



Crude oil remediation in selected soil environment of Niger Delta Area of Nigeria

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General Note



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ABSTRACT

A pilot study was conducted on three different soil type contaminated with crude oil using the application of bio-simulation to examine the effect of the stimulant on the rate of degradation of the crude oil by the indigenous microbes. The contaminated soil was remedied with the application of the *Aloe vera* juice deficient of the essential nutrients which are needed to boost the activities of the microbes which feed on the crude. These nutrients are found in *Aloe vera* juice thereby making it a bio-stimulant. This research shows high efficiency in bioremediation of over 70% with bio-stimulate whereas the sample without the stimulant was found to be 45% within 30 days. The kinetic model developed can be used in monitoring, predicting and simulating the rate of degradation of hydrocarbons present in a polluted soil undergoing bioremediation under the influence of this stimulant.

Key words: Crude oil, remediation, selected soil, environment, aloe vera juice, Niger Delta, Nigeria

1. INTRODUCTION

The effects of crude oil spillage maybe short or long term and this depends on the kind of oil, quantity of oil, distance discharged, time of the year, weather condition, ocean current, and average water temperature. Oil spill have posed several adverse effects on the ecosystem and it is a major source of pollution on land, water and even air [1-2]. Pollution is a change in the environment that is hazardous to man and his ecosystem [3]. Some of its negative effects include: The soil is the home to thousands of different species of bacteria, nematodes, micro-arthropods, microscopic fungi, algae, cyanobacteria, actinomycetes, protozoa, macroscopic earthworms, and insects. The functions of these organisms are summarized. They decompose organic matter to produce humus which helps retain moisture, encourage formation of soil structure and also is responsible for suppressing plant disease [4]. They carry out mineralization which is recycling nutrients to their natural form for plants to utilize. Some soil microbes secrete polysaccharides, gums and glycoproteins which gum the soil minerals needed for plant growth. Some microbes such as *Rhizobium* bacteria carry out nitrogen fixation which is the conversion of atmospheric nitrogen (N_2 gas) to ammonia (NH_3). This account for 60% of the nitrogen fixed on Earth while the remaining is from artificial fertilizers [5]. Some soil microbes produce substances that promote plant growth including auxins, gibberellins and antibiotics. Some soil microbes control plant pest and disease. Examples *Bacillus thuringiensis* (Bt) controls caterpillar pests of crops, *Trichoderma* bio-control fungal disease of plants mainly root disease. The oil clogs the pores of the soil which reduces soil aeration, infiltration of water into the soil, increased bulk density of the soil which may affect plant growth. Crude oil which is denser than water may reduce and restrict permeability [6]. This inhibits the activities of the soil microbes making the soil incapable of sustaining plants and other soil organisms [6]. Oil spill pollution destroys the natural habitations and deprive some organisms of their existence. It poisons and damage several food sources for various habitats. It poses negative on the economy as it kills aquatic life thereby reducing trades [7].

It decreases the insulating competence of birds and this increases inconsistency in their temperature reducing their buoyancy in water. Direct contact with crude can cause irritation and inhaling the volatile components of crude maybe hazardous. Consuming crude oil contaminated food maybe disastrous. Recreational activities areas are sometimes polluted and disrupted [8]. Oil spillage destroys house and other properties and it may cause health hazards [8].

The clean – up and recovery may take days, weeks, months, or even years and depend on certain factors and these include the kind of crude that has been split, the thermal reading of the affected environment (this affects the evaporation as well as biodegradation), the kind of surrounding, the period of contamination, rate or speed in which the contaminated area is able to recycle or restore or itself [9].

The main threats to human health from heavy metals are related with exposure to lead, cadmium, mercury and arsenic [9-14]. Some heavy metals are dangerous to health and the environment (e.g. mercury, cadmium, lead, chromium), some may cause corrosion (e.g. zinc, lead), some are harmful in other ways (e.g. arsenic may pollute catalysts) [15-19]. Some of these elements are actually necessary for humans in minute amounts (cobalt, copper, chromium, manganese, nickel) while others are carcinogenic or toxic, affecting, among others, the central nervous system (manganese, mercury, lead, arsenic), the kidneys or liver (mercury, lead, cadmium, copper) or skin, bones, or teeth (nickel, cadmium, copper, chromium) [20-23].

One of the largest problems associated with the persistence of heavy metals is the potential for bioaccumulation and biomagnification causing heavier exposure for some organisms than is present in the environment alone. Through precipitation of their compounds or by ion exchange into soils and muds, heavy metal pollutants can localize and lay dormant. Unlike organic pollutants, heavy metals do not decay and thus pose a different kind of challenge for remediation.

2. MATERIALS AND METHODS

Degree of degradation

The degree of degradation (DD): is calculated using the formula below

$$DD = \frac{THC_f - THC_i}{THC_i} \times 100$$

Where, THC_i represent the initial amount of hydrocarbon whereas THC_f represent the hydrocarbon residual after the period of the experiment.

The work is concerned with the investigation of the kinetics of crude oil degradation using aloe vera leaf extract. Before an attempt to study the action of this leaf extract on crude oil polluted soil environment it is necessary to find out the characteristic

constituents of the aloe vera leaf extract and the composition of certain important elements/compounds that aid biodegradation that are present in the aloe vera leaf extract and also find out if and microorganism that can thrive in the media of the aloe vera leaf extract. The chemical composition of Aloe Vera was summarized in the table 3.1

From the table it is seen that *Aloe Vera* contains the necessary nutrients that is needed by indigenous microbes to flourish.

There are certain microorganisms that are actually responsible for the bioremediation process and these microbes secrete enzymes that help them to break down this crude oil in the soil into consumable substances. The response of these microorganisms to *aloe vera* leaf extract is of utmost importance to this work. If the *aloe vera* aids the growth of the microbes this in turn will help influence the bioremediation process kinetics of batch culture.

Preparation of the *Aloe Vera* Juice

The aloe vera used for the research was all healthy and fresh, the mature plant is recognizable by its large, green leaves.

- The leaves were properly washed to remove any form of impurities and contamination
- The leaves were carefully sliced into chunks to ease the process of blending.
- A clean blender was used to crushed the leaves
- The juice obtained was applied to the contaminated soil in different ratios

Determination of Total Hydrocarbon Content (THC)

The THC was determined by Gravimetric analysis (GA) which involves the determination of the concentration of a solution by change in mass. The method of GA employed is volatilization. This method separates analyte by application of thermal energy.

5g of each sample was collected and introduced into an airtight container. 50ml of n-hexane was added to each sample to extract the hydrocarbon compounds into a solution. The composition was agitated and allowed to stay for 3 minutes to ensure maximum dissolution. The solution was carefully decanted to separate it from the soil and other solid particles. The solution was heated to vaporize the n-hexane leaving behind the hydrocarbon compounds. The THC was determined using the formula.

$$\%THC = \frac{\text{weight of solute}(W_3 - W_1)}{\text{weight of soluion}(W_2 - W_1)} \times 100$$

Where, W_1 is the weight of the empty beaker, W_2 is the weight of the beaker with solution before heating and W_3 is the weight of the beaker with solution after heating

Experimental Procedures

- 1kg of each of the soil sample was measured into each of the reactor and it was analyzed to determine the THC of the soil before pollution
- There are 6 reactors for each soil types which include 3 controls, making it a total of 18 reactors
- 100ml of crude oil was added to each of the reactor containing the soil samples and it was mixed properly
- The soil samples in the reactor was analyzed after pollution
- The plant extract was measured and added into each reactor in the ratio of 0:1, 1:1 and 2:1. The samples in each of the reactor was analyzed to evaluate the performance of the plant juice.

3. RESULTS AND DISCUSSION

Result of Computation

The result obtained from the experiment proves that *Aloe vera* can be used as an efficient bio-stimulant and that the quantity of extract makes a significant increase in the rate of degradation. Based on the experiment conducted, it was observed that the rate of disappearance of the TPH increased as the amount of the *Aloe vera* juice increases. This is due to the factthat the *Aloe vera* contains nutrients that are very important in bioremediation process because they help to supply nutrients to the soil and in so doing the microbes responsible for the bioremediation feed on this nutrient thereby increasing the population of microbes available to breakdown the crude oil in the soil thus the crude oil present in the soil experiences a continual decrease. The Table of Value is found in Appendix I, Appendix II and Appendix III.

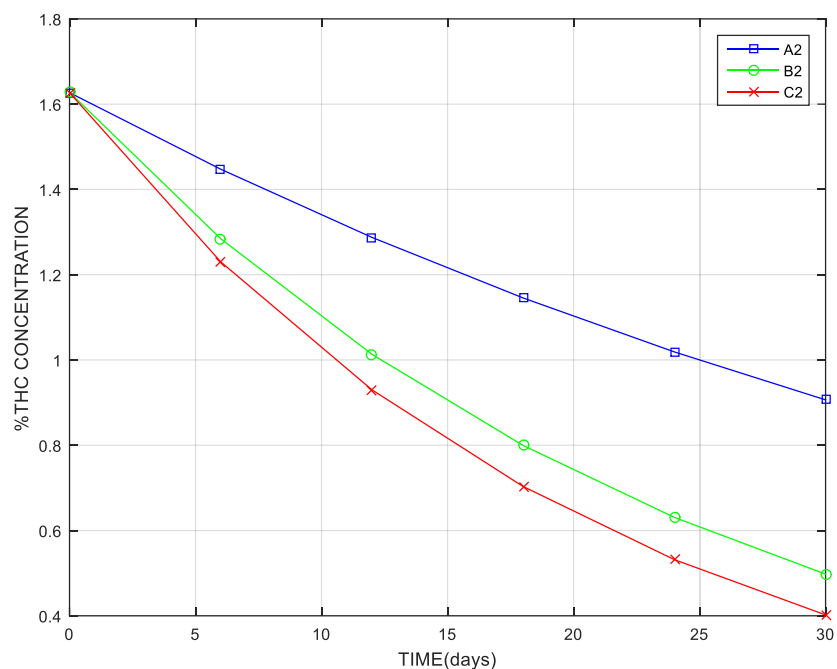


Figure 1 The Concentration of Total Hydrocarbon Content against Time for Sandy Soil

Figure 1 illustrates the relationship between the concentration of the total hydrocarbon content degradation and time for sandy soil. Decrease in THC was observed with increase in time for each reactor as shown in Figure 1. The rate of degradation appears to be faster for the reactor B1 and C1 which contains the bio-stimulant. This plot proves that the bio-stimulant was effective in increasing the rate of degradation in the sandy soil environment in each reactor. The variation in total hydrocarbon concentration in each of the bio-reactor can also be attributed to the variation in time.

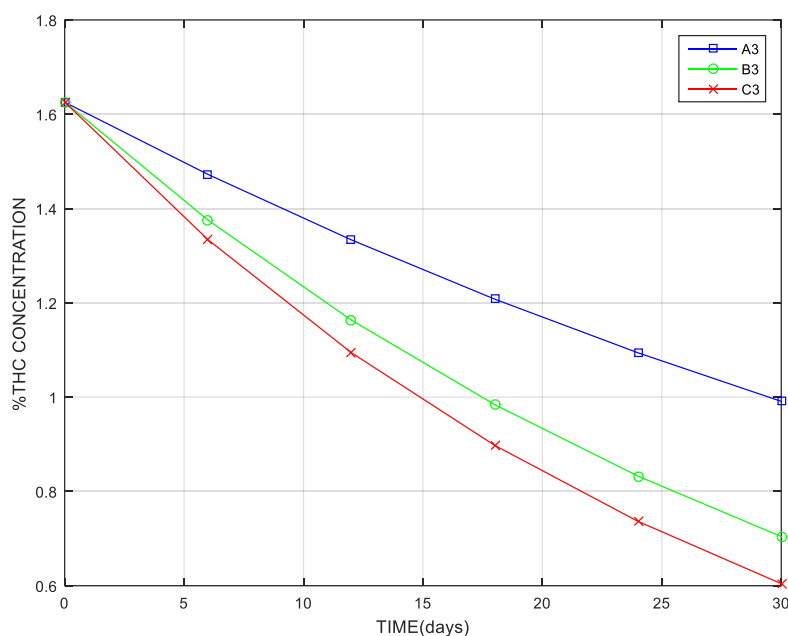


Figure 2 The Concentration of Total Hydrocarbon Content against Time for Loamy Soil

Figure 2 shows the relationship between the concentration of the total hydrocarbon content degradation and time for loamy soil. Decrease in THC was observed with increase in time for each reactor as seen in Figure 2. The rate of degradation appears to be faster for the reactor B2 and C2 which contains the bio-stimulant. This plot proves that the bio-stimulant was effective in increasing

the rate of degradation in the loamy soil environment in each reactor. The variation in total hydrocarbon concentration in each of the bio-reactor can also be attributed to the variation in time.

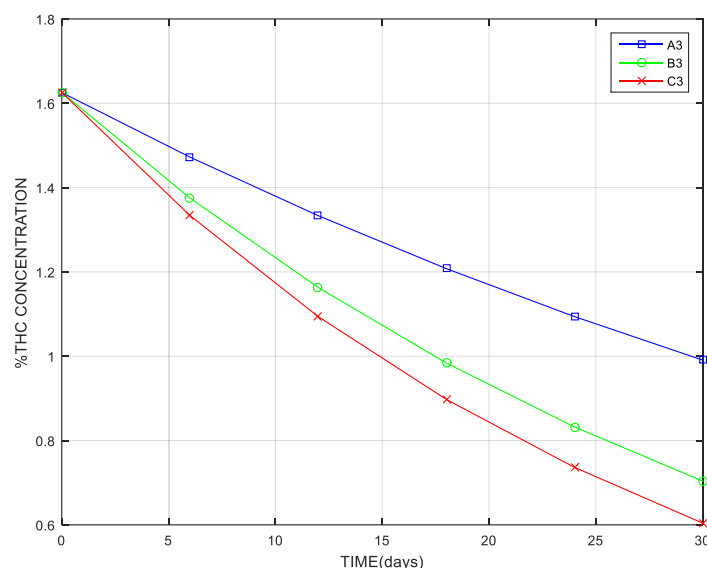


Figure 3 The Concentration of Total Hydrocarbon Content against Time for clay Soil

Figure 3 disclose the relationship between the concentration of the total hydrocarbon content degradation and time for clay soil. Decrease in THC was observed with increase in time for each reactor as seen in Figure 3. The rate of degradation appears to be faster for the reactor B3 and C3 which contains the bio-stimulant. This plot proves that the bio-stimulant was effective in increasing the rate of degradation in the clay soil environment in each reactor. The variation in total hydrocarbon concentration in each of the bio-reactor can also be attributed to the variation in time.

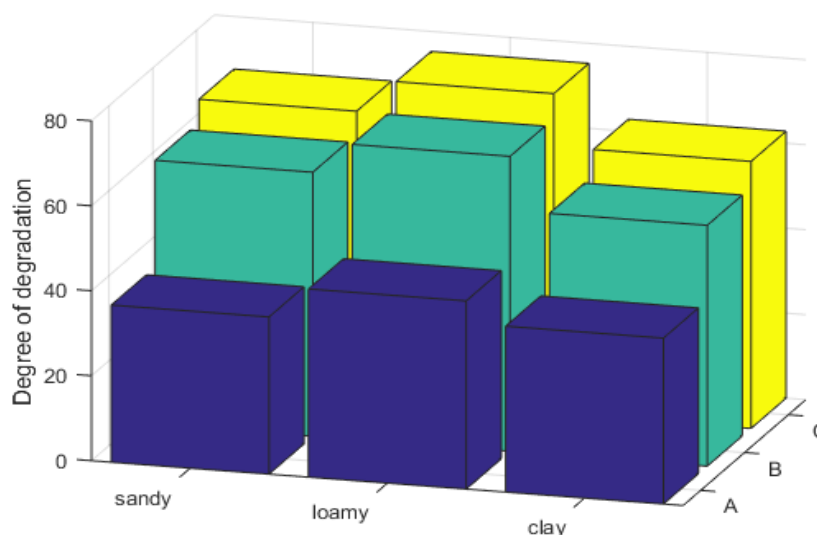


Figure 4 The Degree of Degradation of the Total Hydrocarbon Content in all Soil Types at the end of 30 Days

From Figure 4 it is seen that the degree of degradation is faster in all C reactors containing the 200ml *Aloe vera* as a stimulant. Also, across the various soil types with equal amount of bio-stimulant, Loamy soil has the highest degree of degradation followed by the sandy soil before the clay soil. This result may be due to the different soil properties. This figure also reveals that the degradation can occur without stimulant but it was slow when compared to the other reactors with the bio-stimulant. The rate of reaction of the reactors B and C seems to almost double that of A reactors. The rate of degradation was increased as the amount of stimulant was added.

Order and Rate of Reaction

The order of reaction was obtained by using equation (3.4). And the tables interpreting the order of reaction functional parameters and rate constants are shown below:

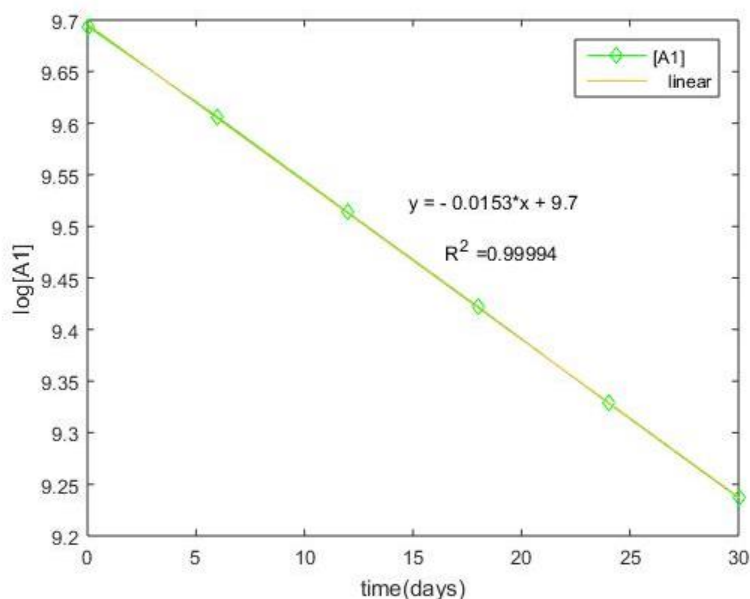


Figure 5 A Graphical Representation of Log(r) Against Log (A1)

From Figure 5, it is seen that the relationship between $\log(r)$ and $\log(A1)$ gives a straight line graph with slope $m = 0.94$ and intercept 1.9 which was obtained from the linear equation of $y = 0.94x + 1.9$ and square root of the best line of the fit is giving as $R^2 = 0.99962$. The slope of the graph is the order of the reaction for the reactor A1. The variation in the $\log(r)$ can be attributed to the variation to the $\log(A1)$ as well the environmental influence.

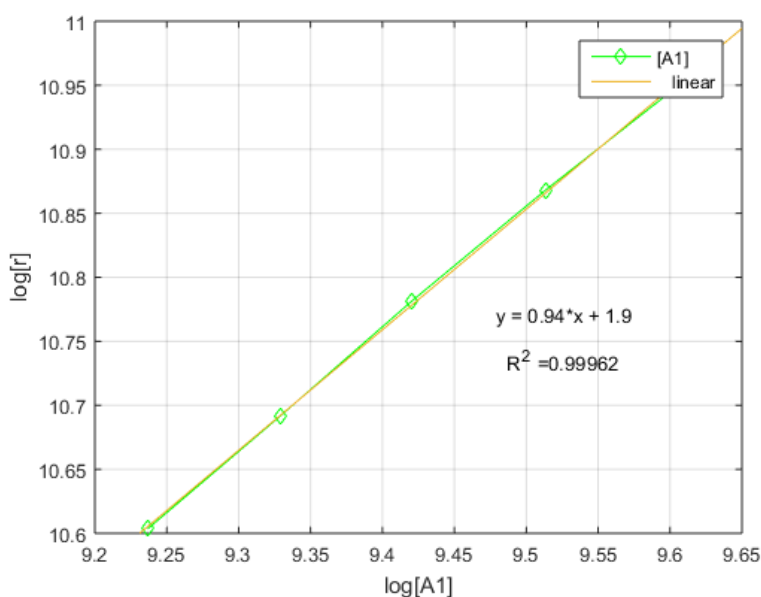


Figure 6 A Graphical Representation of Log (A1) Against Time

Figure 6 shows that the relationship between $\log(A1)$ and time produces a straight line graph with slope $m = -0.0153$ and intercept 9.7 which was obtained from the linear equation of $y = -0.0153x + 9.7$ and square root of the best line of the fit is giving as $R^2 = 0.99994$. The slope of the graph is the constant of the reaction for the reactor A1.

Table 1A The Total Hydrocarbon Content in Sandy Soil as Recorded on a 6 days Interval for 30 Days

Time (days)	Loamy Soil Samples					
	A2 (10 ⁴ ppm)	CA2 (10 ⁴ ppm)	B2 (10 ⁴ ppm)	CB2 (10 ⁴ ppm)	C2 (10 ⁴ ppm)	CC2 (10 ⁴ ppm)
0	1.6270	1.6275	1.6278	1.6276	1.6269	1.6267
6	1.4474	1.4461	1.2843	1.2849	1.2301	1.2314
12	1.2875	1.2849	1.0133	1.0144	0.9300	0.9322
18	1.1454	1.1416	0.7995	0.8008	0.7032	0.7056
24	1.0189	1.0143	0.6308	0.6322	0.5317	0.5342
30	0.9064	0.9013	0.4977	0.4991	0.4020	0.4044
%DD	44.29	44.62	69.42	69.33	75.29	75.13

Table 1B The Total Hydrocarbon Content in Loamy Soil as Recorded on a 6 days Interval for 30 Days

Time (day)	CLAY SOIL SAMPLES					
	A3 (10 ⁴ ppm)	CA3 (10 ⁴ ppm)	B3 (10 ⁴ ppm)	CB3 (10 ⁴ ppm)	C3 (10 ⁴ ppm)	CC3 (10 ⁴ ppm)
0	1.6255	1.6258	1.6259	1.6258	1.6258	1.6257
6	1.4723	1.4699	1.3753	1.3736	1.3338	1.3329
12	1.3335	1.3290	1.1633	1.1604	1.0942	1.0928
18	1.2078	1.2015	0.9840	0.9804	0.8976	0.8960
24	1.0940	1.0863	0.8323	0.8283	0.7364	0.7346
30	0.9909	0.9822	0.7040	0.6998	0.6041	0.6023
%DD	39.04	39.58	56.70	56.95	62.84	62.95

Table 1C The Total Hydrocarbon Content in Sandy Soil as Recorded on a 6 days Interval for 30 Days

Time (days)	SANDY SOIL SAMPLES					
	A1 (10 ⁴ ppm)	CA1 (10 ⁴ ppm)	B1 (10 ⁴ ppm)	CB1 (10 ⁴ ppm)	C1 (10 ⁴ ppm)	CC1 (10 ⁴ ppm)
0	1.6290	1.6289	1.6284	1.6282	1.6289	1.6287
6	1.4852	1.4834	1.3407	1.3438	1.2999	1.2982
12	1.3541	1.3508	1.1038	1.1090	1.0374	1.0348
18	1.2346	1.2301	0.9088	0.9153	0.8279	0.8248
24	1.1257	1.1202	0.7483	0.7554	0.6607	0.6574
30	1.0263	1.0201	0.6161	0.6234	0.5272	0.5240
%DD	36.99	37.37	62.16	61.71	67.63	67.82

Table 1D The Total Hydrocarbon Content in Clay Soil as Recorded on a 6 days Interval for 30 Days

Time (days)	LOAMY SOIL SAMPLES					
	A2 (10 ⁴ ppm)	CA2 (10 ⁴ ppm)	B2 (10 ⁴ ppm)	CB2 (10 ⁴ ppm)	C2 (10 ⁴ ppm)	CC2 (10 ⁴ ppm)
0	1.6270	1.6275	1.6278	1.6276	1.6269	1.6267
6	1.4474	1.4461	1.2843	1.2849	1.2301	1.2314
12	1.2875	1.2849	1.0133	1.0144	0.9300	0.9322
18	1.1454	1.1416	0.7995	0.8008	0.7032	0.7056
24	1.0189	1.0143	0.6308	0.6322	0.5317	0.5342
30	0.9064	0.9013	0.4977	0.4991	0.4020	0.4044

%DD

44.29

44.62

69.42

69.33

75.29

75.13

Table 2 Kinetic Properties to Determine the Order and Rate Constant of the Reaction for Sandy Soil Reactors

Time (day)	A1				B1				C1			
	[A1]	[V _{A1}]	log[A1]	log[VA1]	[B1]	[V _{B1}]	log[B1]	log[VB1]	[C1]	[V _{C1}]	log[C1]	log[VC1]
0	1.6290	-	9.6983	-	1.6284	-	9.6979	-	1.6289	-	9.6982	-
6	1.4852	238.6667	9.6063	10.9501	1.3407	478.3333	9.5039	12.3406	1.2999	548.3333	9.4726	12.6138
12	1.3541	229.0833	9.5135	10.8682	1.1038	437.0000	9.3091	12.1599	1.0374	492.9167	9.2471	12.4007
18	1.2346	219.3889	9.4207	10.7817	0.9088	399.6667	9.1147	11.9813	0.8279	445.0000	9.0215	12.1961
24	1.1257	209.7083	9.3287	10.6914	0.7483	366.6250	8.9204	11.8087	0.6607	403.4167	8.7959	11.9999
30	1.0263	200.7000	9.2369	10.6036	0.6161	337.1000	8.7273	11.6408	0.5272	367.3333	8.5696	11.8125

Table 3 Kinetic Properties to Determine the Order and Rate Constant of the Reaction for Clay Soil Reactors

Time (day)	A3				B3				C3			
	[A3]	[V _{A3}]	log[A3]	log[VA3]	[B3]	[V _{B3}]	log[B3]	log[VB3]	[C3]	[V _{C3}]	log[C3]	log[VC3]
0	1.6255	-	9.6962	-	1.6259	-	9.6964	-	1.6258	-	9.6963	-
6	1.4723	255.3333	9.5972	11.0851	1.3753	417.6667	9.5290	12.0694	1.3338	486.6667	9.4984	12.3752
12	1.3335	243.3333	9.4981	10.9889	1.1633	385.5000	9.3616	11.9091	1.0942	443.0000	9.3004	12.1871
18	1.2078	232.0556	9.3991	10.8940	0.9840	356.6111	9.1942	11.7533	0.8976	404.5556	9.1023	12.0056
24	1.0940	221.4583	9.3002	10.8005	0.8323	330.6667	9.0268	11.6022	0.7364	370.5833	8.9044	11.8302
30	0.9909	211.5333	9.2012	10.7088	0.7040	307.3000	8.8594	11.4556	0.6041	340.5667	8.7063	11.6612

Table 4 Kinetic Properties to Determine the Order and Rate Constant of the Reaction for Loamy Soil Reactors

Time (day)	A2				B2				C2			
	[A2]	[V _{A2}]	log[A2]	log[VA2]	[B2]	[V _{B2}]	log[B2]	log[VB2]	[C2]	[V _{C2}]	log[C2]	log[VC2]
0	1.6270	-	9.6971	-	1.6278	-	9.6970	-	1.6269	-	9.6970	12.9840
6	1.4474	299.6667	9.5800	11.4053	1.2843	571.8333	9.4606	12.6977	1.2301	659.8333	9.4174	12.7235
12	1.2875	282.9167	9.4630	11.2903	1.0133	511.7500	9.2236	12.4757	0.9300	579.2500	9.1387	12.4793
18	1.1454	267.7222	9.3458	11.1799	0.7995	460.1667	8.9861	12.2632	0.7032	512.6667	8.8582	12.2448
24	1.0189	253.3750	9.2291	11.0697	0.6308	415.5000	8.7486	12.0590	0.5317	455.9583	8.5787	12.0219
30	0.9064	240.0333	9.1126	10.9616	0.4977	376.1667	8.5150	11.8601	0.4020	407.8667	8.3000	0.9991

Table 5 Substrate Kinetic Properties for Sandy Soil

Time (day)	A1				B1				C1			
	[A1]	[V _{A1}]	1/[VA1]	1/[A1]	[B1]	[V _{B1}]	1/[VB1]	1/[B1]	[C1]	[V _{C1}]	1/[VC1]	1/[C1]
0	1.6290	-	-	0.6733	1.6284	-	-	0.0614	1.6289	-	-	0.0614
6	1.4852	238.6667	0.0037	0.7385	1.3407	478.3333	0.0021	0.0746	1.2999	548.3333	0.0018	0.0769
12	1.3541	229.0833	0.0039	0.8100	1.1038	437.0000	0.0023	0.0906	1.0374	492.9167	0.0020	0.0964
18	1.2346	219.3889	0.0041	0.8883	0.9088	399.6667	0.0025	0.1100	0.8279	445.0000	0.0022	0.1208
24	1.1257	209.7083	0.0043	0.9744	0.7483	366.6250	0.0027	0.1336	0.6607	403.4167	0.0025	0.1514

30 1.0263 200.7000 0.0045 0.6733 0.6161 337.1000 0.0030 0.1623 0.5272 367.3333 0.0027 0.1897

Table 6 Substrate Kinetic Properties for Loamy Soil

Time (day)	A2				B2				C2			
	[A2]	[V _{A2}]	1/[V _{A2}]	1/[A2]	[B2]	[V _{B2}]	1/[V _{B2}]	1/[B2]	[C2]	[V _{C2}]	1/[V _{C2}]	1/[C2]
0	1.6270	-	-	0.0614	1.6278	-	-	0.0614	1.6269	1.6269	-	0.0615
6	1.4474	299.6667	0.0033	0.0691	1.2843	571.8333	0.0017	0.0779	1.2301	1.2301	0.0015	0.0813
12	1.2875	282.9167	0.0035	0.0777	1.0133	511.7500	0.0020	0.0987	0.9300	0.9300	0.0017	0.1075
18	1.1454	267.7222	0.0037	0.0873	0.7995	460.1667	0.0022	0.1251	0.7032	0.7032	0.0019	0.1422
24	1.0189	253.3750	0.0039	0.0981	0.6308	415.5000	0.0024	0.1585	0.5317	0.5317	0.0022	0.1881
30	0.9064	240.0333	0.0042	0.1103	0.4977	376.1667	0.0027	0.2009	0.4020	0.4020	0.0024	0.2488

Table 7 Substrate Kinetic Properties for Clay Soil

Time (day)	A3				B3				C3			
	[A3]	[V _{A3}]	1/[V _{A3}]	1/[A3]	[B3]	[V _{B3}]	1/[V _{B3}]	1/[B3]	[C3]	[V _{C3}]	1/[V _{C3}]	1/[C3]
0	1.6255	-	-	0.0615	1.6259	-	-	0.0615	1.6258	-	-	0.0615
6	1.4723	255.3333	0.0039	0.0679	1.3753	417.6667	0.0024	0.0727	1.3338	486.6667	0.0021	0.0750
12	1.3335	243.3333	0.0041	0.0750	1.1633	385.5000	0.0026	0.0860	1.0942	443.0000	0.0023	0.0914
18	1.2078	232.0556	0.0043	0.0828	0.9840	356.6111	0.0028	0.1016	0.8976	404.5556	0.0025	0.1114
24	1.0940	221.4583	0.0045	0.0914	0.8323	330.6667	0.0030	0.1201	0.7364	370.5833	0.0027	0.1358
30	0.9909	211.5333	0.0047	0.1009	0.7040	307.3000	0.0033	0.1420	0.6041	340.5667	0.0029	0.1655

Table 1A-1D demonstrates the relationship of total petroleum hydrocarbon degradation on the effect of time for the various level of contaminated soils. Table 2 illustrates the determination of the kinetic parameters in terms of order of the reactors with different level of pollution. The determination of order of the reaction and the rate constant for clay and loamy soil are presented in Table 3 and 4. The substrate kinetic parameter determined from the research work is presented in Table 5, 6 and 7 for sandy, loamy and clay soil.

4. CONCLUSION

The technology for bioremediation that was employed in this study was a simple, effective, inexpensive and environmentally friendly approach. The bio-stimulant is purely organic with its full content intact prior to the experiment. Based on the experiments conducted we can clearly observe that the Aloe vera stimulated the bioremediation of crude oil in the soil this is largely attributed to the nutrients supplied to the contaminated soil by the stimulant juice. The reaction kinetic models obtained as a result of this experiment can be used as a measure to predict the rate of degradation in the different soil types using Aloe vera.

Contribution to Knowledge

This research unravels the importance of Aloe vera as a bio-stimulant which can be utilized in actual field to boost the rate of degradation of crude oil hydrocarbons. It is an efficient bio-degradation stimulator which can yield an efficiency of about 55% and above in a short period if applied in the appropriate ratio based on the initial hydrocarbon content.

This work exposed the degradation rate across the different soil types. The stimulant was applied in same ratio to the different soil types although the degree of degradation was different for same ratio. Bio-remediation can be affected by the different properties of the soil such as composition, humus content, porosity and permeability.

The kinetic models obtained from this research pose as a guide in predicting the time it will take to acquire a desired degree of degradation across the different soil types if this stimulant is used in appropriate quantity in the actual field. There may be some discrepancies due to the influence of natural phenomenon such as climate condition, microbial population, influence of macro-

organisms, constituent of the soil, erosion and flooding. A pilot study should be carried out in the environment to be remediated to attain the effects of this stimulant in that field before large-scale implementation to obtain optimum result.

Conflicts of Interest

None.

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