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# Chemo-Remediation of Crude Oil Polluted Soils Obtained from Recent Polluted Site in Oil Producing Environs in Rivers State Nigeria

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## ABSTRACT

The chemo- remediation of crude oil polluted soils from recent pollution sites in oil producing environs in River state was carried out by both in vivo and in vitro methods using macro-soil nutrients ( Nitrate, Phosphate and Potassium) as index for remediation. The soil samples were labeled A, B, C, D1 to D6, sample A was obtained from pollution free site used as a control. Sample C was crude oil polluted soil not treated with surfactant, sample B was crude oil polluted soil leached with surfactant and not mineralized. Samples D1-D6 were polluted soil samples, leached with surfactant and mineralized with fertilizer. The samples were leached with linear alkyl benzene sulphonate (LABS) and later mineralized with Nitrate, Phosphate and Potassium (N.P.K) fertilizer and returned to the site of excavation to fallow for four months. The samples were later re-excavated and taken to the laboratory for analysis. Nitrate and phosphate contents were obtained with the aid of spectrum lab 725 UV visible spectrophotometer and potassium content was determined by use of a flame photometer. Results showed that sample A had nitrate concentration of 330ppm, sample B had concentration of 21ppm, sample C had a concentration of 54ppm while samples D-D6 had concentrations ranging from300ppm to 420ppm.Similarly, The phosphate concentrations were 68.50ppm, 17.00ppn, 28.00ppm and 48.80-136.40ppm for sample A, B, C.D1-D6 respectively. The potassium concentrations were not different as concentrations of 46ppm, 12ppm, 28ppm and 38ppm-64ppm was recorded for samples A, B, C, and D1-D6 respectively. These results revealed that crude oils not only renders soils unusable but also destroys the nutrient availability in soils. The soils can therefore quickly be reclaimed by leaching them with surfactants and mineralizing them with adequate inorganic fertilizer.

**Keywords:**
Nitrogen. Potassium, phosphorus, mineralization, spectrophotometer

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## INTRODUCTION

Oil spills occur naturally by natural disasters such as ; movement of tectonic plates and also as a result of inadequate trap system. Oil spill can be caused by natural seepage, especially in the ocean, as tectonic plates shift; they may release oil from reserves traps. Oil spills can occur due to man-made reasons which include: carelessness, oil bunkering, Oil siphoning, terrorism and accidents (such as tanker accidents and accident during production operation) [1]. These spills causes a reduction in body temperature which may lead to death of both birds and mammals, this occurs by poisoning of the mammals liver or lungs. It can also cause blindness to certain animals which reduces their ability to avoid predators and they may be killed.[2] These spills exposes the animals and humans to lots of health issues and diseases. Oil hamper proper soil aeration as oil film on the soil surface acts as a physical barrier between air and the soil leading to a reduction or total blockade of oxygen, temperature, nutrient status and pH level. Oiled shoots of crops like pepper and tomatoes may wilt and die off due to blockage of stomata thereby inhibiting photosynthesis, transpiration and respiration [3, 4.5]

Major oil spills in the coastal zone include the Forcado tank 6 Terminal in Delta state incident that spilled 570,000 barrels of oil into the Forcados estuary in July 1979, polluting the aquatic environment and surrounding swamp forest; the Funiwa No.5 Well in Funiwa Field that spilled an estimated 421,000 barrels of oil into the ocean from January 17 to January 30, 1980, destroying 836 acres of mangrove forest; and the Oshika village spillage in River state that spilled 5,000 barrels of oil in 1983, flooding the lake and swamp forest and causing high mortality in crabs, fish, and embryonic shrimp[.6] An average of 240,000 barrels of crude oil are spilled in the Niger delta every year. There were about 5334 reported cases of crude oil spillages between 1976 and 1997, with over 2.8m barrels of crude oil released into the environment. It was reported that about 400,000 barrels of crude oil was released into the sea off Bayelsa State in the Texaco's Funiwa -5 well blow-out in 1980. About 40,000 barrels of crude oil was also released into the sea on January 12 1998 from Mobil producing Nigeria Unlimited Idaho oil Spill which occurred near Akwa-Ibom state due to a burst on corroded oil pipeline conveying crude oil from Idaho oil field to Qua Iboe Terminal at Mkpanak[ 4, 5 7] It has been estimated that there are over 221 oil spills per year in the Niger delta region alone[ 8] . Oil degrading bacteria such as Azotabacter spp has been found to abound in soils polluted with crude oils [9]. The toxicity of crude oil leads to the destruction of soil flora and fauna The water ways are not spared because of its harmful effects and films that block oxygen from dissolving into the water thereby suffocating the water biota [10].Soils polluted with crude oils experiences impeded gas exchange, and destruction of microbes that are necessary for fixation of nitrogen and other essential elements to the soil. Many works on remediation of crude oil polluted lands and water ways have been carried out[ 11].Much success has being achieved in remediation works on soils that were polluted with crude oils and successfully reclaimed by use of macro nutrient supplements as indexes for reclamation. In other words, organic manure has been applied to reclaim polluted soil [12]. Other methods so applied included the use of microbes of biological agents to break down or remove oils bioremediation, application of inorganic fertilizer, (chemo-remediation) and application of heat to the affected soil (thermal-remediation).

## MATERIALS AND METHOD

### FIELD RECONNAISSANCE AND SAMPLING TECHNIQUE

The soil samples were obtained near a busted oil pipeline in Ogoni land Rivers State Sampling plots were erected using a grid system. The soil samples were taken from nine different portions at subsurface area of 0-20 cm

and a depth of about 40cm; each sample was bagged in cellophane bags and labeled. The portions from where they were taken were also pegged with identifying labels. The samples were labeled A to D, with D having six samples-labeled D1 to D6. Sample A was obtained from a portion of land not polluted by crude oil. The Soil samples were taken to the laboratory of Chemistry department, Federal University of Technology Owerri.

## LEACHING AND MINERALIZATION METHOD

Sample A was an unpolluted soil sample reserved as a control, sample C was a polluted soil sample not leached with surfactant, sample B was a polluted soil sample leached with surfactant but not mineralized with fertilizer. Samples D1-D6 was polluted soil samples leached with surfactant and mineralized with fertilizer. To each of the samples B, D1-D6 was leached with equal amount of surfactant made from linear alkyl Benzene sulphonate. Ikg of each sample was treated 500$cm^3$ of 100g/L of solution of surfactant and allowed to stand for three days; the surfactants were allowed to drain out through perforation made at the bottom of the sample containers. This was done knowing that when an emulsifying agent like detergent is added, a suitable emulsion of the linear alkyl benzene sulphonate results, which is safely flushed out into drains. The leached samples D1- D6 were mineralized with 5-25g of NPK fertilizer containing KCl, $KH_2PO_4$ and $(NH_4)_2S0_4$. The samples were returned to their sites and allowed to stay for 4 months before being re-excavation and subsequent laboratory analysis. The essence of returning the samples to the site of excavation is to allow normal microbial activities and aeration.

## DETERMINATION OF NITRATES

10.0g of soil sample was mixed with 2g quantity of 0.5M $K_2S0_4$ in a beaker. This was shaken for 30 minutes and subsequently extracted. The extract was centrifuged at 60rpm. 0.5 $cm^3$ of the extract was pipette into a test tube. Also 0.5 $cm^3$ of a standard Nitrate was pipette into another test tube. To each of them was added 1.0 $cm^3$ of 5% salicylic acid, and later 10$cm^3$ of 4M Na0H solution was added and mixed properly and left to stand for one hour to allow full colour development. The absorbance of the samples was taken at a wavelength of 410-nm using spectrum lab 725 UV visible spectrophotometer. This was repeated thrice with each of the samples and the mean values were recorded. Similarly the absorbances of different standard Nitrate solutions were taken.

## DETERMINATION OF PHOSPHATE

2$cm^3$ of standard phosphate solution was pipette into a test tube and immersed in a water bath at 29ºC, 1$cm^3$ of 2.5% ammonium molybdate was added to the test tube and mixed properly, 0.15 $cm^3$ of stannous chloride was then added and the mixture diluted to 50 $cm^3$ with distilled water and allowed to stand for 5 minutes. The absorbance of the resultant mixture was read at 660nm. The procedure was repeated with different concentrations of standard phosphate solutions and readings obtained. The same procedure was applied to the soil sample extracts and the resultant absorbances were recorded. Each sample was treated thrice and the mean value was recorded

## DETERMINATION OF POTASSIUM

1g of analytical grade potassium nitrate was weighed and dissolved in 1 liter volumetric flask, this was later made up to prepare 1000ppm standard solution. From this stock was prepared 200ppm 400ppm 600ppm and 800ppm of standard potassium solution. These samples were directly aspirated into a flame photometer using potassium filters and the reading taken. Similarly, extracts from the soil samples were treated in similar way. They were also aspirated into flame and the reading taken. This was done thrice and the mean values were obtained

## RESULT AND DISCUSSION

The results obtained from the analysis carried out so far revealed that crude oil pollution of soil samples reduces the nitrate concentration

of soils samples table 1 below. Sample C had a nitrate concentration of 54ppm .Leaching further reduces the nitrate concentration of sample B having a nitrate concentration of 21ppm as most of the nitrate are flushed out . This finding agrees with the work of previous researchers who have proven that there is a reduction in soil nutrients as a result of pollution [13, 14]. This could be due to the destruction of nitrogen fixing bacteria in the soil such as Azotabacter spp. Mineralization therefore restore the nitrogen content of the soil necessary for plant growth. The values are higher with increased addition of the fertilizer samples D1-D6. The nitrate concentrations of the mineralized samples were within the range of those obtained from unpolluted soil samples and the concentration ranges 300ppm in sample D1 to 420ppm in sample D6. The unpolluted soil sample had a nitrate soil concentration of 330ppm. Other researchers had reported the nitrate enhancement of soils neutralized with NPK fertilizers [15, 16, 17, 18]

**Table1: Nitrate Concentration of soil samples**

| Sample | Absorbance | Conc.(ppm) |
|---|---|---|
| A | 0.016 | 330 |
| B | 0.002 | 21 |
| C | 0.005 | 54 |
| D1 | 0.013 | 300 |
| D2 | 0.017 | 340 |
| D3 | 0.019 | 345 |
| D4 | 0.020 | 350 |
| D5 | 0.023 | 370 |
| D6 | 0.032 | 420 |

The result obtained from the analysis of the phosphate concentrations of the soil sample are listed in table 2 below. The unpolluted soil sample A has a phosphate concentration of 68.50ppm. the polluted soil sample C has a concentration of 28ppm while the leached and un-mineralized sample had a concentration of 17ppm. The polluted leached and mineralized soil samples D1-D6 had concentrations ranging from 48.80 to 140ppm.as reported earlier, the values all compare to those of unpolluted soil sample and even got better .The results reveals that addition of inorganic fertilizer as a fast way of reclaiming a crude oil polluted soli. This is in agreement with earlier findings that though the nutrient content of soil is depleted by pollution addition of inorganic fertilizers as well as manures such as animal droppings and compost manure could aid in reclamation of once polluted soil sample. Increase in phosphate availability will eventually increase the soil micro flora and fauna. Most of these microbes returned back to the soil when the samples were returned back to the place of excavation. Therefore there was an increase activity of the soil flora and fauna [.19, 20,21]

**Table2: Phosphate analysis of soil samples**

| Sample | Absorbance | Conc (ppm) |
|---|---|---|
| A | 0.020 | 68.50 |
| B | 0.012 | 17.00 |
| C | 0.015 | 28.00 |
| D1 | 0.017 | 48.80 |
| D2 | 0.019 | 50.00 |
| D3 | 0.021 | 96.20 |
| D4 | 0.024 | 130.00 |
| D5 | 0.030 | 140.00 |
| D6 | 0.026 | 136.40 |

Results for potassium determinations were not different from earlier results as shown in table 3. The was an increase from 38 ppm for sample D1 to 64.00 ppm for sample D6 of the soils polluted and leached and mineralized. The increase is due largely to increase in Macronutrient supplement. [19] . Some other researchers have successfully re-mineralized soils polluted with crude oil by using organic manure, their results were similar to our results, but our results showed a more macro nutrient availability probably because the organic manure had to be broken down before the nutrients could be available.

**Table3: potassium analysis of the leached mineralized soil samples**

| Sample | Absorbance | Conc(ppm) |
|---|---|---|
| A | 0.020 | 46.00 |
| B | 0.012 | 12.00 |
| C | 0.015 | 28.00 |
| D1 | 0.017 | 38.00 |
| D2 | 0.019 | 40.00 |
| D3 | 0.020 | 47.00 |
| D4 | 0.024 | 58.00 |
| D5 | 0.030 | 59.00 |
| D6 | 0.036 | 64.00 |

The presence of high hydrocarbon concentration affects plants growth[ 17]. This explains the reason for leaching the soil samples before mineralization. Leaching of soil samples led to nutrient loss but it is a faster way of breaking oil films, restoring aerations as

well as enhancing microbial activities in soils. Leaching alone will not be useful but mineralization alone will not restore soil properties. The only microbes that are found in polluted soils that were not leached are crude oil resistant heterotrophs [19, 20] . Soils polluted with crude oil have higher moisture content, higher conductivity, total organic carbon, total organic matter. This factor favors mineralization [15 ]it has been shown that mineralized soil sample shows increased soil pH, reduced hydraulic conductivity, diminished crop growth, decreased evapotranspiration, decreased leaf mass water and increase in nitrogen, phosphorus and carbonics [22,23, 24 ] .

## CONCLUSION

Chemical remediation is an effective way to control soil pollution. Mineralization is an efficient method but when the soil is leached and mineralized, soil properties are restored; microbial activities as well as reconditioning the soil for plant growth are achieved. It is evident that mineralization of leached samples has proven to have an advantage over polluted soil samples that were bio-remediated or phyto-remediated.

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