THE REMEDIATION OF OIL POLLUTED SOIL

IN MINNA NIGER STATE, NIGERIA

BY

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(2004/18402EA)

DEPARTMENT OF AGRICULTURAL & BIORESOURCES ENGINEERING

FEDERAL UNIVERSITY OF TECHNOLOGY MINNA

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BEING A FINAL YEAR PROJECT REPORT SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE AWARD OF BACHELOR OF ENGINEERING (B. ENG) DEGREE IN AGRICULTURAL & BIORESOURCES ENGINEERING, FEDERAL UNIVERSITY OF TECHNOLOGY MINNA

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DECLARATION

I hereby declare that this project work is a record of a research work that was undertaken and written by me. It has not been presented before for any degree or diploma or certificate at any university or institution. Information derived from personal communications, published and unpublished work were referenced in the text.

Okeke, Sunday Obumneme

8/3/2010
Date

CERTIFICATION

This project entitled 'The Remediation of Oil Polluted Soil in Minna Niger State' by Okeke Sunday Obumneme, meets the regulations governing the award of the degree of Bachelor of Engineering (B. ENG.) of the Federal University of Technology, Minna, and it is approved for its contribution to scientific knowledge and literary presentation.

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DEDICATION

This project is dedicated to my immediate family, the family of Mr and Mrs.John Okeke who watched after me from when I was a child till date, and to my late brother Oyedikachukwu Okeke.

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I bless the name of the lord, the God of wisdom and the strength of my life for making this work possible. I will forever remain grateful.

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ABSTRACT

Remediation of used motor oil polluted soil is the cleanup of the pollutant from the soil thereby binging back the soil to its original status before pollution. A combination of treatments, consisting of the application of fertilizer and manure and oxygen exposure, was evaluated in situ during period of six weeks. Experimental plot/site measuring 1m by 2m was prepared at an auto-mechanic workshop in Minna, Niger State. The remedial treatment was then applied and the soil characteristic analysed after set period. Soil physiochemical parameters, such as moisture content, pH value, electrical conductivity as well as, organic carbon and total nitrogen contents showed distinct variation as the remediation progressed. The total heterotrophic bacteria [THB] count in the treatment site increased as the remediation progressed. The control site/plot indicated no sign of remediation within the study period. The hydrocarbon loss experienced in the treatment plot revealed the effectiveness in degrading the hydrocarbon contaminant. The result of the study indicates that the application of increased concentration of nutrients [by the application of fertilizers and manure] lead to greater rates of biodegradation of used motor-oil polluted soil.

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INTRODUCTION

.1 Background to the study

Agricultural land plays considerable role in the existence of man. Life would have been difficult if no place existed for man to shelter, farm and reap a harvest. Most families have been maintained today from both subsistent farming and commercial farming. Following the importance of the land to man's existence, any land used should be properly protected.

In fact there has been great deterioration of agricultural lands due to the effect of chemicals and petroleum products during the past century. These spills occur from well heads, distribution lines outlets and from tanks and tankers, drilling mud as well as oil and water produced in the course of drilling.

Government cooperate bodies, interest groups and affected communities have however responded to the problem of oil pollution and its adverse effect on agricultural lands in various ways. The responses ranged from peaceful pressure group activities, in the form of delegations and submission of petitions or the mobilization of international support, to violent protests, and distributions of oil operations and installations.

Notwithstanding the effects of the government, the economic and human losses from oil spillage on farmlands have been tremendous. For the polluted farmlands, there is need to develop the appropriate technology to remedy the farmland for effective agricultural productivity.

The remediation of agricultural lands has remained a challenge to both soil scientists and agricultural engineers. Farm land remediation is the process by which agricultural land is restored to its original state prior to degradation. It entails the removal of the soil pollutant and its products trapped in the pore spaces of the soil or aquifer. This is in fact the major objectives of this project.

1.1.1 Used Motor Oil

Oil spills from the refineries, industries, filling stations, loading and pumping stations, petroleum product depots, during transportation and at auto-mechanic workshops all contribute to soil contamination, and actually make up a larger percentage of polluted ground in the world versus those contaminated by catastrophic spills. The dig and dump method of disposing these oil polluted lands is expensive and only transfer the contamination from one place to another. This disposal technique is very prominent in the developing countries, for example Nigeria where there were no effective regulatory policies on the environment. In no doubt, the dig and dump practices has lead to the contamination of millions of other sites remote from their place of initial contamination and therefore urgent actions need to be taken for environmental safety in general and of importance public health.

In Nigeria, oil spill at auto mechanic workshop have been left uncared over the years and its continuous accumulation is of serious environmental concern because of its hazardous nature. For instance, used motor oil disposed off improperly contains potentially toxic substance such as benzene. Lead, arsenic, zinc and cadmium which can seep into the water table and contaminate ground water. The choice of remediation of soil contaminated with used motor oil in this research work is because it is a representative sample for soils contaminated with minor oil spill. Like other forms of minor oil spill, the content of soil contaminated with used motor oil covers a wide range of hydrocarbons (such as gasoline, diesel fuel, lighter fluids, propane, lubricating oil, etc.) and in addition toxic substances.

1.2 Statement of the Problem

All stages of oil exploration impact negatively on the environment, and the greatest intractable environmental problem caused by crude oil exploration in the host communities is oil. The environmental consequence of oil pollution on the inhabitants of the host communities, for instance in Niger delta are enormous oil spills have degraded most agricultural lands and have turned hitherto productive areas into wastelands. With increasing soil infertility, low crop yield due to destruction of soil micro-organism, and dwindling agricultural productivity and farm income, farmers have been forced to abandon their land to seek non-existent alternative means of livelihood.

Aquatic life have also been destroyed with the pollution of traditional fishing grounds, exacerbating hunger and poverty in fishing communities (Felicia et al 2006)

Also, oil spills result in an imbalance in the carbon-nitrogen ratio at the spill site, because crude oil is essentially a mixture of carbon and hydrogen. This causes a nitrogen deficiency in an oil-soaked soil, which retards the growth of bacteria and the utilization of carbon sources and therefore limiting the rate of growth of crops. Crude oil spill or pollution tend to persist in soil until remediation measures, involving the application of nutrients are restored to because oxygen and nitrogen are limiting factors in all type of petroleum degradation.

1.3 Objectives of the Study

The objectives of this sturdy are:

1. Identifying the different effects of oil pollution on agricultural soil and the extent of pollution

2. The remediation of the used motor oil polluted soil using horse manure and agricultural fertilizer

1.4 Justification

The continuous danger posed by oil spillage on land has dramatically affected the agricultural productivity of polluted farmland. In some of the farmlands and the farming communities, sustainability of life from agricultural land has greatly waned.

As such, the justifications for this project are:

1. In Nigeria, especially the Niger delta area, a lot of sites have been polluted with hydrocarbon products; these sites are fast increasing and need to be addressed.
2. Soil polluted with crude oil needs to be given priority attention because of the hazardous nature of the pollutant.
3. Composting method of remediation and reclamation of oil polluted agricultural land is a simple technique which is cost effective and environmentally friendly and also efficient in soil clean up.
4. Soil contaminated with crude oil defiles the aesthetic nature of the environment.

1.5 Scope / Limitation of this Study

Remediation of any sort on agricultural land has several factors affecting the cost of cleanup namely accessibility to the site, weather condition, quantity of spilled fuel, the extent of environmental damage and the time required for cleanup

This project will be restricted to a mechanic workshop in Minna, Niger state, Nigeria to cub the above mentioned factors.

CHAPTER TWO

LITERATURE REVIEW

2.1 Crude Oil

Crude oil is a naturally – occurring substance found in certain rock formations in the earth. It is a dark, sticky liquid which, scientifically speaking, is a classified as a hydro carbon, this means, it is a compound containing certain carbon and hydrogen, with or with non – metallic elements such as oxygen and sulphur. Crude oil highly flammable and can be turned to create energy. Along with its sister hydrocarbon, natural gas, derivatives from crude oil make an excellent fuel. (www.opec.org.2009).

2.2 Soil

Soil is a thin layer of material on the earth's surface in which plant have their roots. It is made up of many things such as weathered rock and decayed plants and animals matter. Soil is formed over a long period of time.

Soil formation takes place when many things interact, such as air, water, plant life, animal life, rocks and chemicals. (Wikkipedia, 2009)

2.3 Types of Soil

According to www.atinentu.com,2009 soil usually fall into three types namely;

1. Silty soil

2. Sandy soil

3. clay soil

2.3.1 Silty Soil

Silty soil feel like talcum powder when it is dry and have a high level nutrients but they are susceptible to erosion, and compacting because of their fine high texture. Incorporating coarse sand, perlite and humus along with using cover crops and green manure, the tilth of silt soil is build up.

2.3.2 Sandy Soil

Sandy soil is very gritty and crumbles into fine particles. Because of this, the soil drains quickly and is susceptible to extreme fluctuations of heat and cold during the growing season. Due to their super sharp drainage these soil are unable to retain nutrients. This soil can be improved by combining composted organic materials like horse or cow manure, leaves e.t.c.

2.3.3 Clay Soil

Clay soil is slick and greasy feeling when wet, hard and brittle when it is dry. Sometimes tinted whited, red or yellow, these clay soils are rich in materials but have low concentration of organic material clay soil will hold water well when condition are dry but tend to get water logged with heavy or several days of rain. Clay soil can be improved by adding plenty of compost and vermiculite or perlite.

2.4 Agriculture

Agriculture may be more fully defined as all the processes involved in the controlled production of plant and animal materials which are of use to them. Agriculture is primarily concerned with the supply of human needs – food, clothing and shelter through raising the products of the soil and livestock (Uguru, 1981).

Agriculture involves three material sources or living systems, the soil, plants and animals. These systems are interdependent. The soil is the basic raw material of the farmer since it supplies the plant with food and moisture and provides it with firm anchorage. The plant grows in the soil and with the sun's energy builds food materials by the process of photosynthesis. These foods, which are stored in the plant or converted to part of the structure of the plant, can be used directly by man, by eating the plants or indirectly by eating the animals which feed on the plants (Uguru, 1981).

2.4.1 Agricultural System

Sustainable agricultural systems is a system which involves the management and conservation of natural resource base and the orientation of technological and institutional change in such a manner as to ensure the attainment and continued satisfaction of human needs for present and future generation. Such sustainable development (in agriculture, forestry and fisheries sectors) conserves land, water, plant and animal genetic resources and it is economically viable and socially acceptable (Greenland, 1994).

2.4.2 Crude Oil and Soil Interaction

When oil spills on the ground, it penetrates easily to a depth range usually considered vital for agricultural activities. There is an interaction between the spilled oil and soil within the depth occupied by the spilled oil. Rainfall and ground water fluctuations provide the opportunity for the migration of the crude oil from the polluted site, causing extensive threats to the surrounding environment.

Soil constituents, type of petroleum hydrocarbon and the presence of water affect the interactive mechanism of soil and active constituents such as organic amorphous materials and clay materials in the soil matrix affects oil and soil interaction and the soil-oil bonding. Van der Waal's forces, weak hydrogen bonding and cation and water bridging dominate the bonding between oil and soil surfaces. Kings et al (1992). In their contributions, crude oil consists of large molecules with long chain lengths. It is expected that their primary mode of interaction will be by Van der Waal's force. In addition to this, Young et al (1994) highlighted three different situations that co-existed in an oil-soil mixture. These include the absorption of oil into the soil, the existence of oil in the soil pores and the oil formation bond between the particles.

2.5 Pollution

Pollution is the introduction of contaminants into an environment that causes instability, disorder, harm or discomfort to the ecosystem. I.e. physical system or living organism (wikkipedia,2009).

Pollution can take the form of chemical substance, or energy, such as noise, heat or light energy. Pollutants, the elements of pollution can be foreign substance or energies or naturally occurring; when naturally occurring, they are considered contaminants, when they exceed natural levels. Pollution is often closed as point source or nonpoint source pollution. (Wikipedia, 2009)

2.6 Types of Pollution

The major forms of pollution are listed below; (Wikipedia, 2007).

- Air pollution
- Water pollution
- Radioactive contamination
- Noise pollution
- Light pollution
- Visual pollution
- Thermal pollution etc.

A pollutant could be seen as a waste material that pollutes air, water or soil. Three factors determine the severity of a pollutant: it's chemical nature, the concentration and the persistence (Wikipedia, 2009).

Soil contamination occurs when chemicals are released by spills or underground leakage. Among the most significant soil contamination are hydrocarbons, heavy metals, herbicides, pesticides and chlorinated hydrocarbons. (Wikipedia, 2009)

2.7 Land Pollution

Land pollution is the degradation of earths land surfaces often caused by human activities and their misuse of land resources. Haphazard disposal of urban and industrial wastes, exploitation of minerals and improper use of soil by inadequate agricultural practices are a few factors.

Urbanization and industrialization are major causes of land pollution (Wikipedia, 2009).

2.8 Oil Spill

An oil spill is the release of a liquid petroleum hydrocarbon into the environment due to human activity and is a form of pollution. The oil, refined petroleum products (such as gasoline or diesel fuel) or by –products, ship bunkers, oily refuse or oil mixed in waste. Spill take months or even years to clean up.

Oil is also released into the environment from natural geologic seeps on the sea floor. Most human made oil pollution comes from land based activity, but public attention and regulation has tend to focus most on sea going oil tankers (wikkipedia.2009).

2.9 Causes of Spill

Rushton et al,2007 reported that based on data obtained from the seskatchwan spill response centre, the leading causes of spills are equipment failure and accident during road transport and most of the spills documented were from petroleum, transportation and mining companies (Rushton et.al. 2007).

2.10 Effect of Oil Spillage On:

2.10.1Soil Fertility and Crop Production

Felicia, et al 2006,_reported that oil spill on crops causes' great damage to the plant community due to high retention time of oil occasioned by limited flow. The oil hamper proper soil aeration as oil film on the soil surface acts as a physical barrier between air and the soil. In fact, oil pollution affects the physiochemical properties of the soil as temperature, structure, nutrient status and $p^{H.}$ Oiled shoot of crops like pepper and tomatoes may wilt and die off due to transpiration, and respiration. They also observed that germination, growth performance and yield of crops stifled by oil spillage.

2.10.2 Infiltration Rate of the Soil

Infiltration refers to the entry of water, when rain falls on agricultural soil, the soil tends to have infiltration rate which depends on the presence of soil pores. The rate of infiltration is reduced as the pore space blocks and other soil becomes saturated.

Novak et.al. [1994], hinted that when oil pollution occurs, some of the pollutants remain trapped in the pore space of the soil, reducing the rate of infiltration. He referred to this effect as the ganglion effect.

Also Ryan and Dhair [1993] revealed that when oil pollution occurs, films are formed between the soil grains hence reducing the infiltration rate. They are of the opinion that the effectiveness of the films in reducing infiltration rate depends on the viscosity of the crude oil. In their idea, the rate of infiltration of water through the oil polluted soil also decreases as the soil saturation increases.

2.10.3 Soil Permeability

The hydraulic conductivity in an oil polluted soil is highly influenced by the properties of the oil spill. In the opinion of young et al [1994], the soil permeability is enhanced if the oil viscosity is reduced. This in supportive of the finding by Mc Gill [1976], who hinted that the permeability of clay liner in a landfill is attracted as a result of prolonged control with organic liquid.

2.11 Effect of Moisture Content on Oil Recovery

According to McGill and Rowell [1980], moisture content have a high effect on oil recovery from the soil, hence should be considered in the remediation of oil polluted soil. In their opinion, water and oil interacts in the soil forming oil - in - water emulsion, which reduced remediation efficiency. They however, observed that soil must not be completely dried before remediation.

United state environmental protection agency [1998], supported their opinion by stating that the reduction of water content readily enhance remediation of oil from the soil. In its opinion, different mechanisms are used for reducing the water content. These include heating, drying and drainage. It was observed that 96% of oil are removed if soil moisture content is less than 45%

2.12 RemediationMethod

Rushton et al [2007], noted that soil remediation techniques can take place either in-situ or ex-situ using one or more of the current remediation technologies. These in clude: physical, thermal, chemical and biological processes

2.12.1 Physical Processes

Physical remediation technologies include soil washing and land filling.

2.12 .1.1 Soil Washing

Soil washing is when a wash solution (water and / or a surfactant) is added to soil to remove contaminants. The contaminant is transferred from the soil to the wash solution, which then must be treated. Residual sludge is often associated with this method. Water alone is not effective in removing crude oil contaminant. soil washing can also be used to remove 1, 2, 4- trichlorobenzen (T.C.B), aniline, phenol, and 2, 4- chlorophenol (D. C.P) water washing was found to be suitable for removing all contaminants except T.C.B which required washing with surfactant first and then rinsing with water. Other solutions such as hydrochloric acid and sodium hydroxide have also been used in soil washing techniques. (Rushton et al 2007)

2.12.1.2 Landfilling

Landfillng is one of the oldest forms of remediation. Rushtion et al (2007), revealed that contaminated soil is excavated from the site and transported to a landfill where it remains indefinitely. In cases where the soil is brought to a first generation landfill, there is still the potential for the contaminants to enter ground water or bedrock. However, .Rushton et al(2007) reported that methods have been devised for the removal of aromatic organics form soil which may help to control these contaminants in land fill.

2.12.2 Thermal Processes

According to Rushton et al (2007), there are currently three thermal remediation technologies in use: incineration, thermal desorption and radio frequency heating.

2.12.2.1 Incineration

According to Rushton et al (2007), incineration is the destruction of contaminants by burning contaminated soil. This method can achieve greater than 99.99% success in destroying carbon tetrachloride and chlorinated benzenes but is very expensive. He also hinted that however, catalytic incineration is more efficient than thermal incineration in destroying aromatic hydrocarbons.

2.12.2.2 Thermal Desorption

.Rushton et al 2007, hinted that in thermal desorption, soil is heated under an inert atmosphere to increase the vapor pressure of organic contaminants causing the contaminants to volatilize and be released from the soil. In the same journal, Rushtion et al (2007) found that low heating rates practically eliminates gas oil from soil matrices while higher temperatures were required to achieve optimal efficiencies.

2.12.2.3 Radio Frequency Heating

Radio frequency power, according to Rushton et al (2007), has been used in the steam reforming of hydrocarbons. These waves are converted to thermal energy in the soil for heating the contaminants and causing their volatilization. He also noted that the procedure is very expensive but because the heat can be directed, the treatment is more accurate.

2.13.3 Chemical Process

Chemical process is a technique which involve the use of peroxide or an alkaline solution with a p^{H} of 10.5 containing cobalt (111) in addition to contaminated soil to oxidize organic contaminants CO_2 and CO. Superficial water can also be used to oxidize hazardous materials (Rushton et al, 2007)

2.13.4 Biological Processes

There are a number of biological technologies currently in use: land farming, biopiling, composting, bioventing and liquid delivery. It should be noted that hydrocarbon concentration of less than 10ug/l do not usually stimulate microbial growth and hydrocarbons with rings or many branches are slower to biodegrade. (Rushton et al, 2007).

2.13.4.1 Landfarming

The processes involved with this method of treatment include: leaching, adsorption, desorption, photodecomposition, oxidation, hydrolysis, and biological metabolism. Aeration and nutrient are provided by tilling the soil regularly. (Rushton et al, 2007).

There are several disadvantages to this form of treatment:

(a) It requires a large amount of land area which can be difficult to find in populated areas.

(b) It has potential to contaminate groundwater.

(c) It is sensitive to weather.

(d) There is chance of contaminant transport.

2.13.4.2 Biopiling

Biopiling is an ex-situ remediation method that is very effective in nutrient supplementation (Rushton et al). Biopiling require accessible contaminated soil and sufficient land area. It has been found that contaminants in biopiles show the greatest reduction in contamination over the summer month. While treating diesel contaminated soil Rushton et al (2007) found that sand improve pile porosity(and subsequently oxygen diffusion)and surfactants were effective in increasing contaminant (and subsequently oxygen diffusion)and surfactants were effective in increasing contaminant bioavailability. Rushton et al, 2007 mixed nutrient (N.P.K) and microbes in soil biopiles and found mineral oil degradation rates to be the highest in the first months, following a standard first order degradation curve.

2.13.4.3 Composting

Contaminated soil is mixed with a bulking agent such as manure or wood chips, and heaped in a large pile. Manure or sewage sludge are also used for inculcation of the pile to provide high microbial diversity, specifically mesophilic and thermophilic microbes. (Rushton et al,2007). Compositing can be carried out in-situ or ex-situ to treat highly contaminated soils. Machinery is used to turn the pile (aerating it). Moisture, nutrient and PH levels are also controlled.

2.13.4.4 Bioventing

Bioventing is suitable for less volatile contaminants that are biodegradable under aerobic conditions. When volatile compounds are present, off-gases need to be treated, thereby increasing the cost of the operation. This process is most applicable where the water table is greater than 3 meters deep from the surface. The site must be capped if the soil and water table are shallow.

Bioventing should not be used near building because there is the potential for an explosion. Moisture levels of 40% to 60% of field saturation must be maintained in order for the operation to successful. (Rushton et al, 2007).

2.13.4.5 Liquid Delivery System

Liquid delivery system require extensive site characterization and best for sites with fractured rock aquifers, or when control of plume migration is mandated.

The cost of the operation depends on the type of contaminants present, the amount and extent of contamination, sediment characteristics and source of oxygen. For example, low numbers of microbes are associated with clay soils and the addition of 100mg/l of hydrogen peroxide as an oxygen source can be toxic to biota (Rust ton et al 2007). They also reported that hydrogen peroxide is a major source of OH radicals of hydrocarbons in the soil.

2.13.4.6 Bioreactors

There are many different types and sizes of bioreactors ranging from a vessel of a few litres to large systems that can hold millions of litres. Bioreactors have a shorter detention time, low costs than traditional, physical, thermal and chemical reactors take up less space, are simple to use, and offer an economic and technical advantage for contaminated soils having high moisture content.

They are divided into three categories based on the state of the medium: solid, liquid and gas bioreactors. Solid reactors can handle contaminated soil and they include static bed reactors, continuous mix reactors, horizontal drum reactors and fungal compost reactors.

Liquid reactors are designed for liquid medium or slurry and they include slurry phase reactors and dual injection turbulent suspension reactors. Gas bioreactors are usually used in a combination with solid or liquid reactors to remove volatile organic contaminants from the exhaust gas if those reactors and they include a variety of biofilters and packed bed reactors. (Ruhston et al 2007)

2.14 Advantages and Disadvantages of Biological and Non- Biologic Processes

Both biological and non-biological processes have their merits and demerits. A summary of the positive and negative aspects of each process is presented below in table 2.1

PROCESS	ADVANTAGES	DISADVANTAGES
Land farming	- least expensive - can be performed ex-site or in-site	- long residence time - unsuitable in towns (large land area required) - Potential for contaminating water, air, soil. - sensitive to whether - limited capability in degrading complex compounds - possibility of contaminants transport - Requires less than 2% grade slope
Biopiling	- effective nutrient supplementation - second least expensive	- Biodegradation occurs during summer months unless steam is applied. - Soil must be accessible. - Land requirement is relatively large. - Requires infrastructure.
Liquid Delivery System	- Good for fractured rock aquifers. - Good for shallow water tables.	- Requires extensive site characterization. - Longer time frame

Co positioning	- High microbial diversity - Low capital and operating costs. - Simple operation and design. - High treatment efficiency. - Moisture, nutrient, and PH levels can be controlled. - Less threat than incineration. - No mixing with surface. - Shorter treatment time than land farming.	- Large land requirement. - Difficulty sitting. - Time required. - Possible groundwater contamination. - Difficulty to capture off- gasses
Bioventing	- Can be low cost. - High efficiency.	- Site may need to be capped. - Off gasses may need further treatment. - Should not be near buildings (explosion hazard). - Can be difficult to add nutrients. - Can take years. - Requires underground infracture. - Not suitable for volatile organic compounds

Table 2.2 Advantages and Disadvantages of Land Based Biological Methods

Advantages	Disadvantages
- Shorter time- frame (70 times faster than landfarming). - Less space required. - Can capture volatile organic compound. - Can have aerobic conditions for recalcitrant compounds. - Work on concentrated residues. - Can be coupled with other techniques. - Economic and technical advantage for saturated soils. - Can be cheap. - Various sizes (several liters to millions of liters).	- Some reactors can be expensive - Soil sometimes has to be pretreated. - Requires constant mixing. - Off-gasses likely require further treatment

Table 2.2 Advantages and Disadvantages of Bioreactors

2.15 Previous Work done On the Remediation of Crude oil Polluted Soils

There has been a great deal of work done on biological based treatment processes of crude oil contaminated soil. The following notes are extracts from relevant literature on relevant works related to this work.

Odguvwuederhie et al 2006, worked on the effect of oil spillage on crop yield and farm income in Delta state, Nigeria. In their work, they used a sample of 262 crop farmers drawn randomly from ten communities and five local government areas in the oil producing agro ecological zones of Delta state to accentuate the negative impact of oil spill on crop production. They discovered that oil spill reduced crop yield, land productivity, and greatly depressed farm income as a ten percentage increase in oil spill reduced crop yield by 1.3 percent while farm income plummeted by five percent. In order to halt the continual degradation of the Niger Delta environment, the authors recommended the enactment and enforcement stringent environmental laws to protect the areas as well as the implementation of policies to reduce the crusting level of poverty and guarantee a better livelihood for the people. Ayotamuno et al 2006, worked on the bioremediation of crude oil polluted agricultural soil at Port Harcourt, Nigeria. In their work a combination of treatment consisting of the application of fertilizer and oxygen exposure was evaluated in-situ during a period of six weeks. The result obtained from this experimental work was very impressive with 50% to 95% hydrocarbon loses. The result of this study indicated that the application of increased concentration of nutrients (by the application of fertilizers) lead to a greater rate of petroleum products bio-degradation. However, the microbiological characteristics of the contaminated soils and other forms of bioremediation approach needs to be investigated.

Ubochi et al 2006, worked on the effects of inorganic fertilizer (NPK agricultural fertilizer) on microbial utilization of hydrocarbons on oil contaminated soil. They came out with a very promising result in the remediation of oil contaminated soil after seven weeks of bio-stimulation approach of investigation. The result of the study suggested that addition of fertilizer (especially 60g NPK agricultural fertilizer) will further enhance microbial utilization of hydrocarbons.

Ekpo and Udofia 2008, studied the rate of biodegradation of crude oil by micro-organism isolated from crude oil sludge environment in Eket, Akwa Ibom state of Nigeria. The author used mineral salt medium supplemented with crude oil and three most abundant species isolated from a crude oil sludge soil-micrococcus varians, bacillus subtilis and pseudomonas aeruginosa for the degradation test. The result showed that pseudomonas aeruginosa was found to have the highest rate of degradation with 97.2% which is very interesting. However other forms of biodegradation approaches need to be investigated because the microbiology of the polluted soil was not well elaborated.

16 Engineering Structures Used In The Remediation Of Oil Polluted Soil.

As remarked by Ferguson (1992), different engineering structures are used for the remediation of oil contaminated farmlands. The structures are constructed to perform isolation and removal functions. He enlisted the structures below as the structures used for remediation of oil polluted farmlands. These structures are copping, covering, vertical barriers, drains, boreholes, horizontal barriers, vacuum systems, irrigation systems and pumping systems.

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 Study Area

The investigation was undertaken at a mechanic workshop located at Northern by-pass Wushishi road in Minna Niger state. Minna is the capital city of Niger state. Minna is within the tropical Sahara desert zone with longitude 6° 30°E to longitude 5° 30° E Minna has a sum annual rainfall of between 1038.3 to 1423.4mm and mean annual temperature of between 32° and 29° during the dry season.

The study site, situated within the rocky areas of Minna is characterised by flat flying land with concentrated distribution of hills. Soil is classified as sand silt. Remediation was carried out on the moderately drained land.

3.2 Experimental Design

A plot measuring 1m by 2m was used for this work. The plot was demarcated with the aid of pegs and ropes to avoid intrusion and interruption. The plot used was ploughed to a depth of 30cm. The plot was in such a way that the depth and exposed surface area of the soil, and in turn its temperature, nutrient concentration, moisture content and oxygen availability, could be controlled. Furthermore, the cells inhibited excess runoffs of the used motor petroleum product contaminants. Such run-off was inevitable since the remediation study took place from June to September 2009, in the open air and so exposed to the rains.

Cell O was the control volume (i.e. did not receive any treatment), while cell B received 4.2kg of fertilizer, 0.02m^3 of wood dust and 0.186m^3 of horse manure during the remediation period.

.3 Soil Treatment

Prior to nutrient application, the soil was tilled to a depth of 15cm with the aid of digger and shovel (on June 5, 2009) and allowed for three days in an open air for proper aeration of the soil to activate the soil micro-organisms.

On June 7, 2009, one kilogram of agricultural fertilizer was applied on the plot at the rate of 1 kilogram of fertilizer (NPK 20.20.10) per 2m^2 of soil. N.P.K. 20, 10, 10 fertilizer was selected for the relatively high nitrogen content and this fertilizer is commonly available in the market. Plots were tilled again to incorporate these materials to the depth of 15cm.

On June 15 2009, a mixture of sawdust and horse manure was dry applied to the plots. Approximately 0.186m3 of manure was applied once, covering the plot to a depth of 2cm or deeper and then tilled into the soil.

One June 2 21 2009 which is the second remediation week, the soil was tilled prior to collection of composite samples. Composite samples consisted of 5 equally spaced collection sites within the plot. The sample was analysed in a contract laboratory. Following sample collection, N.P.K. 20, 10, 10 agricultural fertilizers was applied or added at the rate of 1kg/m^2 to the plot and then tilled to mix nutrients and aerate.

The soil plot was tilled every two days for proper aeration and to avoid compaction in order to generate an anaerobic condition which disturbs the aerobic micro-organisms. The second composite sample was taken on July 5 2009, after tilling to a depth of 30cm to identify any possible deep leaching of hydrocarbons. N.P.K. 20, 10, 10 fertilizer was applied at the rate of 0.6kg/m^2 and tilled into the soil.

The final and closing composite sample collection was done on 19th July 2009 after tilling the soil to a depth of 30cm. restoration of the site and closure of the study was completed with planting of maize seed.

.4 Soil Samples

These were obtained using a hand-dug soil auger and put in labelled polyethylene bags. The samples for the total hydrocarbon content (THC) measurements were placed in one litre glass bottles and sealed with aluminium foil. This procedure was undertaken three times. The bags and glasses were immediately transferred to the laboratory for analysis

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.5 Analysis of Soil Characteristics

Measures were made of some of the soil physiochemical parameters, such as particle size distribution; total hydrocarbon content; concentration of organic carbon; nitrogen, phosphorus, potassium, and nutrient in the soil; the soil's PH value: its electrical conductivity and bacteria counts. Some heavy metals were also measured like calcium, chromium and lead concentration in the soil.

6 Particle Size Analysis [Hydrometer Method] Determinations

51og of air dried soil which has been passed through 2mm sieve was measured into a 250ml beaker. 100ml of calgon was added and allowed to soak for at least 30 minutes. The suspension was stirred or mixed for about 3 minutes, with a mechanical stirrer in a dispersing cup . the suspension was transferred quantitatively to a sedimentary cylinder and filled to the mark with distilled water while hydrometer is in the suspension. A plunger was inserted and moved up and down to mix the contents thoroughly. The sediment was dislodged with strong upward strokes of the plunger near the bottom and by spinning the plunger while the disk is just above the sediment. The stirring was finished with two or three more strokes and the time was recorded. The hydrometer was carefully lowered into the suspension and reading taken after 40 secons. The temperature of the suspension was taken using a thermometer after moving the hydrometer. The suspension was remixed and the 40 seconds reading was repeated until reliable reading was obtained. Two hours after the final mixing of the suspension another hydrometer and temperature reading was taken and recorded, [Ibitoye 2008]

3.7 Total Hydrocarbon Content Determination

One grain of each soil samples was put into a 500ml volumetric flask and to this was added 200ml of xylene. The xylene/soil mixture was shaken vigorously for five minutes and filtered into 400ml cylinder. The volumetric flask and soil materials were rinsed properly with 500ml xylene and filtered again into the cylinder. Total hydrocarbon content in the xylene/hydrocarbon mixture was thereafter determined by photometric method using utral violent spectrometer at a wavelength of 25mm. total hydrocarbon content was estimated from the calibration curve, obtained by measuring absorbance of a standard prepared by diluting 2.5,,20.0,20.0,25.0 and 30.0 microliters of lease crude oil with 50ml xylene solution. The absorbance measurement was plotted against the concentration of each calibration standard to obtain the calibration curve. [Osuji and Ezebuiro 2006].

8 Soil Moisture Content Determination

Clean and labelled moisture can that has been oven-dried and weight (W1). Enough soil sample was added into the moisture can and weighted (W2). The moisture can containing the soil sample was transferred into thermo-setting oven. The moisture-can was removed and allowed to cool in a indicator for about one hour. Then the oven-dried moisture can containing soil was weighed (W3). The moisture content of the soil was calculated. The loss in weight after drying in the oven is the moisture content of the soil [Ibitoye 2008].

3.9 pH Determination and Electrical Conductivity

Ten grams (10.g) of each soil sample was added 20ml of distilled water. The lump of soil was stirred several times in suspension over a 30 minutes interval to from homogenous slurry, then the pH meter probe [model] was immersed into the samples and allowed to stabilize at 25^0c and pH was recorded [Ibitoye 2008]. Was conductivity was measured using the conductivity meter [model].

0 Organic Carbon/Matter Determination

Soil sample was grinded to a fine powder and one grain was transferred into a 250ml conical flask. 10ml 0.167m$k_2cr_2$07 was added. 20ml of concentrated H_25O_4 was rapidly added, the flask was immediately swirled gently until soil and reagents are mixed, the flask is rotated again and allowed to stand for 30 minutes. 100ml of distilled water was added after standing for 30 minutes. Four drops of ferroin indicator was added and titrated with 0.5m of iron (ii) ammoniumsulphate or iron (ii) sulphate takes a greenish cast and then changes to dark green. A this point ferrous sulphate was added drop by drop until colour changes shaply from green to brownish red. A blank titration in the same manner was made without adding distilled water, 0.167m$k_2cr_20_7$ and H_25O_4 to standardize the iron (ii) solution. The reaction is $k_2cr_20_7$ oxidying carbon and the excess $k_2cr_20_7$ is titrated with iron (ii) solution. [Ibitoye 2008].

The percentage organic carbon and organic matter was determined via calculations using standard formulas.

11 Chromium, Cadmium and Lead

Soil samples was digested, filtered and presented for instrumentational analysis of the element of interest [Cd, Cr, and Pb] using the bulk atomic absorption spectrometer (AAS). The AAS was firstly calibrated using standard solutions of the elements of interest and the sample readings obtained and expressed in cone. The procedure was repeated for all the samples and the result recorded.

Determination of Available Phosphorus

5g of soil which has passed 2mm sieve was weighed 35ml of extracting solution was added. The mixture was shaken for one minute and filtered. Then phosphorus was determined calorimetrically. The extracting solution was the addition of 30ml of 1M NH_4f and 0.5m Hcl to make up a litre.

The procedure was repeated for all samples.

3 Determination of Potassium

Potassium {k} is usually determined using flame photometer. The instrument is of atomic spectrometry for quantitative determination.

When the atoms of an alkali metal are heated sufficiently to high temperature. It absorb energy from the source of heat and became easily exited. The electrons move from lower energy level to a higher energy level, that is from stable configuration to original state as they cool or fall to the original state. The atoms will therefore emit so many radiant energy equivalent in magnitude to the amount of energy absorbed during excitation. The wavelength of emitted radiant energy has direct relationship with the electronic transition that occurred. As every element has its own peculiar electronic configuration, wavelength of light emitted is unique for such a particular element.

In atomic emission spectrophotometry, the frequency emitted is isolated and measured by an optical filter with suitable photo detector placed behind the filter. An electrical is obtained which proportional to the concentration of the element in the test solution. The electrical signal is amplified and used to drive a moving coil meter.

Potassium values for all the soil samples was taken and recorded.1

Nitrogen Determination

The accepted standard method for the determination of nitrogen in samples is the complete digestion of sample in hot concentrated acid, and in the presence of appropriate metal ion catalyst. The catalyst is to convert all nitrogen in the nitrogen materials in the samples into ammonium ion. Upon the addition of alkali to the digest air is released which may then either be distilled out of the sample and determined by acid base titration, or ammonia can be reacted with an appropriate reagent: phenol and sodium hypochlorite, to give a coloured derivative which can be measured with colorimeter or spectrophotometer.

The kjeldahl digestion is usually performed by heating the samples with containing substances which promote oxidation of organic mater by increasing the point of the acid [$k_2 50_4$ or $Na_2\ 50_4$] and se or cu which increase the state of organic matter. These reagents here referred to as catalyst.

5 **Bacteriological Analysis**

One routine method for determining the microbial content of soil is the soil dilution plate method. The method is based on the assumption that each viable cell will develop into a single colour and therefore the number of colonies that develops is regarded as the number of microbes in the sample.

In this test 1ml of appropriate dilution is withdrawn into 9ml of molten agar in the test-tube. The plates were incubated inverted at 35^0 for 48 hours. The number of colonies formed after incubation period was counted and the number of colonies was multiplied by the dilution factor gives the plate count per ml of the soil sample.

CHAPTER FOUR

RESULT AND DISCUSSION

.0 Result Presentation

In order to understand the behaviour of the pollutant during the remediation process or the study, series of tests were carried out. The results of the tests are presented in tables 4.1 to 4.5 the particle size analyses of the 30cm thick, top layer of the soil before treatment showed that the soil texture is sandy silt [see table 4.1]

Treatment Cell	Sand	Silt	Clay
Unpolluted plot	94.2	5.28	0.52
Already polluted plot	96.26	3.9	-0.156

Table 4.1 Summary of the Soil Textural Class

Soil Parameters	Values
% Moisture content	12. 2%
% Organic carbon	0. 15%
% Organic matter	0. 26%
% Nitrogen	0. 06%
pH	7 .5
Available phosphorus	2. 10 ppm
Sodium	0. 59 $cmolkg^{-1}$
Potassium	0. 37 $cmolkg^{-1}$
Lead	0. 30 ppm
Chromium	ppm
Cadmium	ppm
Electrical conductivity	95. 00 Ns\ cm

Table 4.2 Beck Ground Soil Physiochemical Characteristic Values [i.e. unpolluted site data]

Treated Cell	Sampling Period (Wks)	Cr (ppm)	Cd (ppm)	Pb (ppm)
A	0	0.4215	0.0464	0.6154
	2	0.7553	0.0464	0.5824
	4	0.9133	0.0283	0.5824
	5	0.9244	0.0134	0.2200

Table 4.3 Heavy Metals Reduction

Parameters	Treated cell	Sampling period (weeks)			
		0	2	4	6
% Moisture content	A	5.81	8.70	11.2	16. 30
P H	A	6.03	5.80	6.10	6.70
% Organic carbon	A	1.99	2.19	1.99	0.19
% Organic matter	A	3.44	3.78	3.44	0.32
% Nitrogen	A	0.045	0.134	1.10	0. 11
Available Phosphorus [ppm	A	0.017	1.13	1. 05	2. 18
Sodium [cmolkg^{-1}]	A	0.32	0.42	0. 36	0. 67
Potassium [cmolkg^{-1}]	A	0.12	0.20	0.17	0.91
Electrical conductivity [us/cm]	A	50.8	0.32	0.83	105.00

Table 4.4 Soil Physiochemical characteristics during six weeks of remediation (the result is the average of two replicates)

Treated cell	Sampling period (weeks)			
	0	2	4	6
A	3.23	2.10	1.56	0.63

TABLE 4.5 Total hydrocarbon reduction (*10^6 ppm)

About 80% Total Hydrocarbon Content reductions

Treatment cell	Sampling period (weeks)	Bacteria count (x10^6 cfu/ml)
A	0	0.018
	2	1,42
	4	226
	6	0.25

Table 4.6 Total hetotrophic bacteria count

The background [I.e. unpolluted site] sample had a bacteria count of 1. 22x10^6 cfu /ml

Parameters	Sampling period (weeks)	
	0	6
% Moisture content	5.80	8.20
PH	6.03	6.20
% Organic carbon	1.99	2.20
% Organic matter	3.44	3.80
% Nitrogen	0 .045	0.045
Available phosphorus (ppm)	0. 017	0. 09
Sodium (cmolkg^{-1})	0. 32	0. 41
Potassium (cmolkg^{-1})	0.12	0. 20
Electrical conductivity (us/ cm)	50. 8	53.5
Total petroleum hydrocarbon (ppm)	3.23x10^3	4.32x10^3
Cadmium (ppm)	0 .0464	0. 1364
Chromium (ppm)	0 .4215	0 .4515
Lead (ppm)	0. 6154	0. 7130

Table 4.7 Control Site Physiochemical characteristic Parameter result [Untreated polluted sit

Observation and Discussion

The soil moisture content of the unpolluted site averaged 12.2%. It dropped to 5. 81% on the polluted site prior to remediation and later incensed during remediation because of the rainfall. Ayotamuno et al 2006, reported that in heavily polluted soils, water droplets adhere to the hydrophobic layer, and it prevents the wetting of the soil aggregates. As a result, during the study the site was remedied through the introduction of fertilizers, manure and tilling this process continued throughout the month of July during which high rainfall occurred and resulted in significant increase in the moisture content, i .e as high as 16.3% on the treatment site.

Soil pH, or the relative acidity of the soil also affects microbe population development and therefore the rate at which the proceeds. Microbe colonies thrive within a fairly narrow pH range for this study pH was measured in the laboratory.

The soil pH of the polluted site reduced compared to the background result, it further decreased during the remediation treatment. After six weeks total remediation period, the pH increased (see table 4.2). Ayotamuno et al (2006) made similar observation and reported that the decrease in pH during remediation treatment may have resulted from the production of acid radicals through the process of nitrification of the applied fertilizer. Similarly, the electrical conductivity (EC) of the earth in the soil generally increased. The soluble salt-content in the soil which was due to the introduction of the inorganic fertilizer caused a general increase in the electrical conductivity. Ayotamuno et al (2006) made similar observation.

There was a significant increase in the polluted soils carbon content resulting from the used motor oil contamination so corroborating Ayotamuno et al (2006). However, the organic carbon content dropped to near background conditions during the remediation treatment. This situation suggests that the amount of carbon reduced with time as the remediation progressed.

The Nitrogen value of the polluted site was lower compared to the unpolluted site. This decrease in total nitrogen of the polluted soil may be due to temporal immobilization of this nutrient by microbes resulting, which might have increased in population. Agbogidi et al (2007) had earlier reported that oil spills on land resulted in an imbalance in the carbon-nitrogen ration which, if not in the right amount in soils resulted in net immobilization of nutrients by microbes leading to loss of soil fertility. During the remediation period, the total nitrogen increased and reduced a little after six weeks of remediation. This is because a fertilizer was continually fed into the soil via tilling to avoid over utilization of nitrogen due increase in soil microbes. Ayotamuno et al (2006) reported that during biodegradation, nitrogen may be lost to the atmosphere when nitrate ions are converted to gaseous forms of nitrogen by a series of widely-occurring biochemical reduction reactions, brought about by denitrifying bacteria such as pseudomonas, bacillus and micrococcus, especially when localized micro-sites of low oxygen exist well within the soil aggregates.

There was marked decrease in the concentration of total hydrocarbon content in the earth sample in the site. After sis weeks of remediation, the concentration of total petroleum hydrocarbon reduced from 3.234 $x10^3$ppm to 0.63 $x10^3$ppm, which is about 80%

reduction. The result indicate that the applied fertilizer and manure increased the degradation of the hydrocarbon since the total hydrocarbon content of the control site that received no fertilizer treatment was on the increase. This rise in the concentration of the total hydrocarbon content of the control site was due to the existing anaerobic conditions. These resulted because the control-site earth was not tilted at all, so there was insufficient oxygen supply and hence, anaerobic decomposition ensued resulting in inorganic materials being produced and hence the increase in the total hydrocarbon content.

Result of the total heterotrophic bacteria (THB) count showed that there was a great increase in the THB (table 4.5). However, the control cell exhibited different behaviour. The control cell increased at a lower rate. Ayotamuno et al (2006) said that relatively low values obtained in the control cell may have resulted from the toxicity of the used motor oil to the soil microbes, brought about by high concentration of the used motor oil before remediation treatment. After six weeks remediation, THB count of the treated site declined slightly. This may have been due to the retardation of microbial activity resulting from the high concentration of ammonia gas released from the fertilizer, because most commercial fertilizer supply nitrogen in soluble forms, such as nitrate or ammonium. This has been reported previously by Ayotomuno et al (2006). The hydrocarbon-utilizing bacteria types isolated from this site or earth samples were bacillus, pseudomonas, micrococcus, serratia and Escherichia.

Heavy metals were also monitored through the course of this study. These metals have a tendency to complex and are not easily purged from a system. If present in certain chemical form and in elevated concentrations, heavy metals have a toxic effect. Certain heavy metals may occur naturally in soils while others may be introduced.

Background and control soil samples for heavy metals were analyzed. The unpolluted site sample had chromium, cadmium and lead in the concentrations of 0.9202, 0.0082, and 0.300ppm while the control site had chromium, cadmium and lead in the concentrations of 0.4215ppm, 0.0464ppm and 0.6134ppm respectively. From table 4.2, 4.3, and 4.6, the increase in the concentration of cadmium and lead on the polluted site was as a result of the used motor oil pollution because used motor oil derived from crude oil consists of many toxic elements in which lead and cadmium are part. After six weeks remediation, they dropped almost to background condition. This shows that the addition of nutrient and tilling of the soil provided favourable condition for the soil microbes to degrade the hydrocarbon in the soil along with the heavy metal. It also shows that the soil heavy metals were not too high to disrupt microbial degradation.

CHAPTER FIVE

CONCLUSION AND RECOMMENDATION

Conclusion

Results of this study shows that bioremediation process is an effective method for site remediation of use motor oil contaminated soil in certain settings. Nutrient – enhanced bioremediation can achieve the degradation of petroleum hydrocarbon in soils. What is necessary is the supply of the right type (s) quantities or application rates of fertilizer and manure and also the provision of other suitable environmental conditions for the accelerated development of soil microbes. The total hydrocarbon content result (1 . e the basic index of evaluation) of the treated soil (which received 0.186m3 of manure and 4.2kg of fertilizer per 2m2 of soil) recorded above 80% total hydrocarbon content loss after six – week period. For fast biodegradation of hydrocarbons in the soil certain optima should apply, i.e a pH value in the range of 6.0 ----- 6.5 moisture content of between 11 to 16% durian the wet season and a and a tillage rate of between 3 and six times a week.

Recommendation

For an effective bioremediation,

1. Nitrogenous-base fertilizers (preferably NPK) and manures should be used to stimulate the soil microbes because of their effectiveness in the remediation of used motor oil polluted soil.

2. Bioremediation should be applied during the dry season because a wet soil induces anaerobic conditions that impede accelerated biodegradation. When done during the wet season, the rate of tillage should be increased to above two times a day to facilitate adequate mixing of the nutrients and microbes with the contaminated soil and also to enhance the diffusion rate of oxygen to the deeper layers.
3. A team of agricultural engineers that are specialist in waste management, soil and water, and environmental control should be employed and used for the remediation of used motor oil polluted soil.
4. There should be public awareness on the hazards of used motor oil pollution on the soil.

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