Remediation of Petroleum Refinery Waste Contaminated Soil at Alesa-Eleme, River State

Udube C.V, Njoku-Tony R.F, Ejiogu C.C
Department of Environmental Management, Federal University of Technology
Owerri, Nigeria

Abstract:- Soil contamination by hydrocarbons and trace metals has led to adverse environmental and ecological impacts globally. As with the case in most third-world countries like Nigeria, where legal and illegal oil refineries do not follow or implement the national policies and guidelines for the treatment of industrial waste products before these waste products are disposed of into the environment. In this study, petroleum wastes contaminated soil at Alesa, Eleme resulting from the different production processes of petroleum products, was investigated to know the extent of contamination by heavy metals such as Iron (Fe), Zinc (Zn), Lead (Pb), Sulphates (SO4), Phosphates (PO4) and organic hydrocarbons like Phenols which are very dangerous to the environment and how they can be remediated by chemical and biological remediation methods and finding out which method is more cost-effective and environmentally friendly and sustainable. The extent of contamination of the soil was determined by the collection of soil samples from randomized sample points with coordinates 290223.14N 527592.55E, 290260.98N 527694.41E and 290326.19N 527622.51E at the affected area using a Standard Soil Auger at a depth of 15 – 30 cm (subsoil), the soil was then pretreated and their physiochemical properties were determined and later analyzed for the presence of heavy metals under a laboratory controlled experiment. High concentrations of heavy metals and hydrocarbons were found to be present in the soil from the affected area, this could also be seen in a common dominant shrub locally known as stubborn grass (Sida acuta) which was also analyzed for the presence of heavy metals. Chemical remediation (using EDTA/Oxalic acid) and biological remediation methods (phytoremediation) using Sunflower (Helianthus annus) were carried out to treat the contaminated soil and the rate of removal of contaminants through phytoremediation was calculated at 6 weeks and 9 weeks intervals to know the extent to which the contaminants were removed from the soil. The remediation methods were proofed to be very effective. The results of one-way analysis of variance of the contaminated soil at 6 weeks and 9 weeks during the phytoremediation process were 3.014 and 49.2 respectively and this revealed that there was a significant difference between the concentrations of contaminants with an F value of 0.575 which is greater than the F-Critical value for the alpha level selected (0.05). It was recommended that the Government's Ministry of Environment at all levels, should adopt and enforce sound waste management practices for refinery wastes and phytoremediation should be considered in reviving soil contaminated by refinery waste.

Keywords:- Heavy Metals, Contaminants, Remediation Methods, Phytoremediation

I. INTRODUCTION

Nigeria's first Oil refinery at Alesa, Eleme, began operations in 1965 with a capacity of 38,000 barrels per day. Later on in March 1989, another refinery, the fourth refinery in Nigeria, was completed still at Alesa, Eleme, increasing Nigeria's refining capacity to 445,000 barrels in a day (U.S Library of Congress, 1991).

Refinery waste is generally in the form of gaseous and liquid, with the liquid form being wastewater and sludge, containing hazardous trace elements like Ag, Au, Co, Pt, Pd, etc. Also, the refinery discharge water contains large quantities of Arsenic, Antimony, Bismuth, Mercury as well as hydrocarbon compounds which must be neutralized and treated before disposal to the environment but if left untreated will be very hazardous to the man and the environment (S.K.Halder et al., 2014).

In the past three to four decades, hazardous wastes have increasingly assumed a priority of environmental problems (Harrison, 1996).

As a result of poor handling, improper treatment, and wrong disposal methods of these hazardous wastes, industrial communities face serious public and environmental health risks, environmental degradation, and enormous cleanup costs. Improper disposal of waste can make even relatively harmless waste dangerous and very often result in tragedies.

Despite all these, little is still being done by these industries to reduce, reuse or recycle these waste bi-products or make the manufacturing process more environmentally friendly. As a result, the technological age has inherited a legacy of the contaminated environment from the industrial age.

The damage on land by contaminants is physically, biologically or chemically demanding and the contaminated land can contain very high concentrations of contaminants that can be very harmful directly or indirectly to man and the environment as a whole (Sanchez et al, 2012). The main hazards associated with chemically contaminated land are;

A. *Uptake of Contaminants by Food Crops Grown on these Contaminated Solid*
B. *Contact with Skin*
C. *Phytotoxicity*
D. *Fires and Explosion*
E. *Chemical Attack on Infrastructures (Duffy, 2011)*

Land is a very scarce resource especially in urban areas hence, people tend to ignore the hazards posed by contaminated land. It is therefore imperative that attempts should be made to clean up these contaminated land to render them safe and available for man's exploitation. Many options are available for this, ranging from physical, biological, and chemical methods most especially phytoremediation, a novel, cost-effective, and environmentally friendly technique which works by first identifying the contaminant to be remediated (Serrano, 2015).

The identification of the contaminated land or site and its associated problem, is a multistage process involving the suspicion of contaminants, the identification of the individual contaminated sites, sites investigation (including its geology, hydrogeology and engineering properties), assessment through Physical, Chemical and Biological remediation (Smith 2009). In trying to identify the contaminants, the options available are to eliminate the source, remove the target or restrict the pathways and all these options are available singly or collectively in dealing with the contaminated land and the potential threat to identify targets and the intended use of the land (Smith, 2009).

The petroleum refineries at Eleme produce a lot of waste bi-products which could be classified into gaseous, liquid (Effluent), and solid waste. Solid waste and semi-solid waste generated from the refineries are usually in the form of biodegradables (hydrocarbons and Sulphur compounds), non-biodegradables (mostly inorganic elementst like Zinc, Lead etc…) and hazardous compounds.

Within and around the complex are a few heaps of open dumps where the biodegradable waste rich in kitchen waste, spent oils, sludge and other hazardous chemicals are dumped. These are periodically pushed into a dump site called burrow pits surrounded by farmlands and about 200m from available surface waters in the vicinity. These dumpsites are also open for grazing domestic animals like goats etc…

Suffice it to say if prompt remedial actions are not taken, the public health of the community may continue to be at risk as crops produced from the soil would have been severely contaminated by chemical residues that permeate the food chain.

II. STUDY AREA

Alesa is a community in Eleme, a Local Government Area of River State and it's located between 4.7686º N and 7.1090º E.
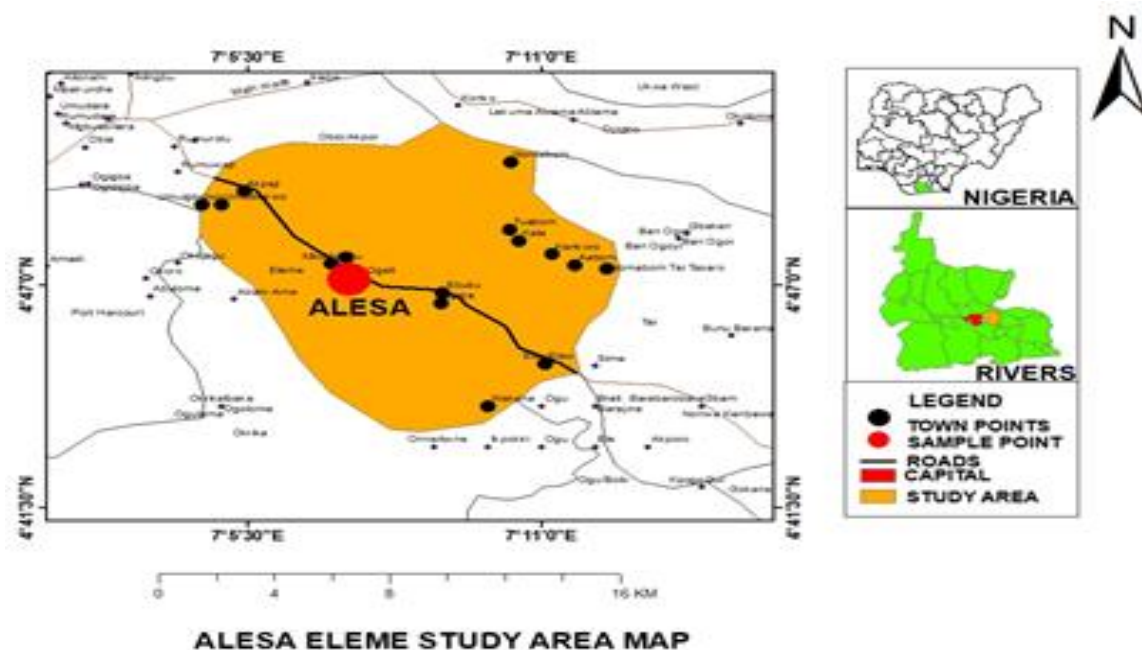

ALESA ELEME STUDY AREA MAP

Fig 1: Study Area Showing Sample Location

A. *Study Design and Scope*

➢ *Collection and Pre-Treatment of Soil Samples*
Soil samples used in this study were collected from 15-30 cm (subsoil) depth with the aid of a Standard Soil Auger. The soil samples of subsoil were collected from 3 identified locations as indicated in (Fig. 3.1). The control soil was collected from somewhere neutral in the Port Harcourt area. Each sample was collected in contaminant-free container bags which were transferred to the laboratory. They were subsequently air-dried and sieved using a 2mm sieve.

➢ *Physical and Chemical Properties of Soil*

- *Soil pH:*
  Fifty milliliters (50ml) of distilled water was added to 20g soil samples in a glass beaker. The mixture was stirred for 10 minutes, left to settle and stirred again for 2 minutes. The pH of the supernatant liquid was determined using an Orion Research pH meter model 407 A.

- *Moisture Content of Soil:*
  A representative sample of the moist soil (0.1g) was placed in a clean dry crucible of known mass with its lid securely in position. The mass of the container and moist soil was determined using a weighing balance Mettler AE 163 thereafter the lid was removed and the crucible was placed in an oven maintained at 110.5°C for 4 hours to obtain a constant weight. The crucible and soil were allowed to cool in a desiccator and the mass was determined. The moisture content of the soil (in %) was calculated as follows:

$$W = \frac{W1\ W2 \times 1000}{(W2 - W1)}$$

  Where W = moisture content of soil
      Wc = weight of container
      W1 = weight of container + moist soil
      W2 = weight of container + oven dried soil

- *Organic Carbon:*
  Reagents 0.167 Potassium dichromate ($K_2Cr_2O_7$) solution concentrated Sulphuric acid (H_2SO_4); Ferroin indicator; 0.5M Ferrous Sulphate heptahydrate ($FeSO_4$. $7H_2O$).

  Organic carbon was determined by Walker – Black Chronic acid digestion method (Anderson and Ingram, 1989). One gram of the sieved soil sample was introduced into a 250ml conical flask and 10ml of 0.167 M, K_2, Cr_2, O_2 was added to it. The flask was swirled gently to wet the soil after which 20ml of concentrated H_2SO_4 was added to it while gently swirling. The flask was left for 30 minutes after which 100ml of distilled water was added. Ferroin indicator (7-8 drops) was added to the suspension in the flask and was later titrated against 0.5M $FeSO_4$. $7H_2O$ at about the endpoint, Iron (ii) sulphate pentahydrate was added dropwise until the colour changed to sharp maroon red. The blank devoid of soil was also titrated against 0.5M $FeSO_4$. $7H_2O$ solution. The mean of the 2 liters value was obtained for each sample and the blank. Subsequently, the organic carbon was determined from the given formula below, using factor F=0.33

$$\text{Organic carbon} = \frac{(\text{ml blank} - \text{ml sample})\ MFe^{2t})\ xK}{\text{Weight of air- dried soil sample (1g)}}$$

  Where K= 0.33x100x1.73
      M=Molarity

- *Organic Matter:*
  The organic matter content of the soil was determined indirectly (Anderson and Ingram, 1989) as follows:
  %organic matter = %organic carbon x 1.73

- *Phosphate:*
  The phosphate content of the soil as determined according to the ASTM standard method with modifications to suit laboratory conditions were as follows:

  50ml of leached soil sample was taken and added 2-3 drops of phenolphthalein indicator. After which 10ml of combined reagent was added and mixed. The mixture was allowed to stay for 10 minutes before taking absorbent readings along with a spectrometer at a wavelength of 880nm. This was repeated for the control soil.

  Concentration mg/kg=Abs/slope

- *Sulphate:*
  50ml of the leached soil sample was taken and added to 10ml of glycerin and 5ml of NaCl solution. After which, a spatula tip of $BaCl_2$ was introduced. The mixture was stirred for 1 minute and allowed to stay for 4 minutes. Again the mixture was stirred for about a few seconds before taking absorbance readings using a spectrometer with a wavelength of 400nm. This was repeated for the control soil.

  Concentration mg/kg=Abs/slope

- *Phenol:*
  Soil sample was leached by taking 10g of it into 250ml conical flask and adding 100ml D/W. The mixture was shaken properly and allowed to stay for about 30 minutes. A clear 100ml of the mixture was filtered out and used for the phenol test. This method was limited to only soluble phenol compounds.

  100ml of the leached sample was added to 5ml of NH_4Cl adjusting the pH between 9.8-10.2 with NH_4OH. After which 2ml of 4-amino antipyrine and 2ml of $K_5Fe(CN)$ were added and mixed immediately. It was allowed to stay for 15 minutes and then measured absorbance at 510nm. This was repeated for the control soil.

  Concentration mg/kg=Abs/slope
                OR
  %Phenol in Soil= Concentration of phenol in soil x 100/ Weight of soil used

B. *Analysis of Soil Sample for Heavy Metals*
  An appropriate amount (0.5g) of the sieved soil sample was weighed using a weighing balance model Mettler AE 163 and placed in a clean and dry 250ml conical flask. $20cm^3$ of a mixture of concentrated hydrochloric acid (in a ratio of 3:1) was poured into the flask, covered with a clean watch glass and replaced for 5 – 10 minutes until brownish fumes of nitric acid disappeared. Thereafter the flask was allowed to cool and its content was filtered with a Whiteman No. 42 filter paper. The filtrate was diluted to 100ml and analyzed for heavy metals like Cd, Pb, Ni, Fe, Zn using

Atomic Absorption Spectrometer Model Unicam 929 (Dorn et al, 1975).

C. Collection and Pre-Treatment of Plant Samples

A sample of the predominant weed, Stubborn grass (Sida acuta) found in and around the dump site was collected in triplicates, labeled and placed in clean contaminated-free polythene bags and conveyed to the laboratory. They were thoroughly washed and rinsed with distilled water to remove all traces of sand on them. The plant was then separated into leaves, stems and roots using a clean stainless steel knife and placed separately in well-labeled porcelain dishes. The sample was dried in a Fisher Econotemp electric oven model 55g maintained at 105°C and allowed to dry overnight to constant weight.

D. Analysis of Plant Samples for Physio-Chemical Parameters

The different parts of the plant leaves, stem and roots were weighed separately using a weighing balance Mettler AE 163 for fresh weight. After this, the plant part was placed in an oven at not more than 120°C and allowed to dry. This was allowed to cool and placed in a desiccator before readings were taken for the dry weight. The dried portion of the plant's parts was burnt to ashes and the ash dissolved in distilled water and digested with acid for various forms of analysis

➤ Fresh Weight of Plant Samples:

The different plant's parts the leaves, stem and roots were weighed separately using the weighing balance, model Mettler AE 163 to determine their fresh weight.

➤ Dry Weight of Plant Sample:

Different plants part, the roots, stems and leaves were dried using a Fisher EconoTemp electric Oven model 55G at temperatures not more than 120°C. There were allowed to cool and stabilized in a desiccator before their weights were taken.

➤ Phosphate in Plants Samples:

1g each of the ashes of the different plant parts was dissolved in 250ml D/W water out of which 100ml was used for the phosphate analysis.

➤ Sulphate in Plant Samples:

Same as above, 1g each of the ashes of the different plant parts was dissolved in 250ml D/W water out of which 100ml was used for the sulphate analysis.

➤ Phenol in Plants:

Same as above, 1g of each of the ashes of the different plant parts was dissolved in 250ml D/W water out of which 100ml was used for the phenol analysis.

➤ Analysis of Plant Samples for Heavy Metals:

1g of each ashes sample of the leaves, stem and roots was dissolved in 5ml, 20% Hydrochloric Acid (HCl) and the solution was carefully transferred to a 100ml volumetric flask. This was made 100ml with distilled water and

analyzed for heavy metals; that is Pb, Zn, Fe, Cr, and Ni using Atomic Absorption Spectrometer (AAS).

E. Treatment of Contaminated Soil (Remediation)

➤ Chemical Method

• Oxalic Acid:

Three different concentrations (0.01M, 0.05M, 0.1M) of oxalic acid (BDH Chemicals Ltd, Poole, England) were prepared by dissolving appropriate amounts of the anhydrous acid in the required quantity of distilled water in clean and well labeled 2 liters plastic container.

F. Disodium Ethylene Di-Amine Tetra-Acetic Acid (EDTA):

Three different concentrations of 0.01M, 0.05M, 0.1M of EDTA (Hopkins and Williams LTD Chadwell Health, Essex, England) were prepared with distilled water in well-labeled 2 liters' plastic bottles.

Apparatus for Soil Leaching Experiment: A column made with PVC pipe, open at one end but close at the other end with a plastic tap was employed. The column was washed several times with tap water and later with distilled water. Thereafter it was rinsed with 30%nitric acid to remove all traces of lead and finally rinsed three times with distilled water. It was inverted with the tap water open and allowed to dry in the air before it was used.

Procedure for Chemical remediation: Five Hundred grams (500g) of the sieved contaminated composite soil was placed in one of the columns and a liter of one of the prepared reagents (i.e. oxalic acid, EDTA) was poured onto the soil in the column. The mixture was allowed to stand for 2 hours with the tap closed before being allowed to drain slowly under gravity. The leachate was collected overnight in a clean glass beaker, later homogenized and filtered using a Whatman No. 42 filter paper. One hundred milliliters (100ml) of the filtrate was collected in a plastic container and its pH was determined using a pH meter model 407. Controls were set up by using distilled water in place of oxalic acid or EDTA. The leachate was analyzed for chemical parameters including heavy metals using AAS and in accordance with standard methods (APHA, 1992. Wasay et al, 1998). This procedure was done in triplicates for the various concentrations and the average values were recorded as shown below.

Table 1: Concentration of Extractants Used.

Extractant	Molarity (M)	Concentration (g/l)
EDTA	0.01	3.7224
	0.05	18.614
	0.1	37.224
Oxalic Acid	0.01	1.2607
	0.05	6.3035
	0.1	12.607

> *Biological Method (Phytoremediation)*
> This method was carried out with Sunflower *(Helianthus annuus)*, a plant known for its remediation potential (Pilon et al., 2016).

G. Materials

> *Contaminant Soil:*
> Representative soil samples (adding up to about 30kg) were collected from the affected area, Alesa. They were thoroughly mixed air-dried and sieved using a 2mm sieved. One kilogram (1kg) of the sieved composite soil was introduced into each polythene bag until 30 such bags were filled.

> *Sun Flower Seeds:*
> Well-preserved seeds were provided by Dr. J. A. Fagbayide of the Department of Agronomy, University of Ibadan.

> *Control Soil Sample:*
> Representative soil samples (adding up to 20kg) were collected from an unaffected area (about 30km away from the dump site) and were thoroughly mixed together to form a composite soil. The composite soil was then air-dried sieve using a 2mm sieve and 1kg of it was introduced into each polythene bag unit six bags were filled. These six bags served as controls.

> *Organic Manure:*
> A good quality organic waste manure (OM) made from Pace Setters Organic Fertilizers Plant in Bodija, Ibadan. The contaminated soil was amended with the OM to improve its fertility. The composition of the organic manure (obtained from the manufacturers) is as follows; Carbon (21.3%), Nitrogen (1.73%), Phosphorous (0.69%), Potassium (1.80%), Zinc (148mg/kg), Cadmium (1.07mg/kg), Lead (35.7mg/kg).

H. Phytoremediation Studies

> *Growth of Sunflower Plants in Contaminated Soil:*
> Apart from the control soil samples, the contaminated soil samples were tested for their ability to support the growth of sunflower plants by mixing it with organic manure to boost its fertility so that there will be considered growth by the time frame of 9 weeks. One kilogram (1kg) of sieved subsoil samples was introduced into six polythene bags. Three bags of control soil samples were also packed. The bags were labeled and watered to 75% field moisture capacity and allowed to stand for 24 hours to give enough room for the water to spread evenly. One to two sunflower seeds were introduced into each to a depth of about 1-2cm and left to germinate. The experiment was laid out in a completely randomized design with three replicates. The plants were observed for 30 days. One kilogram (kg) of sieved contaminated soil mixed with 20g OM was introduced into each polythene bag until 2 bags were filled.

The quantity of OM to be added to the 1kg soil was calculated as shown below:
One hectare (ha) = 2×10^6 kg soil
One ton = 1000kg

The quantity of OM to be added to 1kg of soil is calculated as follows
2×10^6 kg soil requires 1ton of OM
1kg soil requires 1ton ÷ 2×10^6
Therefore 1kg soil would require 1ton x $1 \div 2 \times 10^6$
Where 1 ton = 1000kg   OR $1 \times 10^3 \div 2 \times 10^6$
= 0.5×10^3 kg of OM or 0.5g of OM

The soils in each batch were then watered to 75% field moisture capacity and allowed to stay for 24 hours. One to two sunflower seeds were introduced into each bag to a depth of about 1-2 cm and left to germinate.

The bags were watered every other day for a period of nine weeks, this is so because there must have been enough plant growth to start the determination of heavy metal concentrations. The experiment was laid out in a completely randomized design and at weekly intervals, growth parameters such as plant heights and number of leaves were monitored.

At intervals of 6 and 9 weeks, a set of 3 plants part from the contaminated soil and the control were harvested. The harvested plant parts were thoroughly washed in tap water and later rinsed three times with distilled water, bottled dry in between strips of clean tissue paper and their fresh weight was determined. The plants were later transferred to the hot air oven maintained at 105^0C overnight to dry and their dry weights were subsequently determined.

To determine the amount of contaminant accumulated, the plants were separated into leaves, stems and roots with a stainless steel knife and placed in well-labeled porcelain dishes. They were then burnt to ash in a muffled furnace maintained at $450-500^0$C and subsequently analyzed for the chemical parameters including heavy metals as in 3.3 above.

III. RESULTS

Table 2: Physio-Chemical Characteristic of Contaminated Soil.

S/N	Parameter	Control Sample	Contaminated Sample
1	pH	6.97	8.83
2	Moisture Content (%)	14.3	4.73
3	PO4 (mg/kg)	2.0614	0.597
4	SO4 (mg/kg)	55.0	133.3
5	TOC (mg/kg)	11.418	20.686
6	Phenol (mg/kg)	0.444	2.959
7	Cd (mg/kg)	0.005	0.007
8	Ni (mg/kg)	ND	0.034
9	Fe (mg/kg)	44.4	91.6
10	Zn (mg/kg)	4.40	5.00
11	Pb (mg/kg)	0.069	0.125
12	% Organic Matter	0.0199	0.0348

Table 3: Physio-Chemical Characteristics of Contaminants in Stubborn Grass (Sida Acuta).

S/N	Parameters	Leaf	Stem	Root
1	Wet weight (g)	5.0551	3.936	1.5531
2	Dry weight (g)	4.4760	3.5790	1.3878
3	PO4 (mg/kg)	7.868	10.038	6.51
4	SO4 (mg/kg)	18.33	11.67	25.0
5	Phenol (mg/kg)	0.148	1.334	0.074
6	Cd (mg/kg)	0.007	0.023	0.030
7	Ni (mg/kg)	0.043	0.089	0.147
8	Pb (mg/kg)	0.066	0.284	0.208
9	Fe (mg/kg)	26.2	44.6	131.4
10	Zn (mg/kg)	6.60	13.9	8.20

Table 4: Result of Single Extraction with Oxalic Acid

Parameters	CONCENTRATION (Molarity)/REMOVAL(R)						
	Control Soil	0.01M	%(R)	0.05M	% (R)	0.1M	%(R)
pH Value	8.83	7.95	-	7.50	-	3.25	-
Phenol (mg/kg)	2.959	0.074	2.50	0.360	12.47	1.109	37.48
Iron (Fe) (mg/kg)	0.035	0.70	0.764	3.10	3.38	62.9	68.7
Zinc (Zn) (mg/kg)	0.014	2.00	40	3.90	78	4.50	90
Lead (Pb) (mg/kg)	0.038	0.003	0.24	0.006	1.28	0.642	51.36

Table 5: Results of Single Extraction with EDTA.

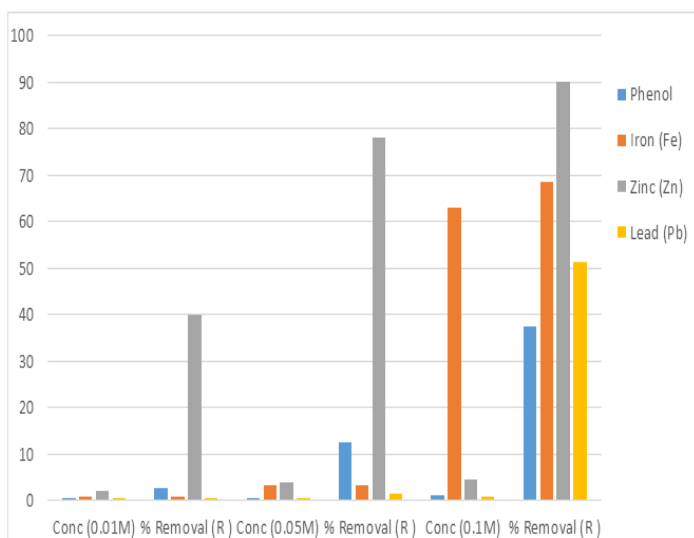| Parameters	CONCENTRATION (Molarity)/REMOVAL(R)						
	Control Soil	0.01M	%(R)	0.05M	% (R)	0.1M	%(R)
pH Value	8.83	4.80	-	5.15	-	7.25	-
Phenol (mg/kg)	2.959	0.222	7.50	1.702	57.52	2.294	77.5
Iron (Fe) (mg/kg)	0.035	27.1	29.59	69.20	75.55	89.10	97.27
Zinc (Zn) (mg/kg)	0.014	2.70	54.0	3.50	70	4.40	88
Lead (Pb) (mg/kg)	0.038	1.602	52.96	14.605	85.2	0.182	94.72

Fig 2: Result of Single Extraction with Oxalic Acid Concentration (Molarity)/Percentage Removal (R) Of Pollutants.
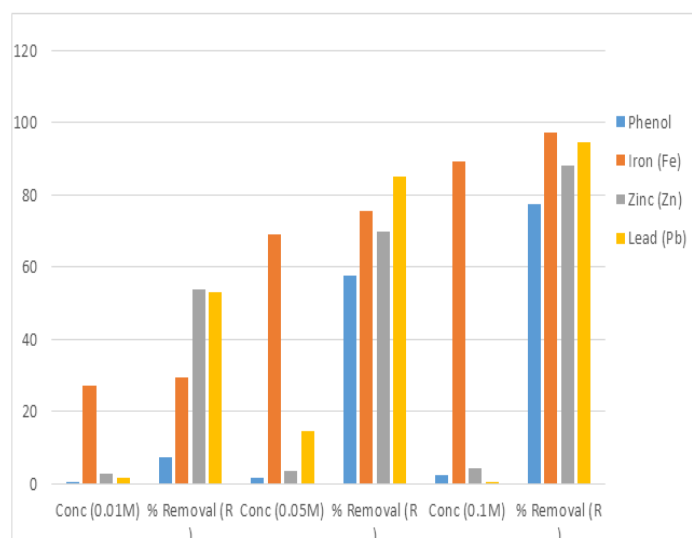

Fig 3: Result of single extraction with EDTA Concentration (Molarity)/Percentage Removal (R) of pollutants.

Table 6: Fresh Weight (FW) and Dry Weight of Sunflower Plants at 6 Weeks.

	Plant Part	Control	Contaminated soil Organic Manure
FW	Leaf	1.9512	3.3204
DW		0.1326	0.2307
FW	Stem	4.6490	2.8316
DW		0.2273	0.3000
FW	Root	1.4976	2.8248
DW		0.6564	0.5403

Table 7: Fresh Weight (FW) and Dry Weight (DW) of Sunflower Plants at 9 Weeks.

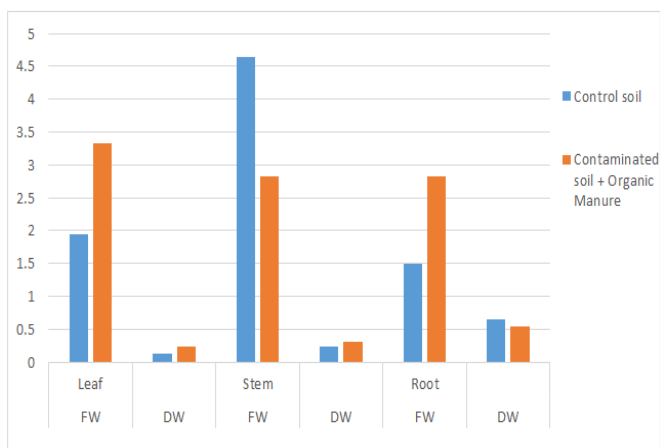|	Plant Part	Control	Contaminated Soil Organic manure.
FW	Leaf	2.0318	2.2463
DW		0.4004	0.8649
FW	Stem	12.3755	17.2430
DW		3.1640	4.2043
FW	Root	4.6165	5.0621
DW		0.7861	1.2043

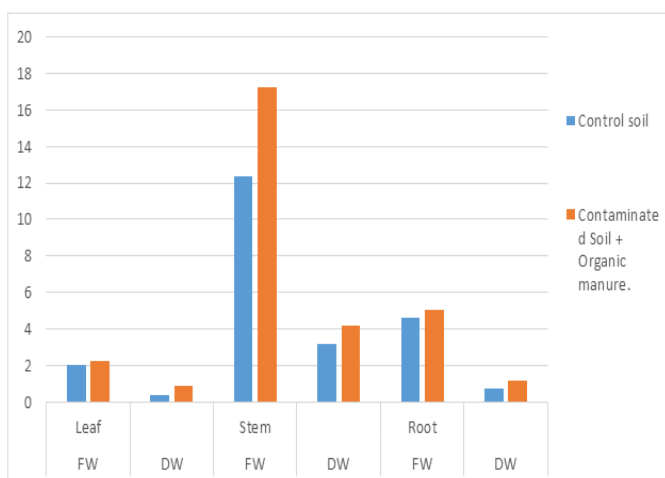

Fig 4: Fresh Weight (FW) and Dry Weight of Sunflower Parts at 6 Weeks

Fig 5: Fresh Weight (FW) and Dry Weight of Sunflower Parts at 9 Weeks

Table 8: Concentration of Contaminants in Sunflower Leaf (Mg/Kg Dry Weight) at 6 and 9 Weeks.

Concentration of contaminants in sunflower Leaf (mg/kg dry weight)				
Selected soil contaminants	Control Soil		Contaminated Soil mixed with OM	
	6 weeks	9 weeks	6 weeks	9 weeks
Phenol	0	0.22	0.30	0.44
Iron (Fe)	0.147	0.087	0.137	0.152
Zinc (Zn)	0.010	0.023	0.012	0.021
Lead (Pb)	0.021	0.057	0.037	0.032
Sulphates (SO_4)	1.7	3.3	10	21
Phosphate (PO_4)	3.26	1.04	2.27	4.34
Nickel (Ni)	0.018	0.035	0.001	0.075
Cadmium (Cd)	0.007	0.012	0.009	0.001

Table 9: Concentration of Contaminants in Sunflower Stem (mg/kg dry weight) at 6 and 9 Weeks.

Concentration of contaminants in sunflower Stem (mg/kg dry weight)				
Selected soil contaminants	Control Soil		Contaminated Soil mixed with OM	
	6 weeks	9 weeks	6 weeks	9 weeks
Phenol	0.22	0.30	0.37	0.74
Iron (Fe)	0.80	0.33	0.035	0.050
Zinc (Zn)	0.018	0.010	0.013	0.052
Lead (Pb)	0.004	0.064	0.067	0.057
Sulphates (SO_4)	6.67	3.40	20.0	41.7
Phosphate (PO_4)	2.27	0.97	2.00	3.25
Nickel (Ni)	0.087	0.028	0.011	0.039
Cadmium (Cd)	0.013	0.09	0.002	0.003

Table 10: Concentration of Contaminants in Sunflower Root (mg/kg dry weight) at 6 and 9 Weeks.

Concentration of contaminants in sunflower Root (mg/kg dry weight)				
Selected soil contaminants	Control Soil		Contaminated Soil mixed with OM	
	6 weeks	9 weeks	6 weeks	9 weeks
Phenol	ND	ND	ND	ND
Iron (Fe)	0.156	0.119	0.062	0.012
Zinc (Zn)	0.013	0.034	0.013	0.017
Lead (Pb)	0.069	0.045	0.047	0.087
Sulphates (SO_4)	1.70	ND	1.70	1.70
Phosphate (PO_4)	0.43	0.27	0.37	0.27
Nickel (Ni)	0.004	0.010	0.039	0.040

Table 11: Concentration of Contaminants in Contaminated Soil Left in Bag (Mg/Kg Dry Weight) at 6 and 9 Weeks.

Concentration of contaminants left in contaminated soil left in the plastic bag (mg/kg dry weight)				
Selected soil contaminants	Control Soil		Contaminated Soil mixed with OM	
	6 weeks	9 weeks	6 weeks	9 weeks
Phenol	0.22	0.35	0.07	0.37
Iron (Fe)	0.183	0.015	0.246	0.148
Zinc (Zn)	0.170	0.095	0.028	0.035
Lead (Pb)	0.018	0.048	0.050	0.052
Sulphates (SO₄)	11.67	10.00	5	20
Phosphate (PO₄)	1.30	0.81	0.21	0.48
Nickel (Ni)	0.099	0.001	0.053	0.059
Cadmium (Cd)	0.077	0.044	0.013	0.023

A. Statistical Analysis

The concentration of contaminants in the contaminated soils remaining in the bags after phytoremediation with the sunflower plants (Helianthus annuus) at 6 weeks and 9 weeks were analyzed using the One-way analysis of variance (ANOVA) method to find out if there was any significant difference between the concentration of contaminants at 6 weeks and 9 weeks respectively. This was done using Microsoft Excel and this revealed that there was a significant difference between the concentration of contaminants in the contaminated soil during and after phytoremediation, that is at 6 weeks and 9 weeks with variances of 3.014 and 49.2 respectively with an F value of 0.575 which is greater than the F-Critical value for the alpha level selected (0.05). Therefore, this is evidence to say at least one of the two samples has significantly different means and thus belongs to an entirely different group. (Gurchetan, 2018).

Table 12: Dependent Variables: Statistical Analysis of Variance of Contaminated Sample left in Bag at 6 and 9 Weeks.

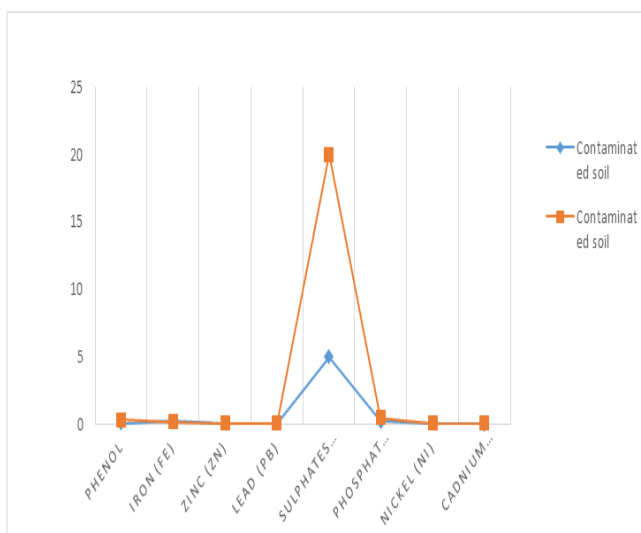| SUMMARY						
Groups	Count	Sum	Average	Variance		
6 weeks	8	5.67	0.70875	3.013881		
9 weeks	8	21.167	2.645875	49.19884		
ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	15.00981	1	15.00981	0.574948	0.460874	4.60011
Within Groups	365.4891	14	26.10636			
Total	380.4989	15				

Fig. 7: Mean Values of Contaminants Between the Contaminated Soil and that of the Soil at 6 Weeks and 9 weeks.

IV.   DISCUSSION

The assessment of the soil quality revealed higher levels of Sulphate (133mg/kg), phenol (2.959mg/kg), Iron (91.6mg/kg), Zinc (5mg/kg) and Lead (1.25mg/kg) in the subsoil than values obtained for the control soil (Table 4.1) an indicator of higher concentrations of these substances in the topsoil were also observed. On the other hand, the subsoil of the control sample contained 0.44mg/kg of phenol, 44.4 mg/kg of Iron, 4.40mg/kg of Zinc and 0.069mg/kg of Lead (Table 2) which were quite low. The presence of toxic waste from the industry accounts for the high levels of these substances in the subsoil suggesting that they were leached from the nature of the topsoil. This result is in agreement with the report given by Fifield and Harris (1995), especially for heavy metals, which stated that the addition of heavy metals to soils normally results in its accumulation in the upper layers of the soil profile. This could be explained by the fact that the soil organic horizon, which is richer in humic substances and organic acids has a high affinity for elements ions.

Stubborn Grass (Sida acuta) was collected from the affected area and analyzed for the selected contaminants. The concentration of the contaminants as shown in Table 3 above was quite high except for Cadmium. The high concentrations were found at the stems and roots which

shows that plants absorb these metal ions in the soil through their roots and translocate them to other areas of the plants through different plant vessels (Pilon et al., 2016).

In the chemical remediation method, the extraction of selected contaminants by the two extractants had significant effects, at increasing concentration, a higher quantity of contaminants was removed as seen in Table 4.5 above. The highest removal rate was with 0.1M EDTA. EDTA has a strong chelating ability for different metals and it also increases the bioavailability and plant uptake of the metals in the soil except for Lead (Pb) which has extremely low solubility in soils and poor mobility. Also, EDTA is highly persistent in the environment and can cause the leaching of heavy metals groundwater table (Slawa Glin'sk et al, 2013).

Oxalic acid is one of the most common organic acids used in the removal of heavy metals because of its ability to form stable chelate complexes with metals. From our results, though its efficiency was lower than that of EDTA, it will be preferred to EDTA in the chemical remediation of contaminated soil because of its lower environmental effects.

The phytoremediation of the contaminated soil was limited to subsoil because of the unarguable assumption that the topsoil would be highly polluted by the contaminants to be able to support any meaningful plant growth. It is believed that the process of contaminants in soil impacts the quality if the soil and fertility. However, the addition of organic significantly increased the uptake of the contaminants by sunflower plants. Evidence of the effectiveness of (OM) on the improvement of soil fertility and enhanced growth of the sunflower plant. This is because organic manure has an overriding importance in heavy metals to a degree limited by pH and soluble organics.

It also revealed the uptake of contaminants by the sunflower plant, this is because there was a greater amount of contaminants found in the leaves, stems and roots of sunflower plants grown on contaminated soils mixed with organic manure (OM). This proves the fact that contaminants are mostly stored at the roots and leave the region of the plants with the stem serving as a means of transport medium. It also shows that the dry weight of plants at the two intervals of (6 and 9 weeks) contributed to and apparently increase uptake of the contaminants at the 9th week. Nevertheless, the diluting effects resulting from enhanced growth rates of the plants in the OM-amended soil were expected to result in an apparently lower concentration of the contaminants at 9 weeks as earlier reported by (Gigliotti et al, 1996), when they study trace metal uptake and distribution of Maize plant grown on a 6-year old urban waste compost amended soil.

V. CONCLUSIONS

This investigation revealed that the soil in the affected area was primarily contaminated with organic compounds like phenols and inorganic compounds mainly heavy metals like iron, Zinc and Lead. Although the affected land at Alesa based on the outcome of this investigation may not have met the Putch soil cleanup (Interim Act of 1983) criteria for remediation, especially for the heavy metals, lead, whose level is far below the criteria limit of 600mg/kg, the soil could still be classified as potentially hazardous to human health.

This study also shows that it is possible to remediate the soil using physical, chemical and biological methods. The choice of any of these methods or a combination of methods will depend on the costs of operation and the risks involved as each method has its own peculiar advantages and limitations. The choice of oxalic acid is based on the fact that it is environmentally friendly unlike the strong mineral acids and chelating agents (e.g EDTA and DPTA) which are known to disturb soil properties by extracting soil nutrients and destroying soil structure thus disturbing biological activities.

Another advantage of using the chemical method is that the extracting agent can be treated in order to remove the contaminants from it thus making the discharge or reused of the extracting agent possible. However, some of the limitations of the chemical remediation method include the fact that in practice, most treatment processes result in sludge containing the pollutant as well as very small soil particles (such as clay) and humus particles. The sludge produced in an extraction process is hazardous and must be properly and safely disposed of.

Phytoremediation however is not without limitations as it is most effective at sites with shallow contaminated soils and may take a long time than traditional approaches to reach cleanup goals or may be limited by soil toxicity. In spite of these limitations, phytoremediation has great potential in developing countries like Nigeria where projects are hindered by financial inadequacy.

RECOMMENDATIONS

A. *The Following Recommendations were Deduced from the Conclusion of this Study:*

➢ More modern, appropriate and environmentally friendly waste treatment methods should be employed in treating refinery waste like sludge and others before being disposed of into the environment

➢ A community base health educational program on health hazards of heavy metal contaminants and other pollutants should be implemented to create awareness of the effects of the pollutants on human health.

➢ There should be routine monitoring of selected contaminants in all aspects of the environment as a whole by Standards and Regulatory agencies like the National Environmental Standards and Regulatory Enforcement Agencies (NESREA) and National Oil Spill and Detection Agency (NOSDRA).

➢ Since the topsoil of the affected area is believed to be highly contaminated, it will be most desirable if the topsoil is excavated and disposed of properly and safely. At a more agreeable and environmentally friendly landfill site. This will make it easier for the application of phytoremediation which happens to be the cheapest of the three methods used in this study.

➢ The potential of other plants such as the Indian mustard (Brassica junicea) to accumulate high tissue concentrations of contaminants should be investigated and if possible applied in tandem with sunflower plants. Phytoremediation of especially metal-contaminated soil not only offers low costs methods for soil remediation, but also offers the possibility of recovering the extracted metals from the harvested plants.

➢ More policies and guidelines on refinery waste treatments and disposals should be developed and enforced, in this manner there will be a drastic reduction in the number of pollutants or contaminants from refineries in the environment.

➢ It would be expedient for the refineries to build a fence around the affected area to prevent straying domestic animals and men from trespassing on these affected areas pending the commencement of remediation work.

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