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Modelling Phytoremediation Augmented Bioremediation Based On Order Of Reaction

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ABSTRACT

Bioremediation and phytoremediation of crude oil contaminated soils has been studied based Total Petroleum Hydrocarbon content, using Locoweed and Sunflower as the plants for phytoremediation. The data was fit to kinetic models based on a substrate concentration driving force. The results reveal that bioremediation and phytoremediation are first order processes whose rates are directly proportional to the substrate concentration driving force. Phytoremediation enhances the rate of the bioremediation process by reducing the ultimate substrate concentration achievable through bioremediation alone, though the first order rate constant is reduced in the process. Locoweed shows higher effectiveness in enhancing the remediation process in comparison to Sunflower. Bioremediation reduces the contaminant concentration by about 65%, while when augmented with Phytoremediation, the contaminant concentration is reduced by 69% and 88% for Sunflower and Locoweed respectively.

Key words: Bioremediation, Phytoremediation, hydrocarbon, substrate, contaminated, model

INTRODUCTION

Petroleum hydrocarbons represent a complex mixture of organic compounds mainly grouped into four fractions: alkenes, aromatics, resins and asphaltenes (Ruijuan et al, 2013). Hydrocarbon pollution of the environment has remained a major challenge for man over the years and has been escalating in proportions with increase in industrial activities. Such pollutions are usually occasioned by human error, equipment failure, vandalism, wars and natural disasters. Prominent among the deleterious effects of such pollutions on land is the destruction of natural flora and fauna thereby ultimately reducing the capacity of the ecosystem to support life. Several techniques have been developed over the years to combat this menace. These techniques are grouped broadly into two namely; In-situ methods (such as leaching or washing, isolation and containment, volatilization, bioremediation and passive bioremediation) and Ex-situ methods (such as incineration, solidification and stabilization, soil washing, and land farming) (Das and Mukherjee, 2007). Bioremediation is a term that describes the deliberate use of organisms to remove or reduce man-made pollution. Bioremediation is the use of biological methods in restoring contaminated land, principally by the addition of bacteria and other micro-organisms that consume or neutralize contaminants in the soil (Gibson and Salyer, 1992). Microorganisms have been known to degrade hazardous compounds considered recalcitrant and resistant to biodegradation. Advantages of biological bioremediation compared to other treatment methods include destruction rather than transfer of contaminants to another medium, minimal exposure of workers to contaminants, longtime protection of public health and possible reduction in the

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duration of the remediation process (Okoh and Trejo-Hernandez, 2006; Machin-Ramitez et al, 2008). The natural bioremediation process usually needs to be enhanced because hydrocarbon biodegradation in soil can be limited by many factors such as nutrients, pH, temperature, moisture, oxygen, soil properties and contaminant presence (Atagana, 2008). Most of these limiting factors can be controlled but metals concentration poses more difficulty as mobility of microbes' enzyme degradation is impaired. This limiting factor and moisture content can be minimized through the employment of phytoremediation technology. Phyto-remediation is the use of living green plants for reduction and/or removal of contaminants from polluted soil, water and air. Phytoremediation is based upon the basic physiological mechanisms taking place in higher plants and associated microorganisms such as transpiration, photosynthesis, metabolism and mineral nutrition (Marmilori et al, 2006). A very promising approach to effective remediation of hydrocarbon contaminated soil is to combine bioremediation with phytoremediation in a hybrid scheme. Investigation into the effectiveness of this scheme and development of models to predict its operations is the major challenge addressed by this research.

Emon (2008) carried out research work on phytoremediation of oil contaminated desert soil using the rhizosphere effect. In his work, four plots of $2x2m^2$ each were delimited in an area with no history of pollution, 0-50cm depth was ploughed on each plot. Ploughed soils were mixed with wreathed crude oil so as to give initial concentration of 2.2-2.3 wt% soil. Each plot received the suitable nitrogen and phosphorus concentration. Plot 1 was seeded with 100 viable Faba seed at the beginning of January. Plot 2 was seeded with 100 viable grain Zea mays at the beginning of May. Plot 3 was seeded with 200 viable triticum aestivuml at the beginning of November while plot 4 was without seeding. After 60 days growth period of each plant, samples were taken from the rhizosphere and non rhizosphere soil of each plant; also at the beginning of the experiment samples were collected. Residual oil and its fraction were determined by adding 10g of anhydrous sodium sulphates to 10g of air-dried soil samples. The hydrocarbons were Soxhlet extracted and evaporated in a pre-weighed dish and the amount of the total petroleum hydrocarbons (TPHs) was determined and the loss (%) of TPH was calculated. Extracted residual oil was suspended in n-hexane and filtered through tared filter paper to remove and determine the insoluble fraction (asphaltenes). Hexane soluble fraction was fractionated by solid-liquid chromatography to have saturates, aromatic and resins. From these results TPH was reduced by 30% in the rhizosphere soil of Viciafaba plant and by 16.8% and 13.7%. In Zea mays and triticum aestivuml respectively. TPH biodegradation was enhanced in the rhizosphere soil of the legume plant (viciafaba) then other two monocotyledon plant.

Freshthe et al (2014) carried out experiment to investigate the quantitative uptake of phenanthrene's (as one of most important PAHs in crude oil) by salicomia eurapea. In their research work salicomia plantlets were taken from Eshtehard plant which is located in Karaj, at Borz, Iran. They were transplanted and exposed to various concentration of crude oil (4.5-16-27.5-32.5g/kg soil). Spectrophotometer and gas chromatography - mass spectroscopy methods were used to determine and identify the phenanthrene uptake, in roots and stalks, also the plants appearance were checked out. From their observation the highest uptake was at 8mg crude oil per 1g of soil.

Olujuyigbe and Aruwajoye (2014) studied rhizoremediation on hydrocarbon contaminated soil with paspalum vaginatum, a stoloniferous, perennial grass of the family poaceae found mainly in the subtropics and tropical regions of the world. The contaminated soil analyses indicated a decrease in the level of hydrocarbons present after phytoremediation. There was equally, a

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significant reduction in growth parameters of the plant such as plant height, leaf number, tiller number and total dry weight, compared to the control. Anatomical studies of sections of the plants, stems did not reveal the presence of accumulated oil within the tissues but rather denatured internal parenchyma cells traction ways observed. Bacteria capable of degrading hydrocarbon were isolated from the rhizosphere of the grass. The isolates include Arthrobactersp, Bacilluspumilus, Bacillus sphaericus and Serratiamarcescens. Growth in mineral salts medium supplemented with 0.5% crude oil for 21 days resulted in 95.9%, 95.6%, 98.3% and 96.7% degradation of oil for Arthrobaiter sp., B. pumolus, S. Macescens and B. Sphaericus respectively. A soil microcosm set up with the consortium of the isolates resulted in 87.70% degradation of crude oil in 45 days.

Ezonu (2013) studied the decomposition of used motor oil in soil as influenced by plant treatment. In their work, soil was contaminated with used motor oil to a concentration of 1.5% w/w. The contaminated soil was seeded with soyabean (Glycine max)/green bean (Phaseolas vulgaris); sunflower (Helianthus annus)/Indian mustard (Brassica juncea); mixed grasses/maize (zea mays); and mixed clover (red clover, Trifoliumpratense/ladino clover, Trifoliumrepens) and incubated Soxhlet-extractable oil and grease remaining in the soil was monitored after 100 and 150 days. After 150days in the clover treatment, the added oil was no longer detected. A total of 67% of the oil was removed in sun-flower/mustard, and with addition of NPK fertilizer, the oil was completely removed. The grass/maize treatment resulted in a 38% oil reduction, which increased to 67% with fertilizer application. The control treatment reduced oil in the soil by 82% when fertilizer was added. At 150 days the sunflower/mustard and wheat/oats treatments produced the greatest biomass in the presence of used oil. Gas chromatograph/Mass spectroscopy (GC/MS) spectra of oil/ grease extracts revealed the presence of new peaks associated with hydrocarbon decomposition. The presence of new hydrocarbons was corroborated by changes in Fourier- transformed infrared spectrometry (FTIR) spectra. Fertilizer addition during treatments resulted in negligible changes to FTIR bands. Based on oil/grease residues and biomass results, the clover and sunflower/mustard are considered superior to the other plant treatments in terms of overall phytodegradation of used oil hydrocarbons.

Ajoy et al (2012) evaluated the use of phytoremediation to clean up soils contaminated with weathered curded oil. Alkane's Total Petroleum Hydrocarbon (TPH) and polycyclic Aromatic Hydrocarbon (PAH) degradation level in the crude–oil contaminated soil was significantly higher in rhizosphere soil as compared to bulk soil. Results from their study showed that TPH levels after 6months were significantly lower in vegetated fertilized plots than in non–vegetated, non–fertilized plots. Vegetation establishment and fertilizer addition result in increased bacterial and fungal degradation levels.

Kinetics of Biodegradation

The kinetics of biodegradation is a set of empirically derived rate laws. Three suffice to describe most biological reactions are:

$$\frac{dC_A}{dt} = -k_0 \quad \text{Zero order} \quad (1)$$

$$\frac{dC_B}{dt} = -k_1 C_A \quad \text{First order} \quad (2)$$

$$\frac{dC_B}{dt} = -k_1 C_A C_B \quad \text{Second order} \quad (3)$$

k_0, k_1, k_2 are rate constants in units of mol/1-sec, 1/sec and 1/mol-sec respectively

C_A, C_B are some reacting species.

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Osoka and Onyelucheya (2010) presented a modified approach that will be adopted for zero order, first order and second order kinetics:

$$\frac{dS}{dt} = -k \quad (4)$$

$$\frac{dS}{dt} = -k(S - S_\infty) \quad (5)$$

$$\frac{dS}{dt} = -k(S - S_\infty)^2 \quad (6)$$

Where S is substrate concentration, t is time, k is the reaction rate constant and S∞ is the ultimate substrate concentration.

Zero Order

Integrating equation (4) subject to the condition that $S = S_o$ when $t = 0$, we have;

$$S = S_o - k\,t \quad (7)$$

Where S_o is the initial substrate concentration

First Order

Integrating equation (4) subject to the condition that $S = S_o$ when $t = 0$, we have;

$$ln\left(\frac{S-S_\infty}{S_o-S_\infty}\right) = -k\,t \quad (8)$$

Equation (8) gives;

$$\left(\frac{S-S_\infty}{S_o-S_\infty}\right) = \exp(-k\,t) \quad (9)$$

Re-arranging equation (9) gives;

$$S = S_\infty + (S_o - S_\infty)\exp(-k\,t) \quad (10)$$

If $S_\infty = 0$, equation (10) reduces to

$$S = S_o \exp(-k\,t) \quad (11)$$

Second Order

Integrating equation (6) subject to the condition that $S = S_o$ when $t = 0$, we have;

$$\left(\frac{1}{S-S_\infty}\right) - \left(\frac{1}{S_o-S_\infty}\right) = k\,t \quad (12)$$

On simplification of the above equation we have;

$$\frac{S_o-S}{(S-S_\infty)\,(S_o-S_\infty)} = k\,t \quad (13)$$

Further re-arrangement of equation (13) gives;

$$S = \frac{S_o+S_\infty(S_o-S_\infty)k\,t}{1+(S_o-S_\infty)\,k\,t} \quad (14)$$

If $S_\infty = 0$, equation (14) reduces to

$$S = \frac{S_o}{1+S_o\,k\,t} \quad (15)$$

Table 1: Summary of the Kinetic equations and parameters for different reaction orders

s/no	Order of Reaction	Kinetic Equation	Kinetic Parameters
1	Zero Order	$S = S_o - k\,t$	K
2	First Order	$S = S_o \exp(-k\,t)$	K
3	First Order	$S = S_\infty + (S_o - S_\infty)\exp(-k\,t)$	K, S∞
4	Second Order	$S = \frac{S_o}{1 + S_o\,k\,t}$	K

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5	Second Order	$S = \frac{S_o + S_\infty(S_o - S_\infty)k\,t}{1 + (S_o - S_\infty)\,k\,t}$	K, S∞

METHODOLOGY

Soil samples were collected from Erema town of Ogba-Egbema-Andoni LGA of Rivers State, Nigeria on 4^o 55' 55"N and 6^o 32' 48" E. Experimentation was carried out in microbiology and Chemical/Petrochemical Engineering laboratories in Rivers State University of Science and Technology, Port Harcourt. Mud auger were used at 0-30cm depth to collect muddy polluted soil. Glass containers fitted with plastic lids were used. The microbiology laboratory was used to isolate existing native microbes present in each sample. Microbes so isolated were cultured and identified. The soil samples were inoculated with the cultured microbes and nutrients addition was controlled to allow for increase in microbial population and hence increase in degradation rate of carbon source. This involved the application of nitrogen and phosphorus fertilizers. Sunflower and Locoweed Plantlets were sought for and planted in two of the polluted soil samples and studied with aim of examining the effect of flora and fauna applications in bioremediation, while the third soil sample had nothing planted on it.

Residual oil and its fraction were determined by adding 10g of anhydrous sodium sulphates to 10g of air-dried soil samples. The hydrocarbons were Soxhlet extracted and evaporated in a pre-weighed dish and the amount of the total petroleum hydrocarbons (TPHs) was determined and the loss (%) of TPH was calculated. This was done in two weeks intervals for twenty weeks and recorded.

RESULTS AND ANALYSIS

The graphical fit results for bioremediation based on kinetic equation models for various reaction orders are shown in the following figures.

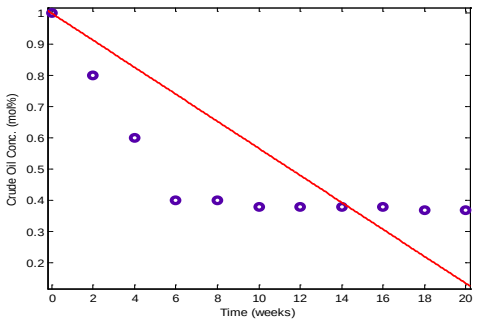

Fig. 1: Zero Order for Bio-remediation

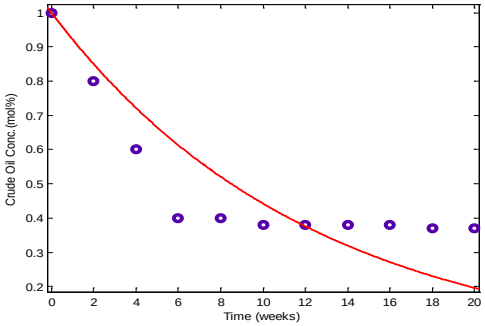

Fig. 2: 1st Order for Bio-remediation(S∞ = 0)

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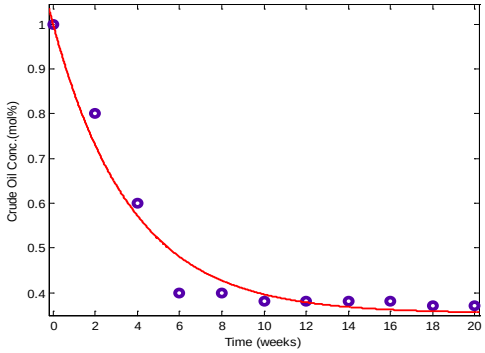

Fig. 3: 1st Order for Bio-remediation(S∞> 0)

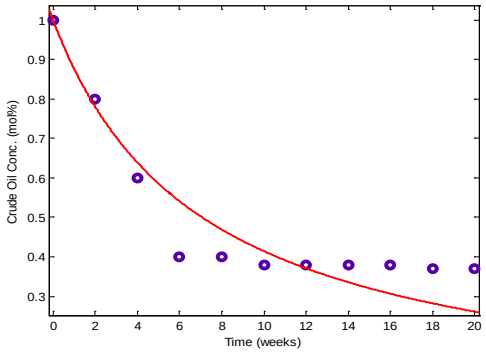

Fig. 4: 2nd Order for Bio-remediation(S∞ = 0)

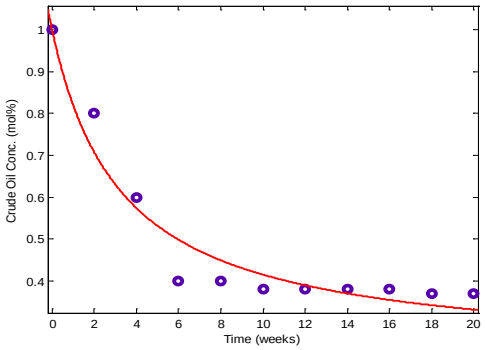

Fig. 5: 2nd Order Model for Bio-remediation(S∞> 0)

The summary of the numerical fit result for the bioremediation based on kinetic equations for different reaction orders is given in Table 2 below.

Table 2: Numerical fit result summary of the different reaction orders for bioremediation

Kinetic equation	k	S∞	R^2	Adj-R^2	RMSE	SSE
$S = S_o - k\,t$ (Zero Order)	0.04323	-	0.1916	0.1916	0.1931	0.3729
$S = S_o \exp(-k\,t)$ (First Order)	0.08137	-	0.6823	0.6823	0.1210	0.1465
$S = S_\infty + (S_o - S_\infty)\exp(-k\,t)$ First Order	0.2712	0.3535	0.9695	0.9661	0.03954	0.01407
$S = \frac{S_o}{1+S_o\,k\,t}$ (Second Order)	0.1412	-	0.8812	0.8812	0.07401	0.05478
$S = \frac{S_o + S_\infty(S_o - S_\infty)k\,t}{1 + (S_o - S_\infty)\,k\,t}$ Second Order	0.3856	0.2208	0.9443	0.9381	0.05344	0.02571

It can be observed from Fig. 1 to Fig. 5, that Fig. 3 and Fig. 5 which represent first order and second order reactions with an ultimate substrate concentration greater than zero (S∞> 0) respectively, fit well to the experimental data, while other models have poor fits. The numerical fit results reveal that the first order reaction with an ultimate substrate concentration greater than zero (S∞> 0) gave the best fit. Thus suggesting that bioremediation is a first order reaction. The graphical results for the locoweed assisted phyto-remediation based on the kinetic equation for different reaction orders are given in the following graphs.

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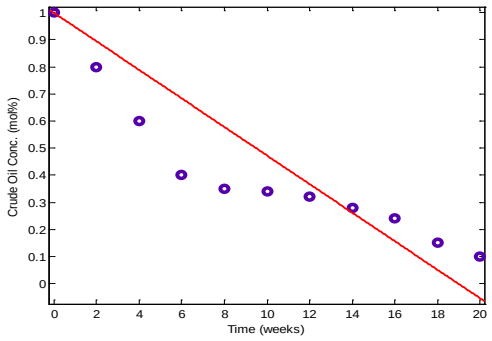

Fig. 6: Zero Order for Locoweed

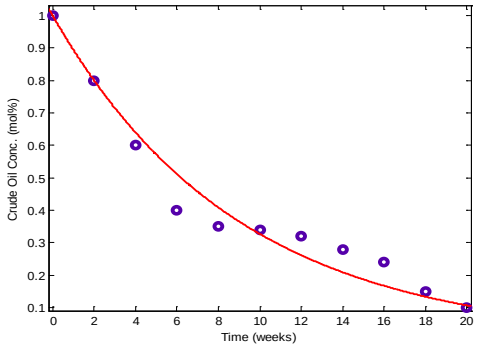

Fig. 7: 1st Order for Locoweed (S∞=0)

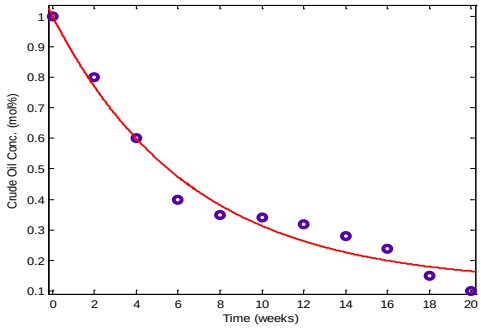

Fig. 8: 1st Order for Locoweed (S∞>0)

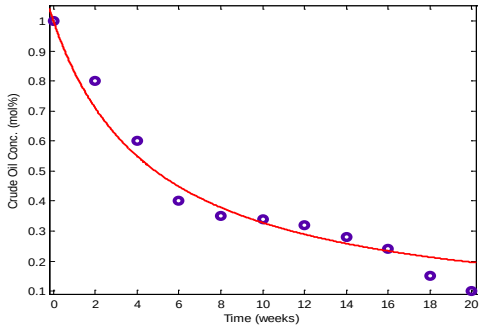

Fig. 9: 2nd Order for Locoweed (S∞=0)

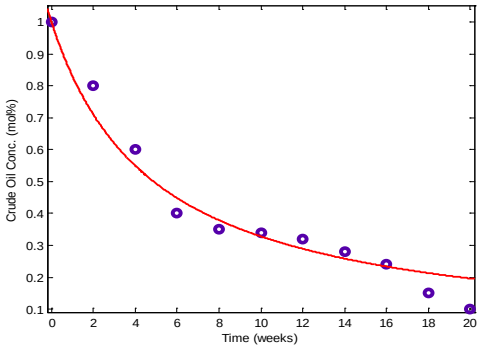

Fig. 10: 2nd Order for Locoweed (S∞>0)

Table 3: Numerical fit Results for Locoweed enhanced Phytoremediation based on reaction order

Kinetic equation	k	S∞	R^2	Adj-R^2	RMSE	SSE
$S = S_o - k\,t$ (Zero Order)	0.05266	-	0.6876	0.6876	0.1543	0.2381
$S = S_o \exp(-k\,t)$ (First Order)	0.1115	-	0.9585	0.9585	0.05626	0.03166
$S = S_\infty + (S_o - S_\infty)\exp(-k\,t)$ First Order	0.1527	0.1241	0.9727	0.9696	0.04811	0.02083
$S = \frac{S_o}{1+S_o\,k\,t}$ (Second Order)	0.2045	-	0.9622	0.9622	0.05367	0.02881

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$S = \frac{S_o + S_\infty(S_o - S_\infty)k\,t}{1 + (S_o - S_\infty)\,k\,t}$ Second Order	0.2045	2.121e-11	0.9622	0.9622	0.05367	0.02881

It can be observed from Fig. 6 to Fig. 10 that Fig. 7, Fig. 8, Fig. 9 and Fig. 10 which represent first order and second order reactions respectively fit well to the experimental data, while the zero order model has a poor fit. The numerical fit results reveal that the first order reaction with an ultimate substrate concentration greater than zero (S∞> 0) gave the best fit. Thus suggesting that phytoremediation is a first order reaction and the ultimate substrate concentration will never go to zero.

The graphical results for the sunflower enhanced phyto-remediation based on the kinetic equation for different reaction orders are given in the following graphs.

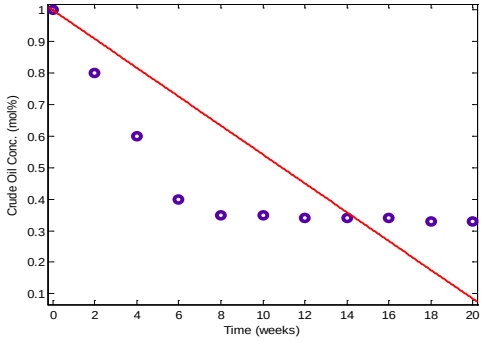

Fig. 11: Zero Order for Sunflower

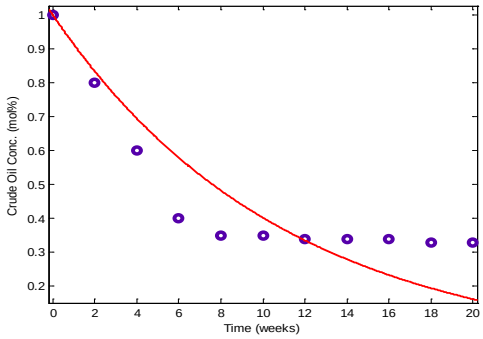

Fig. 12:1st Order for Sunflower (S∞ = 0)

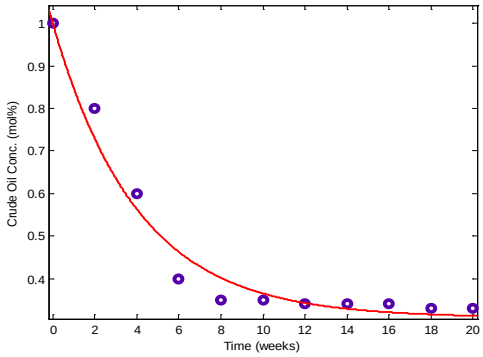

Fig. 13: 1st Order for Sunflower (S∞> 0)

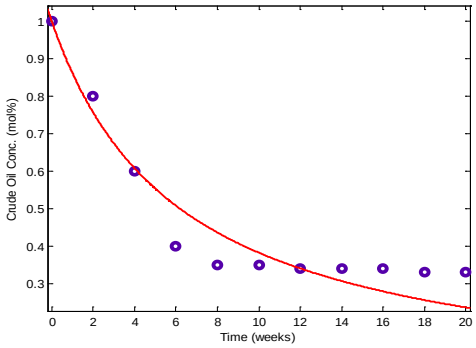

Fig. 14: 2nd Order for Sunflower (S∞ = 0)

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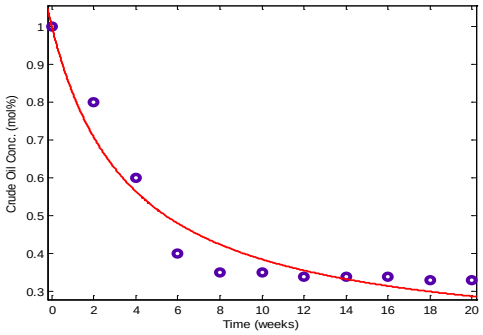

Fig. 15: 2nd Order for Sunflower (S∞> 0)

Figure 4:Numerical fit results for Sunflower enhanced Phytoremediation based on reaction order

Kinetic equation	k	S∞	R^2	Adj-R^2	RMSE	SSE
$S = S_o - k\ t$ (Zero Order)	0.04577	-	0.2759	0.2759	0.1960	0.3840
$S = S_o \exp(-k\ t)$ (First Order)	0.09095	-	0.7655	0.7655	0.1115	0.1244
$S = S_\infty + (S_o - S_\infty)\exp(-k\ t)$ First Order	0.2493	0.3082	0.9728	0.9698	0.04002	0.01441
$S = \frac{S_o}{1+S_o\ k\ t}$ (Second Order)	0.1612	-	0.9223	0.9223	0.0642	0.04121
$S = \frac{S_o + S_\infty(S_o - S_\infty)k\ t}{1 + (S_o - S_\infty)\ k\ t}$ Second Order	0.3127	0.1530	0.9494	0.9437	0.05462	0.02685

It can be observed from Fig. 11 to Fig. 15 that Fig. 13 and Fig. 15 which represent first order and second order reactions with the ultimate substrate concentration being greater than zero (S∞> 0) respectively fit well to the experimental data, while the other models have poor fit. The numerical fit results reveal that the first order reaction with an ultimate substrate concentration greater than zero (S∞> 0) gave the best fit. Thus suggesting that phytoremediation is a first order reaction and the ultimate substrate concentration will never go to zero.
It can be observed that the first order model fit well to both bioremediation and phytoremediation processes with the ultimate substrate concentration never going to zero. The summary of the fit is given in table 5 below.

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Table 5: First order model fit results for all three processes

Remediation Process	k	S∞	R^2	Adj-R^2	RMSE	SSE
Bioremediation	0.2712	0.3535	0.9695	0.9661	0.03954	0.01407
Phytoremediation (Locoweed)	0.1527	0.1241	0.9727	0.9696	0.04811	0.02083
Phytoremediation (Sunflower)	0.2493	0.3082	0.9728	0.9698	0.04002	0.01441

CONCLUSION

Bioremediation and phytoremediation augmented bioremediation are based on the same mechanism, based on the result of this study. Bioremediation and phytoremediation are first order processes whose rates are directly proportional to the substrate concentration driving force. Phytoremediation enhances the rate of the bioremediation process by reducing the ultimate substrate concentration achievable through bioremediation alone, though the first order rate constant is reduced in the process. Locoweed shows higher effectiveness in enhancing the remediation process in comparison to Sunflower. Bioremediation reduces the contaminant concentration by about 65%, while when augmented with Phytoremediation, the contaminant concentration is reduced by 69% and 88% for Sunflower and Locoweed respectively.

REFERENCES

Ajoy K.M., Priyangashu M.S, Jayaseelan C.P., Veerana A.C, Bina S., Banuwari L and Jagatai D.,(2012)“Large Scale Bioremediation of Petroleum Hydrocarbon Contaminated Waste at Indian Oil Refineries: case studies”, International Journal of Life Science and Pharma Research, Vol 2, Issues 4.

Atagana, H. I. (2008), “Compost bioremediation of hydrocarbon contaminated soil inoculated with organic manure”, African Journal of Biotechnology, 7(10); 1516 – 1525.

Das, K. and Mukherjee (2007), “Crude Petroleum Oil Biodegradation Efficiency of bacillus Subtilis and Pseudomonas Aeruginosa Strain Isolated from a Petroleum Contaminated Soil from North-East India”, Bioresource Technology, 98: 1339 – 1345.

Emon A.D. (2008),“Phytoremediation of oil contaminated desert soil using the rhizosphere effect”, Global Journal of Environmental Research, 2(2) ; 66- 73.

Ezonu C.S., (2013), “Phytoremediation and Crude Oil Bioaccumulation Potential of Zea Mays L.”, Journal of Environmental Science, Toxicology and Technology, vol. 7, Issue 2, Pp 24-26.

Freshthe G., Mohammed M. Z,Sajjad G., Seyedah H.M., Malihe F., Hamed G., Mash Z , Azam B., Nayer A.K S. and Mashen A (2014), “Bioremediations of the Crude Oil Contamination of Soil by the Indigenous, Herbaceous plant Salicorniacurapra in Iran”, Thirata 3(2): 17409.

Gibson, D. T. and Sayler, G. S. (1992), “Scientific Foundation for Bioremediation”, American Academy of Microbiology, Washington DC, 1- 24.

ISSN 2348 – 7968

Machin-Ramitez, C. A. I, Morales, M. and Mayolo-Deloisa, R. (2008), "Slurry phase bioremediation of weathered oily sludge waste", Chemosphere 70, 734 – 744.

Marmiroli, N., Marmiroli, M., Maestri, E. (2006). Phytoremediation and phytotechnologies: A review for the present and the future. In: Twardowska, I., Allen, H.E, and Haggblom, M.H. (eds). Soil and water pollution monitoring, protection and remediation. Springer, Netherland.

Okoh, A.I., Trejo-Hernandez, M.R. (2006) Remediation of petroleum polluted systems: Exploiting the bioremediation strategies. African Journal of Biotechnology 5(25): 2520 – 2525.

Olujuyigbe S.O. and Aruwajoye D.A. (2014), "Phytoremediation of Diesel Oil Contaminated Soil using Seeding of two Tropical Hardware Species (KhayaSenegalensis and Terminal Superba)", International Journal of Life Scientific and Engineering Research Volume 5, Issue 5.

Osoka, E.C. and Onyelucheya, O.E. "Data-Driven Model for Palm Bunch Ash Enhanced Bioremediation of Crude-Oil Contaminated Soil", Inter. Journal of Engineering, 4 (3), 2010, 357-364.

Ruijuan, F., Shuhai, G., Tingting, L.,Fengmei, L, Xuelin, Y., Bo, W. (2013), "Continuous of electrokinetics and bioremediation in the treatment of different petroleum compounds", Clean-soil, Air, water, 43(2), 251-259.