

ORIGINAL RESEARCH PAPER

Application of Steam Enhanced Extraction method on BTEX contaminated soil in a Nigerian petroleum depot and Automobile workshop sites in Ilorin metropolis, Nigeria.

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Received: 21 May 2021/ Accepted: 23 August 2021/ Published: 15 September 2021

Abstract: The contamination of soil in the environment is a natural consequence of industrialization and urbanization. Organic chemical pollutants dissolve into groundwater, absorb and adsorb into soil grains. Benzene, toluene, ethylbenzene and xylene (BTEX) are major causes of contaminated soil. This is due to fuel leakages or spillages, various forms of hydrocarbon burning/combustion and land disposal petroleum base oil. Contaminated soil samples were excavated from two different locations within the Ilorin metropolis; pipelines and products marketing company, a Nigerian petroleum depot, Ilorin depot and auto mechanic workshop of over ten years. Steam enhanced extraction method was employed through injection of steam to contaminated soil from steam generator into soil pot where contaminated soil was placed. The condensation of steam on soil particles provides energy to release desorbed contaminants molecules from the soil and the mobilized contaminants vapor was transferred into the recovery pot via the pipe that was connected to the soil pot. After the remediation process, the steamed soil samples were taken to the laboratory where the sonication extraction technique was used to extract the contaminants (BTEX) from the steamed soil samples of 30, 60 and 90 minutes respectively. The extract from the steamed soil samples of 30, 60 and 90 minutes was subjected to Gas Chromatography fitted with flame ionization detector analysis to determine the exact amount of BTEX removed after the remediation process. Pre-treated soil sample of auto mechanics workshop was found to be 4.5004×10^{-1} mg/kg and post-treated soil samples were found to be 1.8164×10^{-1} mg/kg, 8.7519×10^{-1} mg/kg and 5.7006×10^{-2} mg/kg for 30, 60 and 90 minutes respectively after remediation process while Pre-treated soil sample of a Nigerian petroleum depot was found to be 6.6049×10^{-1} mg/kg and post-treated soil samples were found to be 2.9320×10^{-1} mg/kg, 1.9855×10^{-1} mg/kg and 1.0237×10^{-1} mg/kg for 30, 60 and 90 minutes respectively after the remediation process. This study established the effectiveness of the remediation process of hydrocarbon contaminated soil using steam enhanced extraction method an In situ remediation technique.

Keywords: soil pollution; remediation process; Ex-situ technique; In-situ technique; hydrocarbon contamination



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1.0 Introduction

Soil pollutions build up unwanted chemicals in the soils such as persistent organic compounds, heavy metals, radioactive materials and other chemicals which have adverse effects on plant growth, human and animal health and degrade the ecosystem. Petroleum products are not only the primary source of fuel but also contamination source of soil and groundwater (Esmailzadeh et al., 2020). The contamination of soil and groundwater by petroleum hydrocarbons and solvents are major and widespread problems facing the world today. Soil and groundwater contamination problems exist as a result of soil's exposure to spills or leakage of hydrocarbon and hydrocarbon combustion. Major causes of hydrocarbon/crude oil-contaminated soil include leaking

storage tanks, leaking pipelines, corrosion of pipelines, land disposal of petroleum waste and accidental or intentional spills (Wilson and Moore, 1998). BTEX (benzene, toluene, ethylbenzene and xylene) are volatile, monocyclic aromatic compounds present in petroleum products and various organic chemical product formulations (Cohen and Mercer, 1993). BTEX is a class of chemicals in Light oils that are generated in far larger quantities (10-100 times more) than heavier tar oil and is the only organics that travel extensively. Light oils are known to reach several kilometers underground and precipitate the carried heavier fractions of Polycyclic Aromatic Hydrocarbons (Hatheway, 2006). Larger amounts of BTEX can enter the environment from leaks from underground storage tanks, overfills of storage tanks,

fuel spills and landfills. BTEX compounds easily move through the soil and can make their way into the groundwater, contaminating public and private water systems and the soil in between. Besides gasoline, BTEX can be found in many of the common household products and typically of about 18% gasoline (US Environmental Protection Agency, 2010). Luty et.al (1994) reported that most complex chemical compound of BTEX tends to have a potential to cause severe health concern of particular importance on building and environmental standpoints. Most people are exposed to small amounts of BTEX compounds in the ambient (outdoor) air, work and in the home (US Environmental Protection Agency, 2010). The possible health effects of BTEX exposure vary greatly and depend on the amount and duration of a person's exposure, **as well as** their personal circumstances.

Soil treatment technologies are developed and evaluated to conform to regulatory demands which may require or suggest that residual total petroleum hydrocarbon concentrations in soil be reduced below the remediation objective. There are many technologies available for treating sites contaminated with petroleum hydrocarbons and coal gas contaminants specifically. The treatment selected depends upon contaminant and individual site characteristics, regulatory requirements, costs and time constraints (Riser– Roberts, 1998). Ex-situ remediation techniques involve removing the soil from the subsurface to treat it. The major disadvantage of Ex-situ techniques is that are too expensive and old fashion of remediation compare to In-situ remediation techniques which are more vibrant, economical, timely and environmentally friendly. In-situ remediation techniques involve leaving the soil in its original place and bringing the treatment mechanisms to the soil. In situ treatment techniques have found wider acceptance among Brownfield stakeholders (Riser-Roberts, 1998). Remediation schemes should be chosen to suit the circumstances of a particular site to achieve cost-effective solutions to soil complex problems (US Environmental Protection Agency, 2010). In this study, the Steam Enhanced Extraction (SEE) treatment method was adopted. Steam Enhanced Extraction (SEE) involves the injection of steam into contaminated soil and the recovery of mobilized groundwater. This method is selected because it can be used in difficult locations such as in between buildings, beneath buildings, in deep zones, and locations where there are established infrastructures such as buried utilities and aboveground piping. They are also relatively fast, meaning that the contaminants can be treated and removed on time. It has been demonstrated that heating the soil can greatly accelerate the removal of volatile hydrocarbon compounds (Scientific American, 1999; Buettner et. al., 1992). Heating the contaminated area with steam will reduce the treatment time, depending on site characteristics, compared to treatment at ambient temperatures. Steam injection techniques were first used in 1933 (White and Moss, 1983) and approximately 80% of tertiary oil produced worldwide has been recovered by

thermal methods, primarily steam injection (Ahner and Sufi, 1994).

This study is aimed to remediate BTEX contaminated sites in auto-mechanic workshops and a petroleum depot

2.0 Research Methodology

2.1 Description of Study Area

Kwara State is one of the States in Nigeria that is located in the North Central and it has an estimated population of 2.3 million people with sixteen Local Government Areas (Population census, 2006). The sites selected for this research work are located in Ilorin East Local Government Area. The NNPC depot (gas station) site as the case study, where the transfer of diesel, petrol and kerosene from the storage tank takes place and it has been in existence for more than three decades. It is on latitude and longitude 8°33'38.73"N and 4° 45'33.88" E respectively. While the auto-mechanic workshop which was the second site selected for this study where the repairing of motor vehicles has been carried out for more than ten years. It is on latitude and longitude 8°28'14.15"N and 4° 34'05.49"E respectively.

2.2 Excavation of the Soil Samples from the Contaminated Site

The petroleum depot is very close to essential places like farmland. The spillage of gasoline, diesel and kerosene occurred as a result of transferring of petroleum products from the storage tanks to other tanks, accidental spills and leakage from the pipelines. Some specific spots in the depot were considered due to spillage that occurs during the normal depot operations. Spots considered at the Auto-mechanic workshop were locations where the grass has not grown. A small portion of the soil was excavated from the selected sites and the location was dug in rectangular shape with the following dimensions; 25cm depth, Length 25cm and width 30cm in the selected sites and the soil samples were stored in the polythene bag to guide against environmental influence.

2.3 Set-Up of the Experimental Apparatus for the Remediation Process

Since thermal remediation process requires a form of heat for the remediation process to take place. Considering Steam Enhanced Extraction (SEE) method of reclaiming/remediating the soil as a form of thermal remediation process/procedure which involves the injection of steam through the contaminated well and the recovery of the contaminants from the soil. The steam was supplied by locally made steam generator set to generate the heat needed/required for the remediation process. It is, therefore, necessary for the steam to be injected into the soil to be considered which goes a long way in determining the effectiveness of the remediation process. Since, for good remediation to take place steady energy in form of heat (steam) must be supplied to the contaminated soil, which is corresponding to the time/duration.

2.3.1 Steam Generating Set

The steam generating set consists of two parts; a furnace in which combustion of fuel takes place and fed water that was converted into steam by the absorption of heat produce by the combustion of charcoal.

2.3.2 Soil Pot

This is made of mild steel material of 2 mm thickness rolled into a cylindrical shape and placed few meters beside the steam-generating set mainly to store the contaminated soil and to constantly receive the supply of steam from the steam set to remove the (BTEX) contaminants from the soil. This pot contained two pipes, the steam injection pipe and the extraction pipe. Both pipes are perforated from the beneath to the middle and the injection pipe conveyed the steam into the contaminated (BTEX) soil sample and the extraction pipe absorbed the desorbed contaminants (BTEX) from the soil and transferred it to the recovery pot.

2.3.3 Recovery Pot

This is made of mild steel material of 2 mm thickness rolled into a cylindrical shape and connected to an extraction pipe. The extraction pipe conveyed the desorbed contaminants (BTEX) from the soil pot to the recovery pot for further action.

2.4 Principle of Steam Enhanced Extraction (SEE) Method

Steam Enhanced Extraction (SEE) involves the injection of steam through the injection pipes and the recovery of mobilized contaminants and vapor from the recovery pipes. The steam was injected into the contaminated (BTEX) soil in the soil pot through the injection well for a period of 30, 60 and 90 minutes respectively. The steam-heated the soil matrix, causing the more volatile compound to vaporize. The heat increases the vapor pressure of the less volatile compound and decreases their viscosity which made them easier to desorb from the soil particles. The condensation of steam on soil particles provides energy to release desorbed contaminants molecules from the soil and the mobilized contaminants vapor was transferred into the recovery pot via the pipe that was connected to the soil pot from the extraction pipe. After the remediation process, the steam soil samples were taken to the laboratory where the sonication extraction technique was used to extract the contaminants (BTEX) from the steamed soil samples of 30, 60 and 90 minutes respectively. The extract from the steamed soil samples of 30, 60 and 90 minutes were taken to the laboratory where they were injected into HP 6890 gas chromatography flame ionization detector (GC-FID) machine to determine the exact amount of BTEX composition of Benzene, Toluene Ethylbenzene, Para-Xylene, Ortho-Xylene and Meta-Xylene present after the remediation process.

2.5 Sonication Extraction Technique

McCartney bottles were dried in the oven at temperature 105°C and were transferred to the desiccator

to cool to laboratory temperature and the weights of the bottles were measured. 5.0g of the soil sample was weighed into the McCartney bottle and covered with the appropriate threaded cover-lined with silicone. 10ml of the extracting solvent, carbondisulphide (CS₂) was measured and poured into the soil sample in the bottle. The bottle containing the soil samples with the extracting solvent was placed in the sonicator for about 2hrs for the extraction at the temperature 27°C. The filtrate was recovered in a fast manner through the filter paper and 1.0ml was transferred into the 2ml gas chromatography vial for the injection into gas chromatography system.

2.6 Gas Chromatography Analysis:

HP 6890 gas chromatography with a flame ionization detector (GC-FID) was used to analyze the BTEX content in the soil sample in selected locations. A capillary column type HP 5MS with the following dimension length, inner diameter and particle size set at (30 m× 0.25 mm× 0.25 μm) was attached to the injection port. The flow rate of carrier gas (hydrogen) was 1.0 mL/min, the hydrogen pressure and compressed air were set at 22psi and 28psi respectively. The injection temperature was split injection set at 150°C, the detector temperature at 320°C and the oven temperature was programmed at 50°C with the 1st ramped 5°C/min to 150°C and 2nd ramped at 10°C/min to 250°C . A 1mL aliquot of the final solution was injected in the GC (split ratio; 20: 1).

2.7 Geotechnical Test: Soil Porosity, Soil Permeability, Moisture Content and Soil Texture.

The geotechnical test was performed on the soil samples to determine the identity of the soil samples used in the experiment.

2.7.1 The Soil Porosity

The Fetter C.W 1994 method was adopted to determine the porosity of the soil sample. A beaker filled up with soil sample to 100ml; 100ml of water was measured and poured into a graduated cylinder. Water in the graduated cylinder was poured slowly and carefully into the beaker until the water reached the top of the soil sample. The remaining volume of water in the graduated cylinder was measured and recorded. The remaining volume of water was subtracted from the total volume and this represents the volume of water added to the soil sample. The volume of water added to the soil sample was noted, this is the pore space. The procedure was repeated with the second soil sample (Sample B) The porosity of the soil samples was determined by using the equation below

Where;

The total volume of water = V1

The total volume of water remaining= V2

Volume of water added to the soil sample=V1 –V2, Pore space= V1-V2

% porosity= (pore space)/ (Total volume of water)×100

% porosity = (V1-V2)/ (V1) ×100

$$\% \text{ pore space} = (\text{pore space} / \text{total volume}) \times 100$$

2.6.2 The Soil Permeability

Permeability is a property of a porous material that permits passage of fluids through interconnecting conditions. The principle behind the test is Darcy's law for laminar flow. The permeability was calculated using the equation:

$$KT = \frac{QL}{Ath} \quad (2)$$

Where;

KT = coefficient of permeability at temperature T, cm/sec

L = length of specimen in centimeters

t = time for discharge in seconds

Q = volume of discharge in cm³ (assume 1 mL = 1 cm³)

A = cross-sectional area of permeameter ($= \pi D^2 / 4$, D = inside diameter of the permeameter)

h = hydraulic head difference across length L, in cm of water; or it is equal to the vertical distance between the constant funnel head level and the chamber overflow level.

2.7.3 Moisture Content

The oven-drying method of English Standard Institution (E.S.I) part II-1973 was adopted to determine the moisture content of the soil sample. A clean container of non-corrodible material with a lid was weighed and recorded. A small quantity of moist soil was placed in the clean container weigh and recorded. The lid was taken off and the clean container with the moist soil was placed in an oven for 24 hours and the temperature was maintained at 105°C-110°C. After the drying, the clean container was cooled in a desiccator. The lid with the clean container and the drying soil was weighed and recorded. The procedure was repeated for soil sample B.

Using equation 3

where;

W1 = Weight of an empty clean container with lid

W2= Weight of clean container with lid + wet soil

W3=Weight of clean container with lid+ dry soil

$$W_{\text{content}} = \frac{(W2 - W3)}{(W2 - W1)} \times 100 \quad (3)$$

2.7.4 Soil Texture

Soil textural determination was done using the hydrometer method described by Bouyoucos (1951). The soil samples were air-dried and sieved then 50g was measured for the test and 10% of calogon (sodium hexametaphosphate) was added to it in a measuring cylinder. It was stirred and allowed to settle for 40 secs and a hydrometer reading was taken. In another 2hrs another hydrometer was taken again. The percentage of sand, clay and silt in the soil samples can be determined. After 40 seconds, the sand has settled and the hydrometer reading reflects the grams of silt + clay in 1 litre of the suspension.

$$\% \text{ Sand} = \frac{(\text{Sample mass} - 40 \text{ second reading})}{\text{Sample mass}} \times 100$$

$$\% \text{ Clay} = \frac{(\text{Two hour reading})}{\text{Sample mass}} \times 100$$

$$\% \text{ Silt} = (100\% - \% \text{ sand} - \% \text{ clay})$$

3.0 Discussion of Results

3.1 BTEX Composition from the Pre-treated (PRT) and Post-treated (PST) Soil Samples in the Selected Locations.

Table 1 presents the amount of BTEX in the pre-treated Soil Sample of the auto-mechanic workshop. From Table 1, the total amount of BTEX was 4.50043×10^{-1} of which Benzene is 4.41952×10^{-3} , Toluene is 4.23005×10^{-3} , Ethylbenzene is 1.10544×10^{-2} , Para-Xylene is 3.80953×10^{-2} , Meta-Xylene is 3.78430×10^{-1} and Ortho-Xylene is 1.95715×10^{-2} respectively. From the results, the amount of BTEX composition in ascending order of Meta-Xylene, Para-Xylene, Ortho-Xylene, Ethylbenzene, Toluene and Benzene.

Table 1: Amount of BTEX composition in a pre-treated soil sample of auto-mechanic workshop

BTEX COMPOUNDS	AMOUNT OF BTEX PRESENT BEFORE THE REMEDIATION PROCESS (mg/Kg)
Benzene	4.41952×10^{-3}
Toluene	4.23005×10^{-3}
Ethyl benzene	1.10544×10^{-2}
Para-Xylene	3.80953×10^{-2}
Meta-Xylene	3.78430×10^{-1}
Ortho-Xylene	1.95715×10^{-2}
TOTAL	4.50043×10^{-1}

Table 2 shows that there is variation in the total amount of BTEX present after the remediation process in the selected soil samples of the Auto-mechanic. 1.81638×10^{-1} mg/kg of the contaminants BTEX was recorded after the steaming time of 30 minutes while 8.75194×10^{-2} mg/kg and 5.70056×10^{-1} mg/kg of the BTEX was present after the steaming time of 60 minutes

and 90 minutes respectively. The Porosity of the sandy loam allows the persistence penetration of the steam into the soil and thereby reducing their viscosity and makes it easy for BTEX to vaporize and desorb from the soil particles which eventually caused the reduction in the amount (Art, 1993).

TABLE 2: Amount of BTEX composition in post-treated soil samples of the auto-mechanic workshop at different time (30, 60 and 90 minutes)

BTEX COMPOUNDS	AMOUNT OF BTEX PRESENT AFTER THE REMEDIATION PROCESS (mg/Kg)		
	Steaming Time of 30minutes	Steaming Time of 60minutes	Steaming Time of 90minutes
Benzene	2.81413×10^{-3}	1.84494×10^{-3}	3.98423×10^{-5}
Toluene	2.84738×10^{-3}	2.02276×10^{-3}	8.64963×10^{-4}
Ethyl benzene	4.76630×10^{-3}	2.21812×10^{-3}	6.16978×10^{-4}
p-Xylene	1.31578×10^{-2}	2.71119×10^{-3}	1.61992×10^{-3}
M-Xylene	1.49299×10^{-1}	7.47449×10^{-2}	5.12145×10^{-2}
O-Xylene	7.370432×10^{-3}	3.97748×10^{-3}	2.64947×10^{-3}
TOTAL	1.81638×10^{-1}	8.75194×10^{-2}	5.70056×10^{-2}

From Table 3, 6.60493×10^{-1} mg/kg is the total amount of BTEX present in the petroleum depot soil sample. The BTEX composition has Ethylbenzene and Toluene to be 1.83230×10^{-3} mg/kg and 3.70916×10^{-4}

mg/kg respectively, while Benzene, Para-Xylene, Meta-Xylene and Ortho-Xylene were 2.55226×10^{-5} mg/Kg, 5.75611×10^{-2} mg/Kg, 5.85317×10^{-1} mg/Kg and 1.53865×10^{-2} mg/Kg respectively.

Table 3: Amount of BTEX composition in pre-treated (PRT) soil sample of Petroleum depot

BTEX COMPOUNDS	AMOUNT OF BTEX PRESENT BEFORE THE REMEDIATION PROCESS (mg/Kg)
Benzene	2.55226×10^{-5}
Toluene	3.70916×10^{-4}
Ethyl benzene	1.87006×10^{-3}
P-Xylene	5.75611×10^{-2}
M-Xylene	5.85317×10^{-1}
O-Xylene	1.78700×10^{-2}
TOTAL	6.60493×10^{-1}

Table 4 shows the amount of BTEX present after the remediation process in gas-station soil sample. 2.93203×10^{-1} mg/kg of the amount of BTEX recorded after the steaming time of 30 minutes while 1.98546×10^{-1} mg/kg and 1.02370×10^{-1} mg/kg of steaming time of 60 minutes and 90 minutes respectively. From table 4, further steaming of the BTEX polluted soil samples led to the reduction in the amount of BTEX present in the soil. These

consecutive reductions can be attributed to the evaporative temperature of VOCs which usually occur at a temperature less than 100°C (Art, 1993). The porosity of the soil allows the persistence injection and movement of the steam within the soil particles; this makes the steam stay longer thereby increasing the temperature of the soil samples and caused the BTEX to vaporize and then a further reduction in BTEX composition.

Table 4: Amount of BTEX composition in post-treated (PST) soil samples of Petroleum depot at a different time of 30, 60 and 90 minutes

BTEX COMPOUNDS	AMOUNT OF BTEX PRESENT AFTER THE REMEDIATION PROCESS (mg/Kg)		
	Steaming Time of 30mins	Steaming Time of 60mins	Steaming Time of 90 mins
Benzene	8.02369×10^{-6}	5.36115×10^{-6}	3.63368×10^{-6}
Toluene	1.81765×10^{-4}	1.20443×10^{-4}	9.87794×10^{-5}
Ethyl benzene	1.83230×10^{-3}	3.82337×10^{-4}	2.95379×10^{-5}
P-Xylene	7.92318×10^{-3}	4.50436×10^{-3}	2.71146×10^{-3}
M-Xylene	2.65350×10^{-1}	1.81781×10^{-1}	9.24602×10^{-2}
O-Xylene	1.53865×10^{-2}	1.17526×10^{-2}	7.03393×10^{-3}
TOTAL	2.93203×10^{-1}	1.98546×10^{-1}	1.02370×10^{-1}

3.2 The Geotechnical result test of the soil samples.

The results from the Geotechnical test present 0.4 and 0.5 as porosity values for auto-mechanic and gas-station soil samples respectively. The permeability test gives 1.6cm/minute for Auto-mechanic soil and 1.5cm/minute for Petroleum depot soil. The moisture content for the two soil samples was 20.27% and 20% for

the Auto-mechanic workshop and Petroleum depot soil samples respectively. The soil texture analysis presents the auto-mechanic workshop soil sample to be 64% Sand, 9.4% clay and 26.6% Silt while the Petroleum depot soil sample composed of 65.52% Sand, 10.48% clay and 24% Silt. The sand, silt and clay values distribution obtained from the textural analysis were measured from the soil

texture triangle and the corresponding soil samples in both locations were identified as sandy loam. The values obtained from the geotechnical test in this study fall within the limits of ASTM'S international geotechnical engineering standard for the sandy loam Ahaneku (2011).

3.3 Effectiveness of the Steam Enhanced Extraction (SEE) Method

The effectiveness of the remediation process at a different time of 30, 60 and 90 minutes respectively in the selected sites were evaluated using equation

Where;

E = Effectiveness

CB = amount of BTEX in pre-treatment

CA = amount of BTEX in post-treatment

$E = (CB-CA)/CB \times 100\%$

Effectiveness= (amount of BTEX in pre-treatment)-(amount of BTEX in post-treatment)/ (amount of BTEX in pre-treatment) $\times 100\%$

For the Auto-mechanic workshop soil sample

From Table 1, the total amount of contaminants (BTEX) present before the treatment was 4.50043×10^{-1} mg/kg and after the steaming period of 30 minutes, the total amount of contaminants (BTEX) present after the remediation process was 1.8163×10^{-1} mg/kg in the soil sample. Therefore, the effectiveness was evaluated

$$ESEE \ t30 = (0.450043)-(0.81638)/(0.450043) \times 100 = 59.63988\%$$

$$ESEE \ t30 = 59.64\%$$

$$ESEE \ t60 = (0.450043)-(0.0875194) /0.450043 \times 100 = 80.55\%$$

$$ESEE \ t60 = 80.55\%$$

$$ESEE \ t90 = (0.450043)-(0.0570056)/0.450043 \times 100 = 87.32\%$$

$$ESEE \ t90 = 87.32\%$$

For Petroleum depot soil sample

From Table 3, the total amount of contaminants (BTEX) present before the treatment is 6.60493×10^{-1} mg/kg and but after the steaming period of 30minutes the total amount of contaminants (BTEX) present after the

remediation process was 2.93203×10^{-1} mg/kg) Therefore, the effectiveness is evaluated

$$ESEE \ t30 = (0.660493) -(0.293203)/0.660493 \times 100 = 55.608\%$$

$$ESEE \ t30 = 55.61\%$$

$$ESEE \ t60 = (0.660493)-(0.19854)/ 0.660493 \times 100 = 69.9406\%$$

$$ESEE \ t60 = 69.94\%$$

$$ESEE \ t90 = (0.660493)-(0.102370) /0.660493 \times 100 = 84.501\%$$

$$ESEE \ t90 = 84.50\%$$

Table 5 shows the summary of the effectiveness of the steam enhanced extraction process for auto-mechanic workshop and gas-station soil sample at a different steaming time. In the auto-mechanic workshop, 59.64 % effectiveness was obtained for the steaming time of 30minutes but after a steaming time of 60 minutes, the effectiveness of the remediation process increased to 80.55 % and for a steaming time of 90minutes further increase was observed in the effectiveness of the remediation process (87.32%). In gas-station, 55.61% of the effectiveness was obtained for a steaming time of 30 minutes but for a steaming time of 60 and 90 minutes, the effectiveness was found to be 69.94% and 84.50% respectively. This shows that the more the steaming time the more the effectiveness of the remediation process. The surge in the effectiveness of the remediation process was attributed to the decrease in the amount of BTEX present after the remediation process. The soil type may influence the process of removal of BTEX considering the porosity of the soil which allows the persistence penetration of steam into the soil and in turn aid BTEX to vaporize and desorb from the soil particles. Sleep and McClure (2001) described volatile organic compounds as those compounds that vaporize at a temperature usually less than 100°C. The more the steam is injected into the soil sample the more the BTEX vaporize from it because of its nature of volatility and this led to the reduction in BTEX and which eventually increases the effectiveness of the remediation process.

Table 5: Summary of the Effectiveness of the remediation process in the auto-mechanic workshop and petroleum depot soil sample

Steaming Time (minutes)	Effectiveness of remediation process (%)	
	Auto-mechanic	Petroleum depot
30.00	59.64	55.61
60.00	80.55	69.94
90.00	87.32	84.50

3.4 Regression Analysis

The effectiveness of the remediation process was evaluated for each time of 30, 60 and 90 minutes respectively. Effectiveness for auto-mechanic workshop

in 30, 60 and 90 minutes were found to be 59.64, 80.55 and 87.32%; for petroleum depot, the effectiveness of the process were found to be 55.61, 69.94 and 84.50% respectively.

In order to elucidate the relationship of correlation between the time of treatment and effectiveness of the remediation process, a regression analysis of the results obtained was carried out on results obtained. The line fit is shown in Figures 1 and 2 respectively for both the auto-mechanic workshop and petroleum depot. The R² values obtained for the time of treatment with the effectiveness of the remediation process employed for both auto-mechanic workshop and gas-station are 0.984 and 0.993 respectively.

The linear equation is:

For auto-mechanic workshop: $Y = 0.475x + 47.11$, $R^2 = 0.984$

For gas-station: $Y = 0.482x + 40.99$, $R^2 = 0.993$

Where;

Y= effectiveness of the remediation process

X= time of treatment

R= Coefficient of determination

The linear regression model developed shows an increase in the effectiveness of the remediation process as the time of treatment increases in the selected soil samples. These results agree with the results obtained by Van Eyk and Vreeken (1991) in the use of the Steam Enhanced Extraction technique for the removal of BTEX from the gas-station soil sample.

Figure 1 shows the graph of the effectiveness of the remediation with time. As the time of treatment increases the effectiveness of the remediation process also increases. The effectiveness is a dependable variable on the time of treatment. But at 110 minutes of the treatment time, total remediation will be achieved in the auto-mechanic workshop. The R² value shows that 98.4% of the data from the effectiveness are predicted from the time of treatment and the R² value obtained also shows a good fit of the remediation method employed in the study.

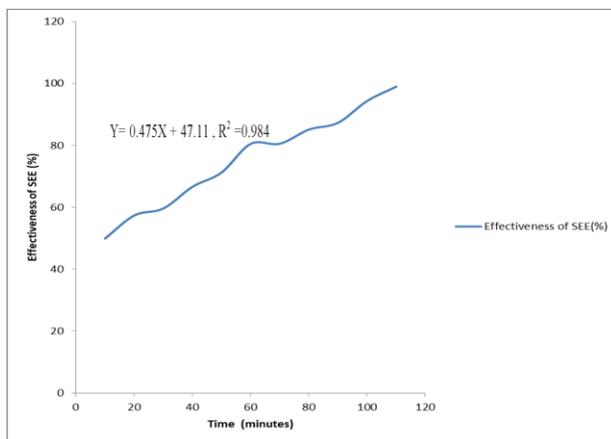


Figure 1: The effectiveness of the SEE process varied with time in the Auto-mechanic workshop soil sample

The graph of the effectiveness of the remediation with time of treatment in the petroleum depot soil sample is shown in figure 2. As the steaming time increases the effectiveness of the remediation process increases. Also effectiveness is a dependable variable on time of treatment. But at 120 minutes of the treatment time, total

remediation will be achieved in the petroleum depot. The R² value shows that 99.3% of the data from the effectiveness are predicted from the time of treatment and it also show a good fit of the remediation method employed in the study.

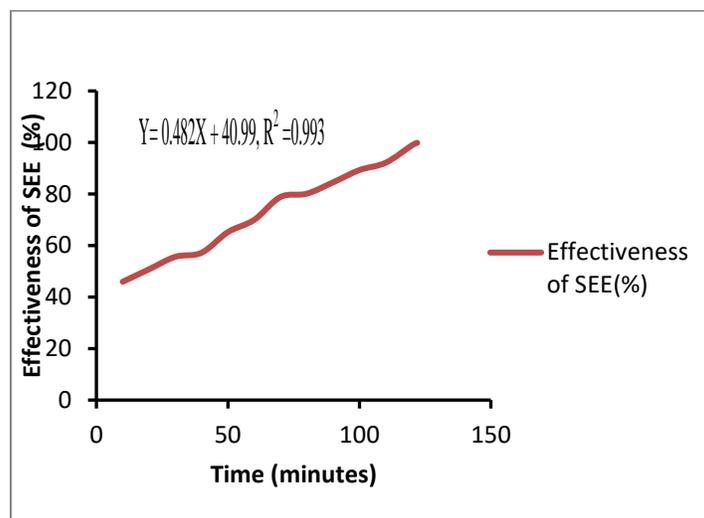


Figure 2: The effectiveness of the SEE process varied with time in the petroleum depot soil sample

6.0 Conclusion

The results obtained from the study revealed that steam enhanced extraction method of in-situ thermal treatment technology can be employed to remediate hydrocarbon (BTEX) polluted sites. Benzene, Toluene, Ethyl benzene and Ortho-Xylene composition is higher in auto-mechanic workshop while Meta-Xylene and Para-Xylene composition is higher in the petroleum depot. Benzene, Toluene and Ethyl benzene were insignificant in the selected soil samples. The study revealed that the total amount of BTEX composition (6.60493×10^{-1} mg/kg) in the petroleum depot is more than that of the auto-mechanic workshop (4.50043×10^{-1} mg/kg) and this can be attributed to the long years (30) of use of the site for petroleum discharge activities compared to the auto-mechanic workshop established more than 10 years ago.

Effectiveness for the auto-mechanic workshop in 30, 60 and 90 minutes were found to be 59.64, 80.55 and 87.32% while that of the petroleum depot were found to be 55.61, 69.94 and 84.50%.

A regression analysis was used to forecast the time to achieve the total remediation of the sites. The R² values obtained for auto-mechanic and petroleum depot showed that there was a strong relationship between the effectiveness and time of treatment. It can be predicted that with a treatment of 110 minutes and 120 minutes for auto-mechanic and gas-station respectively, complete remediation could be achieved.

This study therefore established that BTEX contaminated soil can be remediated effectively using steam enhanced extraction method an in situ remediation technique.

7.0 Conflict of interest

The authors declare that they have no conflict of interest.

References

- Ahaneku I.E. (2011). Infiltration Characteristics of Two Major Agricultural Soils in North Central Nigeria. *Agricultural Science Research Journals* vol. 1(7); pp.166-171, September 2011
- Art, H.W., (1993). Volatile Organic Compounds in Art, H.W., ed., *A dictionary of ecology and environmental sciences*: New York, Henry Holt and Company. p.581
- Baker, R.S. and G. Heron. (2004). In-situ delivery of heat by thermal conduction and steam injection for improved DNAPL remediation. *Proceedings of the 4th International Conf. on remediation of Chlorinated and Recalcitrant Compounds*, Monterey, CA, May 24-27, 2004. Battelle, Columbus, OH.
- Beyke, G. and D. Fleming. (2002). Enhanced removal of separate phase viscous fuel by electrical resistance heating and multi-phase extraction. *9th Annual International Petroleum Environmental Conference*, October 22-25, 2002, Albuquerque, NM.
- Beyke, G. and D. Fleming. (2005). In situ thermal remediation of DNAPL and LNAPL using Electrical resistance heating *Remediation*, 15(3):5-22pp
- Bouyoucos CJ (1951). A recalibration of the hydrometer mechanical analysis of soil. *Agron.J.* 43: 434- 438pp
- Blundy, R. and P. Zionkowski. (1997). Final Report: Demonstration of Plasma In Situ Vitrification at the 904-65G K-Reactor Seepage Basin, WSRC-RP-97405. Westinghouse Savannah River Company, 192 pp.
- Block, P., R. Brown, and D. Robinson (2004). Novel activation technologies for sodium Per sulphate in-situ chemical oxidation. *Proceedings of the Fourth International Conference on the*

- Remediation of Chlorinated oxidation Recalcitrant Compounds, Monterey, CA
- Cohen, R.M., and Mercer, J.W., (1993), DNAPL site evaluation: C.K Smoley, 384 p.
- Cole, G.M (1994) Assessment and Remediation of Petroleum Contaminated Sites CRC Press Boca Raton, Florida
- Davis, E. (1997). Ground Water Issue: How Heat Can Enhance In-situ Soil and Aquifer Remediation: Important Chemical Properties and Guidance on Choosing the Appropriate Technique, EPA 540/S-97/502. U.S. EPA., Office of Research and Development, 18 pp.
- Davis, E. (1998). Steam Injection for Soil and Aquifer Remediation, EPA 540/S-97/505. US EPA, Office of Research and Development, 16 pp.
- Davis, E., et al. (2005). Steam Enhanced Remediation Research for DNAPL in Fractured Rock, Loring Air Force Base, Limestone, Maine, EPA 540/R-05/010.
- English standard institution (E.S.I) part II-1973. Determination of moisture content by oven-drying of soil sample
- Esmailzadeh, H., Fataei, E., Saadati, H. (2020). NH₃ Removal from Sour Water by Clinoptilolite Zeolite: A Case Study of Tabriz Refinery. Chemical Methodologies, 4(6), 754-773. doi: 10.22034/chemm.2020.113660
- Fetter C.W (1994) applied hydrogeology, 3rd edition, new York .Macmillan college publishing company 691p , porosity measurement is on p 81
- Hatheway, A. (2006). Long-Term Fate And Transport Characteristics Of Manufactured Gas Plant Residuals And Wastes.
- Luthy, R.G., Dzombak, D.A., Peters, C.A., Roy, S.B., Ramaswami, A. (1994). Remediating Tar-Contaminated Soils at MGP Sites. Environmental Science and Technology, 28(6), 226- 276pp.
- Pope, D. et al. (2004). Performance Monitoring of MNA Remedies for VOCs in Ground Water, EPA/600/R-04/027, U.S. EPA, Office of Research and Development.
- Riser-Roberts, E., (1998). Remediation of petroleum contaminated soils: Biological, Physical and Chemical processes. Boca Raton: Lewis Publishers.
- Sleep and McClure (2001). Removal of Volatile and Semi-volatile Organic Contamination from Soil by Air and Steam Flushing.
- Thornburg, T. et al. (2005). Effectiveness of in situ cement stabilization for remediation of sediment containing coal tar derived hydrocarbons. The Annual International Conference on Contaminated Soils, Sediments, and Water, October 17-20, 2005, University of Massachusetts, Amherst. <http://www.umasssoils.com/abstracts2005/Thursday/evolving%20strategies.htm>
- US EPA. (1990). Control technique for volatile organic emission from stationary source. Report no: EPA 450/2-78-022. Research Triangle Park NC. National Technical information service. May 1990
- US EPA. (1991). Engineering Bulletin: In Situ Soil Flushing, EPA 540/2-91/021. Office of Research and Development, 7 pp.
- US EPA. (1995). Geosafe Corporation In Situ Vitrification Innovative Technology Evaluation Report, EPA 540/R-94/520. Office of Research and Development, 148 pp.
- US EPA. (1997). Analysis of Selected Enhancements for Soil Vapor Extraction, EPA 542/R 97/007. Office of Solid Waste and Emergency Response, 246 pp.
- US Environmental Protection Agency. (2010). Waste and cleanup risk assessment glossary: U.S. Environmental Protection Agency, access date May 26, 2010.
- Van Eyk, J., and Vreeken C. (1991). In Situ and On-site subsoil and Aquifer restoration at retail Gas-station: Robert E. Hinchee and Robert F. Olfenbuttel (ed) Insitu Bioreclamation Butterworth-Heinemann, Stoneham Massachusetts pp.303-320
- Van Cauwenberghe, L. (1997). Electrokinetics. Technology Overview Report. Ground Water Remediation Technologies Analysis Center.
- Wilson, W.E., and Moore J.E., (1998). Benzene, toluene, ethyl benzene, xylene, Glossary of Hydrology: Alexandria, Virginia, America Geological Institute, p.20