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Chemical interactions of synthetic and natural remediating agents with crude oil on agricultural soil

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ABSTRACT

Altered chemical system of an Agricultural Soil resulting from crude oil spillage was subjected to NPK fertilizer and compost manure for remediation. The effect of the remediating agents was observed in-situ by examining the soil parameters before, during and after the interactions. An Ultraviolet(UV) Spectrophotometer V180 was used for the evaluation of the Total Hydrocarbon content of the soil. Remediated state of 92.5% TPH reduction, pH, moisture balance and soil restoration was achieved with a combination of 150g NPK fertilizer and 150g compost manure per meter square(300g remediating agent /m^2) plot of land, after seven weeks of application.

Keywords: soil contamination, hydrocarbon degradation, in-situ remediation, NPK fertilizer, compost manure

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INTRODUCTION

The earth (soil) has been the crude oil's reservoir as well as the first victim of its contaminating abilities. The extraction (transportation and storage) of crude oil beneath the earth surface without spillage is inevitable. Crude oil pollution has therefore been a persistent environmental problem [1]. Oil spillage incidents in various countries around the world have been recorded. The Exxon Valdez oil spill in Alaska United State is considered to be one of the most devastating human caused environmental disasters [2]. The British Petroleum (BP) oil spill incident at Louisiana, United State as well as respective sources of oil spills in France, Canada, Mexico, Angola, Saldanha bay South Africa and a recent oil spill that occurred in India have also been documented[3].In Nigeria, the obvious oilspill incidents include Chevron's oil spill in Ilaje, Ondo state, Shell's oil spill in Barrale, Ogoniland, Rivers state, Shell's oil spill in Gana and Urhobo community in Delta state [4], [5],[6].

Improper treatment of these oil spills will lead to great depreciation of the environmental resources due to alteration in the natural chemical system of the soil [7]. This alteration involves the adsorption of excess carbon which results to its unavailability for microbial use. Limitations in soil Nitrogen and phosphorous have also been attributed to the adsorption process [8],[9] and [10].Consequently, there is a delay in the natural rehabilitation process in crude oil polluted soils. Various soils treatment measures have been used to hasten the process, these include the use of surfactants, carbon substrates, both organic and in organic fertilizers, as well as application of microbes and bacteria[11]. Studies on the possibility of using water hyacinth as a source of nutrient in bioremediation process of soil contaminated with heavy crude oil and also the possibility of it serving as a soil conditioner have also been documented [12].In the present study, the restoration of the natural chemical balance of crude oil contaminated agricultural soil was investigated by evaluating the efficacy of various concentrations of organic manure and inorganic fertilizer. The study was also designed to evaluate the maximum load capacity of the experimental soil with respect to the remediating agent. The restoration agents were applied directly (in situ) to the experimental portion of a farm land.

MATERIALS AND METHODS

The crude oil used was a Nigerian Forcados blend obtained from Jawura Environmental Services, Port Harcourt in Nigeria. The compost manure was obtained from the school of Agriculture at Federal University of Technology Owerri (FUTO) in Nigeria. An uncultivated parcel of land behind ICT building in FUTO was used as the experimental plot. The NPK fertilizer was obtained from the National Fertilizer Company (NAFCON), Port Harcourt, Nigeria.

Experimental: The compost manure was air dried, crushed and stored in the laboratory at room temperature (29^{o}C) before use [13]. The experimental plot of land was divided into four phases. Soil samples collected from the phases were analyzed and recorded as initial characteristics of the natural soil. Phase one was used as a control, while phases two, three and four were each divided into five(5) treatment cells and labeled A to E. Each cell was of the same area of 1m^2, and was two meters away from others. Each cell was spilled with 200ml of the crude oil. The top soil was thoroughly mixed and allowed to stand for eight days after which the remediating agents were applied. Soil samples collected within the eight days indicated establishment of contamination. Soil samples from the cells were collected at intervals and analyzed. Phase one received no remediating agent and was therefore labeled as a control. Each cell in phase two was treated with compost manure of specific quantity. Cells in phase three were treated with NPK fertilizers of various quantities, while phase four was with various compositions of NPK fertilizers-compost manure mixtures. The remediation process was monitored by regular weekly sample collection and analysis during the study period of eight weeks. The monitoring was also used as a determinant factor for the end of remediation.

Analysis of the soil samples: 2g of oven dried soil samples were mixed with 50ml of chloroform in five separate 60 ml experimental bottles. Each bottle was properly shaken, allowed to settle, decanted and then filtered. The absorbance of each filtered portion was measured with the UV spectrophotometer at a wavelength of 290nm. A calibration curve was also prepared by measuring the absorbance of standard petroleum hydrocarbon (TPH) in chloroform at the same wavelength.

RESULTS AND DISCUSSION

The value of the soil parameters before and after spillage was an indication of established contamination. In table 1, the total hydrocarbon value increased from 3.99mg/dm^3 to 5630mg/dm^3(milligram of crude oil in one decimeter cube of solvent) in 1kg of excavated contaminated soil sample. The moisture content of the soil also increased from 7% to 25%, while the pH reduced from 7 to 4.

Table 1: Soil parameters before and after crude oil spillage

TPH(mg/dm^3)		Moisture content (%)		pH	
Before	After	Before	After	Before	After
3.99	5630	7%	25%	7	4

The general observation implied that, the contamination resulted to a humid and an acidic farm land. The observed increased acidity of the contaminated soil was in agreement with the studies carried out by previous workers [14], [15].

The acidic state of the contaminated soil could be attributed to residual sulfur compound (in the form of mercaptant)and organic sulfides as found in light naphtha content of the spilled oil which must have reacted with atmospheric moisture to yield sulfuric acid mist and hydrogen sulfide. The reduced acidic state of the remediated soil must have resulted from the principles of "hydrotreating". This is a catalytic hydrogenation process that reduces the concentration of sulfur, nitrogen, oxygen, metals and other contaminants in a hydrocarbon spill. In more severe forms, hydro treating saturates olefins and aromatics with the hydrogen. The obtained data recorded in table 1 showed increased moisture content of the contaminated soil. This observation could be attributed to lack of air circulation and hindered natural water transportation in soil system. The application of the remediating agents attempted to neutralize the acidic state and normalize the moisture content of the soil. This observation was implied in the reduction trend of TPH concentration as well as the obtained percentage of remediation with respect to the amount of compost manure and NPK fertilizer.

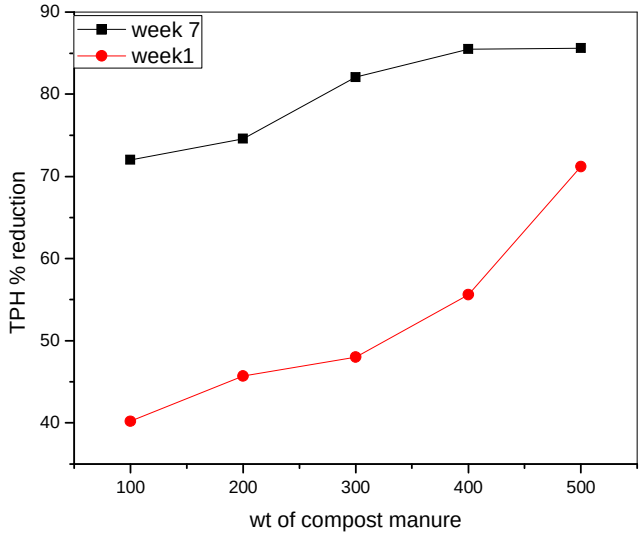
TPH concentration in the contaminated soil was effectively reduced with increase in compost manure (comp. man.) concentration as shown in table 2.

Table2: Effect of compost manure on the TPH content of the contaminated soil

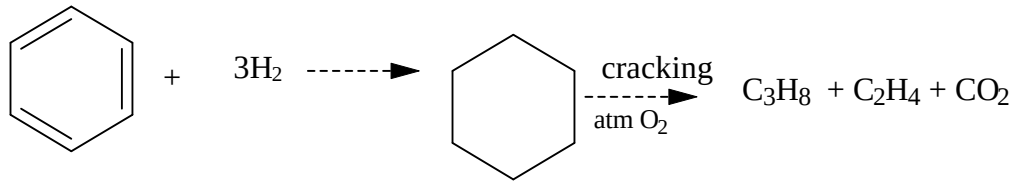
Wt. of com. man. In exptal. cells	% reduction of TPH value per kg of soil						
	1wk	2 wks	3 wks	4 wks	5 wks	6wks	7wks
F (100g)	40.2	47.2	53.0	54.9	59.9	65.0	72.0
G (200g)	45.7	57.7	59.0	71.0	72.0	74.6	74.6
H (300g)	48.0	58.0	62.7	72.7	74.4	77.7	82.1
I (400g)	55.6	63.6	66.3	74.1	75.6	80.0	85.5
J (500g)	71.2	74.5	77.9	80.2	85.6	85.6	85.6

The trend of the obtained data for the first and seventh week as shown in figure 1 indicated that the remediating effect of compost manure was consistent with respect to the 100g, 200g and 300g application, while there was not much difference in the remediating effect of 400g and 500g on the soil for the seventh week. The load capacity of the experimental plot could therefore be stated as 400g/m^{2}cell, with respect to compost manure.

Fig.1: Variation of percentage reduction of TPH with respect to quantity of applied compost manure



The given properties of the *Forcardos* crude oil showed that the most probable soil contaminants in it must have been Benzene, Toluene, Naphtha, kerosene and gas oil. These constituents are complex mixtures of molecules called hydrocarbons [16] and [17].The chemical composition of the spilled oil therefore explained the remediating effect of the compost manure. The principle is based on the provision of hydrogen-rich blanket (by the compost manure) which supplied the amount of hydrogen required to saturate the aromatic rings. Consequently, restoration of the soil balance must have resulted partially from the hydrogenation of benzene and toluene(aromatic compounds) and subsequent cracking of the resulted cyclohexane rings. Studies have shown that cycloalkanes also behave like their corresponding open chain analog in terms of undergoing cracking in the presence of atmospheric oxygen [18].
The observed restoration was therefore deduced to be based on the equation of a reaction given as:



consequently, the effect of the operating conditions on cycloalkane (product of aromatic hydrogenation) ring opening is based on the effect of hydrogen in the cracking mechanisms, thus the cracking mechanisms are directly affected by hydrogen as products (alkenes) and intermediates (carbonium ions) are saturated. The overall effect of rising hydrogen partial pressure is an enhancement of (hydro)isomerization and monomolecular cracking, that is, yields like methane, ethane, penthane and isoalkanes are generated. The total significance of the process is that: the original nature of the crude oil was degraded and its negative effect on soil fertility was also reduced.

On the experimental plots treated with the NPK fertilizer, it was observed that the amount of remediating agent had a linear relationship with the percentage reduction of TPH except for the cells treated with 400g and 500g

respectively, which showed a decrease in TPH reduction rate. It implied that the maximum remediation occurred with 300g of NPK fertilizer as seen in cells 'K' to 'O' of table 4.

Cells in the fourth phase exhibited an enhanced remediated effect with a percentage TPH reduction of 92.5% from 150g/150g NPK-Compost manure mixture as shown in figure 2. The observed trend is attributed to the joint function of the two remediating agents.

Figure 2: Effect of NPK-Compost manure mixture on the oil spilled soil

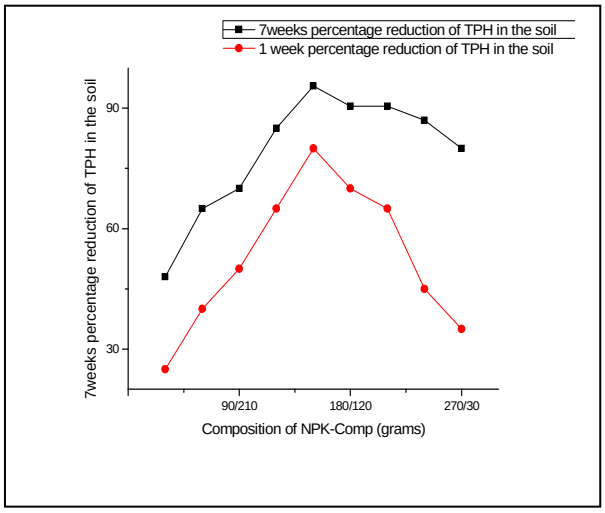


Table 4: Summary of Experimental Results and their Implications

Experimental Cells	Remediating Agent	Oil Content (mg/kg)	Removed Oil Content (mg/kg)	% reduction of Oil Content
F	Compost Manure (100g)	5630	4068	72.1
G	Compost Manure (200g)	5609	4185	74.6
H	Compost Manure (300g)	5673	4660	82.1
I	Compost Manure (400g)	5597	4791	85.5
J	Compost Manure (500g)	5640	4834	85.6
K	NPK (100g)	5680	4615	81.3
L	NPK (200g)	5557	5030	90.5
M	NPK (300g)	5597	5182	90.5
N	NPK (400g)	5665	4217	74.4
O	NPK (500g)	5649	3128	55.3

The highest remediation rate of 90.5% was observed on sample M, where the total petroleum hydrocarbon of 5182mg/dm^3 was removed from the initial concentration 5597 mg/dm^3 in 1 kg of the excavated soil sample.

CONCLUSION

Both NPK fertilizer and compost manure showed good remediating effects on the crude oil polluted soil. The NPK fertilizer remediated faster than the compost manure at the remediation percentage of 90.5 % when compared with 85. 6% obtained with compost manure within the same study period. A maximum TPH reduction and remediation rate of 92.5% was obtained after seven (7) days with a combination of the NPK-Compost manure mixture on 1:1 ratio with respect to the 300g/m^2 load capacity of the experimental soil.

Acknowledgement
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