DISCOVERY

58(319), July 2022

Characteristics of Nitrate and Total Hardness on Sedimentation of Crude Oil Degradation in Stagnant Water Media

Ukpaka CP, Okirie FU

To Cite:
Ukpaka CP, Okirie FU. Characteristics of Nitrate and Total Hardness on Sedimentation of Crude Oil Degradation in Stagnant Water Media. *Discovery*, 2022, 58(319), 817-823

Author Affiliation:
Department of Chemical/Petrochemical Engineering, Rivers State University Port Harcourt, PMB 5080, Rivers State, Nigeria.
Email:chukwuemeka24@yahoo.com

Peer-Review History
Received: 14 May 2022
Reviewed & Revised: 18/May/2022 to 21/June/2022
Accepted: 23 June 2022
Published: July 2022

Peer-Review Model
External peer-review was done through double-blind method.

ABSTRACT

In this research the characteristics of nitrate and total hardness of contaminated water media was monitored in view with degradation and sedimentation due to action of the microorganisms present in the bio-reaction, which was subjected into stagnant condition. The variation in the concentration of the nitrate and the total hardness was monitored with respect to variation in time and depth as the dispersion occurs in the bio-reactor. Decrease in nitrate and total hardness concentration was observed in view of increase in time and depth of the stagnant water media. It is revealed that the variation in salt water medium was more significance compared to the variation in fresh water medium for both nitrate and total hardness concentration. The concentration of nitrate in salt water medium was higher than the concentration of nitrate in fresh water medium as revealed in this research and the high concentration of the nitrate favours the microbial activity in the bio-reaction, because the organisms uses the nitrate as a source of nutrient for cartelizing the degradation process of total petroleum hydrocarbon in the stagnant water media. Similarly, the degree of the total hardness concentration in the bio-reactor was reduced due to the dispersion, sedimentation and biodegradation processes that occurs. However, this investigation has predicted the significance of nitrate and total hardness characteristics of crude oil degradation in stagnant water media.

Key words: Characteristics, nitrate, total hardness, sedimentation, crude, degradation, stagnant water media

1. INTRODUCTION

This research on the nitrate and total hardness characteristics on crude oil degradation in stagnant water environment is focus on the contribution in aiding the remediation processes. However, research on remediation of contaminants in both soil and water environment has been studied extensively, especially on the various factors that induces the reaction processes [1-6]. Indeed, it is observed that allot of studies has been considered on these factor that influence bioremediation programme or processes and the cost implication in term of effectiveness in the process with optimum performance [7-9].

ISSN 2278–5469 EISSN 2278–5450 I OPEN ACCESS

Other researchers has look at the constrain factors in crude oil remediation with application of microbes and observed that the variation in some of the physicochemical properties of the system induced other parameters simultaneously [10-13]. The variation in the dissolved, temperature, organic matter, electrical conductivity, total hardness etc. influence the pH value [14]. This physicochemical parameters really induced the microbial growth rate as well as reduces the efficiency of crude oil degradation and resulted to waste of materials and increase in capital financial involvement [14-15].

Bioremediation is a process that involves the application of microorganisms to enhance restoration on polluted environment and the process is classified to be environment friendly due to fact that reaction results to products with no impact on the ecosystem [16]. Considering the conditions that favours bioremediation of contaminated environment and the action of the organisms in the situation will experience exponential growth and rapid action will occur on contaminants degradation, meaning less cost will be incurred as well as the mission well achieve [17-20].This investigation was aim in revealing the contribution of nitrate and total hardness in crude oil degradation, dispersion and sedimentation in the stagnant water media.

2. MATERIALS AND METHODS

Sampling

The research samples were obtained from Rivers State of Nigeria and all analysis conducted in Rivers State University Port Harcourt of the Department of Chemical/Petrochemical Engineering for the determination of the total hardness and nitrate concentration with respect to the effect of dispersion, sedimentation and bio-degradation of water media subjected into a stagnant plastic GP tank.

Determination of Total Hardness

2.5.0ml of the Sample was diluted to 50ml with distilled water in a 250ml conical flask. 2ml of buffer solution obtained by dissolving 16.9g NH_4Cl in 143ml concentrated NH_4OH with the addition of 1.25g of Magnesium Salt of EDTA and dilution to 250ml with distilled water were added to the diluted sample. 2 drops of indicator solution obtained by dissolving a mixture of 0.5g of the dye Eriochronic Black T with 4.5g hydroxylamine in 100ml of 95% ethyl or isopropyl alcohol were also added. 0.01M Standard EDTA titrant obtained by dissolving 3.723g of dry disodium ethylenediamine tetra-acetate dehydrate in water and diluting to 1000ml was slowly added with continuous stirring until reddish tinge disappeared from the solution and last few drops added at 3-5 seconds intervals changed the colour to blue which was the end point. This was calculated as:

$$\text{Hardness (EDTA) as mg/L } CaCO_3 = \frac{A \times B \times 1000}{\text{Ml Sample}} \quad (1)$$

Where A = ML Titration Sample

B = Mg $CaCO_3$ equivalent to 1.00Ml EDTA Titrant

Determination of Nitrate

Nitrate was determined by Ultraviolet Spectrophotometric Screening method. The analysis procedure involved the addition of 1mL HCl solution to 50ml filtered sample and the preparation of calibration standards in the range of 0 to 7mg NO_3 N/L by diluting to 550mL. The following volumes of intermediate nitrate solution 2.00, 4.00, 7.00 – 35ml standards NO_3 were treated in the same manner as the samples.

Absorbance or transmittance was read against re-distilled water set at zero absorbance or 100% transmittance. A wave-length of 220mm was used for NO_3 reading and a wave-length of 275nm was used to determine interference due to dissolved organic matter. For samples and standards, twice the absorbance reading at 275nm was subtracted from the reading at 220nm to obtain absorbance due to NO_3^-. A Standard curve was constructed by plotting absorbance due to NO_3^- against NO_3- concentration of standard using corrected sample. Absorbance and sample concentration were obtained directly from standard curve.

3. RESULTS AND DISCUSSION

Variation in Nitrate Concentration

The nitrate in the stagnant fresh and salt water samples determined over the period of the experimental investigation is shown in Figures 1 and 2.

ISSN 2278–5469 EISSN 2278–5450 I OPEN ACCESS

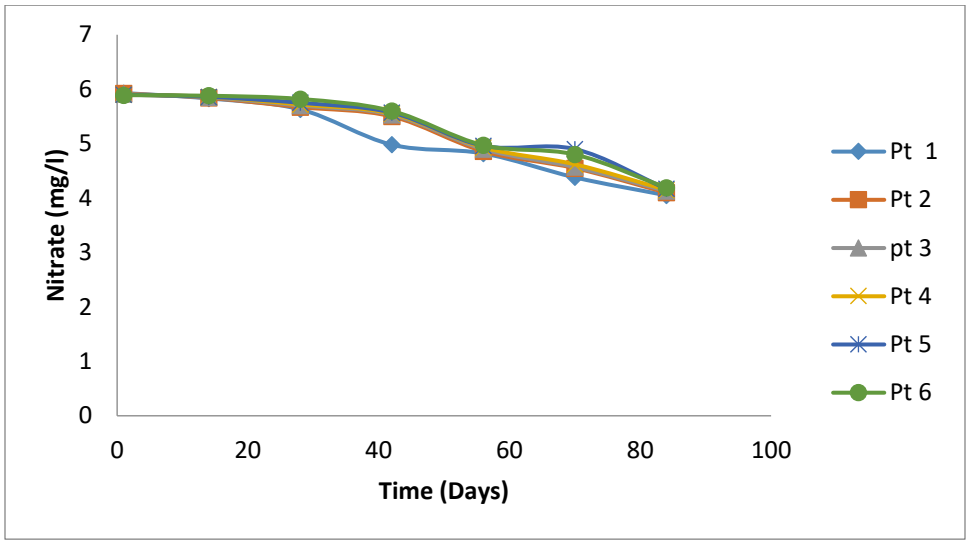

Figure 1: Variation of Nitrate in the Polluted Stagnant Fresh Water
Pt 1 (0m), pt 2 (0.25m), pt 3 (0.5m), pt 4 (0.75), pt 5 (1m) and pt 6 (1.25).

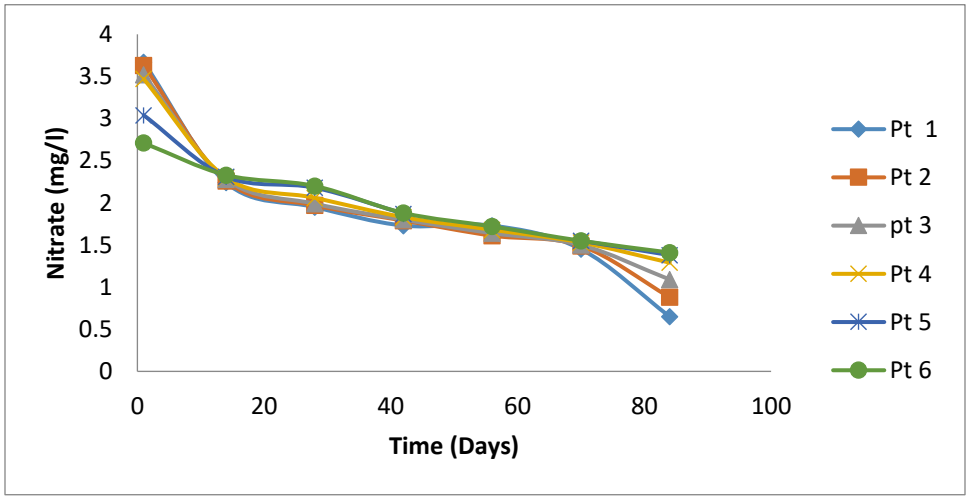

Figure 2: Variation of Nitrate in the Polluted Stagnant Salt Water
Pt 1 (0m), pt 2 (0.25m), pt 3 (0.5m), pt 4 (0.75), pt 5 (1m) and pt 6 (1.25).

Figure 1 shows the profiles of nitrate content with time at various depths for polluted fresh water, while Figure 2 shows the profiles of nitrate with time in polluted salt water. Before the crude oil pollution, nitrate content in fresh water was just 1.36mg/l and 2.9mg/l in salt water, but after pollution, it increased to 5.93mg/l in the fresh water and 3.67mg/l in the salt water. Again, nitrate content in fresh and salt water generally decreased with increase in time and randomly varied with increased in depth.

Nitrate content across the sampling points over the period of the analysis ranged between 4.05mg/l and 5.93mg/l in fresh water and 0.65mg/l and 3.67mg/l in salt water. Nitrate level across the sampling points in fresh and salt water is within the permissible limit of 50mg/l set by WHO. The results for nitrate content are shown in Tables 1 and 2 of Appendix for fresh and salt water. Reduction in nitrate over time may be attributed to interactions between microorganisms in the water system and the nitrates, which may act as nutrient for bacteria species in the system [21-23] Again, nitrate content in fresh water was higher than in salt water before and after pollution. This also implies the biological characteristics of the fresh water may be easily influenced over time, leading to biodegradation of hydrocarbon content if favourable hydrocarbon degrading bacteria are present in the water [24-26]. Lower concentration of nitrate (0.03 – 0.38mg/l), as compared to the range of nitrates obtained in the fresh water system, and was reported in Orashi River located in Ahoada West, Rivers State [27]. This Rivers was described as fresh water by the authors.

Variation in Total Hardness

Hardness in water is another important parameter, especially for drinking purpose. Calcium and magnesium levels, as well as pH and alkalinity interactions, can have a significant impact on water hardness levels in different communities. The total hardness of

the polluted stagnant fresh and salt water samples that was determined over the period of the experimental investigation is shown in Figures 3 and 4.

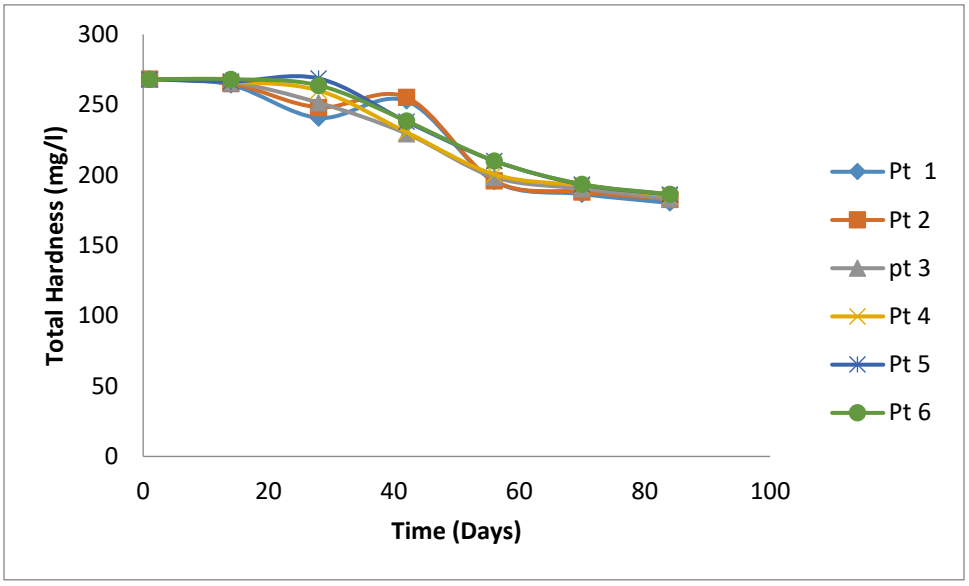

Figure 3: Variation of Total Hardness in the Polluted Stagnant Fresh Water

Pt 1 (0m), pt 2 (0.25m), pt 3 (0.5m), pt 4 (0.75), pt 5 (1m) and pt 6 (1.25).

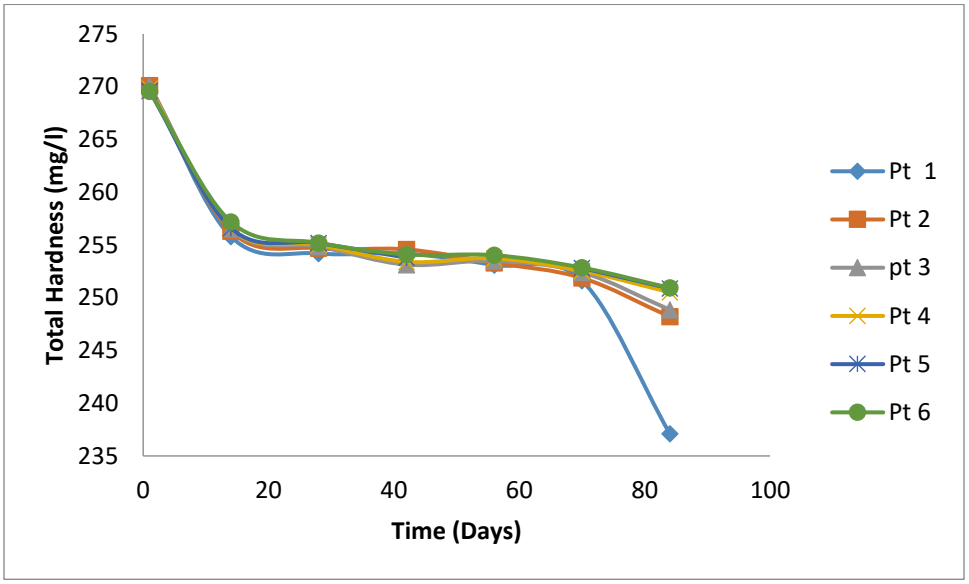

Figure 4: Variation of Total Hardness in the Polluted Stagnant Salt Water

Pt 1 (0m), pt 2 (0.25m), pt 3 (0.5m), pt 4 (0.75), pt 5 (1m) and pt 6 (1.25).

Figures 3 and 4 showed the profiles of total hardness with time at various depths for polluted fresh water and salt water, respectively. Again, before oil pollution, total hardness of fresh water was recorded as 53.9mg/l and 159.16mg/l in salt water, but after pollution, it increased to 268.4mg/l in the fresh water and 270.14mg/l in the salt water. Total hardness of fresh and salt water generally decreased with increase in time and marginally increased with increased in depth, especially in fresh water. Across the sampling points over the period of the analysis, the value of total hardness ranged between 180.2mg/l and 268.4mg/l in fresh water and 237.11mg/l and 270.14mg/l in salt water. Total hardness results are shown in Tables 3 and 4 of Appendix for fresh and salt water. Total hardness across the sampling points in fresh and salt water is within permissible limit of 500mg/l specified by the World Health Organisation for drinking water quality.

Total hardness of fresh water was higher than in salt water before pollution, but after pollution, there was increased concentration in salt water than in fresh water. In addition, total hardness reduction in salt water after pollution was also higher compared to the fresh water. Thus, 45.93% total hardness was reduced within 84 days in salt water compared to just 9.85%

ISSN 2278–5469 EISSN 2278–5450 I OPEN ACCESS

reduction recorded in fresh water. This may be due to more ionic compounds present in the salt water, and was evident in the high amount of conductivity and chloride recorded in the salt water. Hardness in water is caused by dissolved polyvalent metallic ions, predominantly calcium and magnesium ions.

4. CONCLUSION

This research illustrates the following conclusion:

i. The concentration of the nitrate decreases with increase in time and dispersion depth
ii. The concentration of the total hardness also decreases with increase in time and dispersion depth
iii. The variation in the total hardness induced the concentration of the nitrate concentration in the stagnant water media
iv. Variation in nitrate and total hardness was high in salt water medium than fresh water medium
v. This research predicts the significance of nitrate and total hardness in enhance bioremediation of crude oil on the effect of sedimentation and dispersion.
vi. This research has also revealed that nitrate as nutrient can act as an activator or inhibitor in bioremediation process as well as the total hardness, especially base on the available concentration of the medium.

Appendix

Table 1: Nitrate Measurement in Fresh Water

Time (Days)	Nitrate (mg/l)					
	Pt 1	Pt 2	pt 3	Pt 4	Pt 5	Pt 6
1	5.93	5.92	5.91	5.9	5.9	5.89
14	5.83	5.84	5.85	5.86	5.86	5.88
28	5.63	5.67	5.7	5.72	5.75	5.82
42	4.98	5.5	5.53	5.55	5.57	5.6
56	4.82	4.86	4.9	4.93	4.96	4.97
70	4.38	4.55	4.57	4.62	4.9	4.8
84	4.05	4.1	4.13	4.15	4.17	4.19

Table 2: Nitrate Measurement in Salt Water

Time (Days)	Nitrate (mg/l)					
	Pt 1	Pt 2	pt 3	Pt 4	Pt 5	Pt 6
1	3.67	3.63	3.52	3.47	3.04	2.71
14	2.24	2.26	2.28	2.3	2.31	2.33
28	1.95	1.97	1.99	2.06	2.18	2.2
42	1.73	1.79	1.8	1.83	1.87	1.88
56	1.73	1.61	1.64	1.68	1.7	1.72
70	1.45	1.49	1.5	1.53	1.55	1.55
84	0.65	0.88	1.09	1.29	1.38	1.41

Table 3: Total Hardness Measurement in Fresh Water

Time (Days)	Total Hardness (mg/l)					
	Pt 1	Pt 2	Pt 3	Pt 4	Pt 5	Pt 6

ISSN 2278–5469 EISSN 2278–5450 I OPEN ACCESS

1	268.4	268.27	268.25	268.24	268.23	268.2
14	264.19	265.24	266.1	266.38	266.51	268.18
28	240.7	248.18	251.46	260.12	268.72	263.8
42	225.77	225.33	229.52	230.51	238.1	238.45
56	195.6	196	198.55	200.52	210.13	210.19
70	186.52	188.1	190.4	192.6	193.3	193.57
84	180.2	182.91	183.24	185.4	186.2	186.41

Table 4: Total Hardness Measurement in Salt Water

Time (Days)	**Total Hardness (mg/l)**					
	Pt 1	Pt 2	Pt 3	Pt 4	Pt 5	Pt 6
1	270.14	270.12	270.08	269.84	269.6	269.58
14	255.8	256.3	256.51	256.55	256.6	257.19
28	254.2	254.69	254.87	255.02	255.18	255.2
42	254.18	254.58	253.13	253.4	253.8	254.1
56	253.1	253.31	253.5	253.74	253.95	254.03
70	251.61	251.87	252.4	252.53	252.81	252.85
84	237.11	248.2	248.86	250.52	250.88	250.93

Funding

This study has not received any external funding.

Conflicts of interests

The authors declare that there are no conflicts of interests.

Data and materials availability

All data associated with this study are present in the paper.

REFERENCES AND NOTES

1. Ukpaka, C. P. & Ogoni, H. A. (2013). Model to Monitor and predict the total hardness density of Trans-Amadi River using the Application of Conversion and Dispersion, *Journal of modeling, simulation and control AMSE*, 74(2), 1-30.
2. Ukpaka, C. P. (2018). Predictive Model of Plug Flow Reactor for Sodium Benzoate Production, *Science and Technology*, 4, 158 – 172.
3. Ukpaka, C. P. (2018a). Performance Evaluation of Batch Reactor for Sodium Benzoate Production, *Discovery*, 54(274), 387 – 386.
4. Ukpaka, C. P. (2018b). Remediation of Crude Oil in Loamy Soil: The Integration of Improved Oil Palm Fiber (*Tekena Species*) Dried in Dark Environment, *Discovery Science*, 14, 65 – 73.
5. Chukwu, E. O & Ukpaka, C. P. (2018). Investigation on characteristics of potato Waste degradation in an anaerobic digester: The influence of pH, *Science and Technology*, 4, 173 – 182.
6. Ikenyiri, P. N., Abowei, F. M. N., Ukpaka, C. P & Amadi, S. A. (2019). Application of Langmuir Isotherm on Adsorption to Monitor the uptake of oil using Aburu sawdust in Seawater medium, *Science and Technology*, 5, 30 – 37.
7. Nneke, P. O & Ukpaka, C. P. (2019). Adsorption of Kerosene by locally formulated adsorbent from clay and sawdust, *Indian Journal of Engineering*, 16, 46 – 59.
8. Wecheonwu, B. C, Ukpaka, P. C, Puyate, Y. T & Ehirim, E. O. (2019). Influence of Microorganisms on Aluu Crude Oil polluted soil environment in Niger Delta. *Indian Journal of Engineering*, 55, 285.
9. Okwu, N. O & Ukpaka, C. P. (2020). Crude oil remediation in selected soil environment of Niger Delta area of Nigeria, *Discovery*, 56(289), 16-25.

10. Ukpaka, C. P & Okwu, N. O. (2020). Integration of oil palm fibre for remediation of crude oil polluted soil environment, *Discovery*, 56(289), 1-15.
11. Ukpaka, C.P., Sinee, B.L & Harmony, N. (2020). Crude Oil Degradation in Loamy Soil Using Neem Root extracts: An Experimental Study. *International Scientific Organization: Chemistry International*, 6(3) 160-167.
12. Ukpaka, C. P. (2020). Development of mathematical model to predict the quantum energy of an electron in an orbit of hydrogen, lithium and sodium, *International Scientific Organization: Chemistry International*, 6(4), 179-186.
13. Kio, V. I., Ukpaka, C. P & Goodhead, T. O. (2020). Bioremediation of Diesel Contaminated Loamy Soil using Corn Cob, *International Journal of Chem-informatics Research*, 6(1), 12-21.
14. Ugiri, A. C., Ukpaka, C. P & Ikenyiri, P. N. (2020). Evaluation of Petroleum Hydrocarbon Remediation on Soil Environment Using *Mangnifera Indica* (Mango) Seed., *International Journal of Chem-informatics Research*, 6(1), 22-36.
15. Ukpaka, C. P & Gift-Onyesoh, J. B, (2020). Examination of Microbial and pH Contribution of *Azadirachta Indica* Leaf on Crude Oil Degradation in Soils, *International Journal of Chemical and Molecular Engineering*, 6(1), 10-17.
16. Essiet, C, Ekong., Ukpaka, C. P & Nkoi, B. (2020). Improvement of solid waste management system in Port Harcourt city using reliability tool, *Journal of Newviews in Engineering and Technology*, 2(1), 25-33.
17. Ukpaka, C.P. (2020). Comparison of Treatment and Purification of Salt Water Using *Moringa Oleifera* Leaf: The Concept of Photo-integration. *International Journal of Photochemistry*, 6(1), 44–53.
18. Ukpaka C. P. & Gift-Onyesoh, J. B. (2020). Modeling of the Enzymatic Hydrolysis of various wood saw dust. *International Journal of Prevention and Control of Industrial Pollution.* 6(1), 18-26.
19. Onusaka, S. A., Ukpaka, C. P., Orji, C. (2020). Development of momentum transfer and kinetic model for hydrocarbon degradation in a flow system, *International Journal of Chemical Separation Technology*, 6(2), 17-34.
20. Ukpaka, C. P. (2020). Overview of petrochemical solid waste composition and impact on environment, *International Journal of Chemical Engineering and Processing*, 6(2), 6-11.
21. Ukpaka, C.P., Uku, Philip Eruni., Amadi, S.A., Dagde, K. K. (2020). Characteristics of Physicochemical Parameters of Elephant Grass Mixture for the Remediation of Crude Oil Polluted Swampy Soil, *International Journal of Petroleum and Petrochemical Engineering*, 6(4), 33-41.
22. Ukpaka, C.P., Uku, Philip Eruni., Amadi, S.A., Dagde, K. K. (2020). Mathematical modeling of the effect of functional parameters on the biogradation rate of hydrocarbon. *Research and Reviews: Journal of Bioinformatics*, 7(3), 34-43,
23. Ukpaka, C. P & Pepple, L. N. (2020). Comparative Study of Biodegradation of Hydrocarbons in Soils under Nipa Palm (Nypa Fruticans wurmb) Treatment. *Research & Reviews: Journal of Ecology*. 9(3), 20-32.
24. Ukpaka C.P. (2022). Examination of the Physicochemical Properties of Lube Oil on the Effect of Load Utilization in a Generator Set. Journal of Thin Films, Coating Science Technology and Application. 9(1), 1–9
25. Cunningham, C.J., Ivshina, L. B., Lozinsky, V. I., Kuyukina, M. S. & Philip, J. C. (2004). Bioremediation of Diesel-Contaminated Soil by Micro-organisms immobilized in Polyvinyl Alcohol. *International Biodeterioration and Biodegradation*, 54(2-3), 167-174.
26. Das, K. & Mukherjee, A. K. (2007). Crude Petroleum Oil Biodegradation Efficiency of Bacillus Subtilis ad Pseudomonas Aeruginosa Strains isolated from a Petroleum-Oil contaminated soil from North-East India. *Bioresource Technology*, 98(7), 1339-1345.
27. Daugulis, A. J. & McCracken, C. M. (2003). Microbial Degradation of high and low molecular weight poly-aromatic hydrocarbons in a two phase partitioning bioreactor by two strains of *Sphingomonas Sp*. *Biotechnology Letters*, 25(17), 1441 – 1444

ISSN 2278–5469 EISSN 2278–5450 I OPEN ACCESS