities.
PBP, Pay Back Period.
ROI, Rate of Return on Investment.
THC, Total Hydrocarbon Content.
PAHs, Polycyclic Aromatic Hydrocarbons.
PPM, Parts Per Million.
GC – MS, Gas Chromatography and Mass Spectrophotometry.
TABC, Total Anaerobic Bacterial Count.

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