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Enhancing Green Synthesis using Zinc Oxide/*Musa Paradiascal* Nanoparticles for Soil Remediation Within the Coastal Region of Niger Delta, Nigeria

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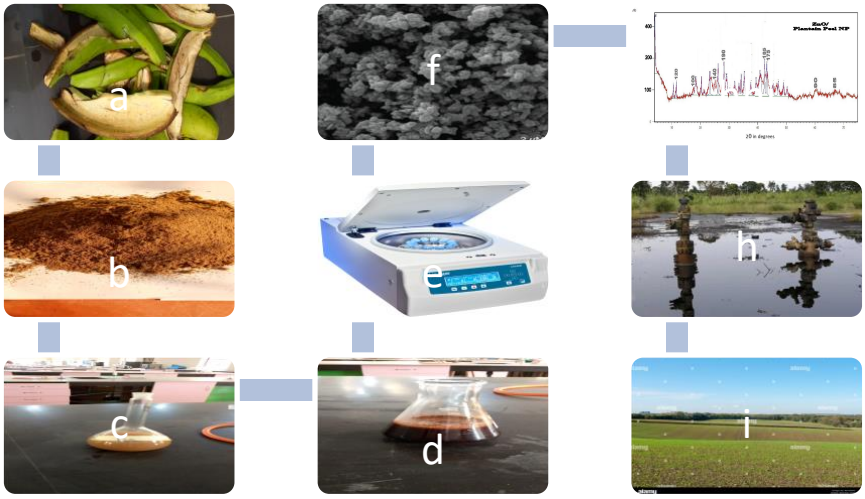
Abstract

This study aimed to evaluate the efficacy of biosynthesis of zinc oxide (ZnO) nanoparticles using plantain peel (*Musa paradisiacal*) extract (MPE) for remediation of oil spill contaminated soil sites within the Niger Delta zone of Nigeria. This study became of paramount importance due to substantial retrogression in agricultural activities off the coastal region and vegetation which has resulted in acute food shortage, land degradation, malnutrition which in turn has brought the Nigerian economy from "grace to grass" MPE/ZnONPs was characterized using scanning electron microscope (SEM), X-ray powder diffraction (XRD) and Fourier infrared spectroscopy (FTIR) taking in cognizance of the physicochemical parameters of the soil before and after analysis so as to ascertain the efficacy of remediation technique. SEM revealed the image of an irregular morphology and a porous surface which can enable oil entrance into the internal parts of the nanomaterial for easy sorption purposes. The XRD revealed a hexagonal wurtzite structure with a particle size of 22 nm. The synthesized MPE/ZnONPs exhibited adsorption properties when used on the oil spill contaminated soil samples and the degradation efficiencies were found to range between 1.87 – 9.48%(CSOA1); 1.38 – 12.06% (CSPB1); 44.87 – 88.79% (CSOA2) and 38.95 – 79.24% (CSPB2) for the oil contaminated samples suggesting that the synthesized MPE/ZnONPs had good efficacy for oil spill removal in the contaminated soil samples. Kinetic of remediation gave a linear graph and took a pseudo-first order reaction with R^2 values close to 1 (R^2 = 0.980, 0.901, 0.957 and 0.935).Analysis of Variance (ANOVA) employed in the course of this study revealed that there is significant difference ($p< 0.05$) at 95% confidence limit in the diminishing trend of TPH of the CSOA1 and CSOA2 and likewise that of CSPB1 and CSPB2. It is therefore recommended that for optimum remediation efficacy most especially in oil saturated soil medium,, surfactant enhanced ex-situ soil washing may be employed.

Keywords: Adsorption, Morphology, Nanoremediation, Kinetics, Pseudo-first order

Graphical Abstract



(a) Plantain peels (b) Dried and ground plantain peels powder (c) Filtrate of plantain peel extract (d) Filtrate + Zinc acetate (e) Centrifuge and oven dry (f) SEM (g) XRD (h) Oil spill contaminated soil site (i) Remediated tilled soil for Agricultural purposes

1.0 Introduction

Surface water pollution and land degradation often caused by oil spill and its setback to green environment actualization has remained a challenge since the discovery and exploration of crude oil in Niger-Delta, Nigeria. Oil spills emanating from unforeseen disasters (Knap and Rusyn, 2016), accidental leakages (Olayinka and Abimbola, 2017) and youth restiveness (Chukwuemeka and Agbara, 2010) have been recorded over the years in the Niger Delta zone of Nigeria. Spill experts have estimated about 30-50% of oil spills to be caused either directly or indirectly by human error while 20-40% is caused by equipment failure or malfunction (Michel and Fingas, 2016).

Serious global health impacts ranging from physical and mental disorders, organ dysfunction, neurological disorder, respiratory problem cancer, reduced life expectancy, weakening of the body's immune system, respiratory problems and death have often resulted from oil spill and related issues (Kuppusamy *et al*., 2016; WHO, 2013; Perera and Herbstman, 2011) while other health related issues emanating from oil pollution may involve high levels of emotional stress and psychological distress resulting from living under such environmental adversity (Kadafa, 2012).

Methods employed in remediating soil and water differs and often depends on factors such as adequate procedure, type of contaminants involved and nature of contaminated site. Contaminated soil may involve the use of soil vapor extraction, pump and treat systems, degradation, and bioremediation (Fingas and Fieldhouse, 2011) while conventional methods often applied for water clean-up may include physical, chemical, thermal and biological methods (Larson, 2010; Hamby, 2012). Though these conventional methods have moved oil experts a step forward in remediation advancement, they are not adequate to solve the problem of massive oil spills as most often, technical difficulties

associated with contaminant rebound, matrix diffusion, degradation intermediates and by-products are encountered in the process (Nnaji, 2017).

Recently, **nanotechnology** seems to offer a reliable solution to the impending problem of oil spill all over the world. Nanotechnology is the science of production, manipulation and use of nanoparticles at quantum energized level for ultimate processes and goals. Nanoparticles are particles between 1 and 100 nanometres (nm) in size with a surrounding interfacial layer consisting of ions, inorganic and organic molecules. In nanotechnology, a particle is defined as a small object that behaves as a whole unit with respect to its transport and properties which are further classified according to diameter (Mohamed *et al.,* 2017). Nanoparticles often possess unexpected optical properties as they are small enough to confine their electrons and produce quantum effects (Hewakuruppu *et al.,* 2013). Nanoparticles with one half hydrophilic and the other half hydrophobic are termed Janus particles and are particularly effective for stabilizing emulsions (Mohamed *et al.,* 2017) . They can self-assemble at water/oil interfaces and act as solid surfactants. Remediation using Nanotechnology offers faster transformation kinetics, better penetration of contaminated matrices, extension of the spectrum of degradable contaminants and avoidance of remediation intermediates (Elloit, 2016; NanoRem 1, 2016). Nanomaterials can be used to remediate environmental matrices polluted by volatile organic fractions of petroleum, chlorinated benzenes, persistent organic pollutants (POPs), carbon tetrachloride, heavy metals (As, Cr, Hg, Zn, Ni) etc (Nnaji, 2017). Therefore the necessity to enhance the applicability of nanotechnology in remediating oil spill land and surface water in the Niger Delta region of Nigeria is of paramount importance.

Statement of Problem

Oil exploitation, exploration and production activities within the Niger Delta region of Nigeria has created unprecedented negative environmental impacts on the entire populace of Ogonoland since the commencement of oil activities and practices in 1956. The four LGAs namely; Eleme, Gokana, Khana and Tai are the main sites of oil industry operations in Rivers State and have experienced calamities of oil spill disaster, anthropological environmental degradation, food shortage-persistent and poverty. These have caused a substantial retrogression in agricultural activities off the coastal region and vegetation. There is acute food shortage, malnutrition and death and in turn has brought the Nigerian economy from "grace to grass" Moreover, residual chemical toxicity caused after chemo-remediation, long duration time spent on achieving effective bioremediation and other constraints has justified the need to explore nanoremediation technology so as to find a lasting solution to impending quest for a green environment and economic sustainability

Purpose of the Study

The purpose of this study is to investigate the effectiveness of nanoremediation on oil contaminated soil and surface water within Niger Delta region of Nigeria. The specific objectives are to;

1. Evaluate the physicochemical parameters of the soil and water samples.
2. Investigate the mechanism of nanoparticles so as to ascertain its efficacy in remediating contaminated soils and water
3. Employ nanoremediation technology on the crude oil contaminated soil and water samples
4. Examine the kinetics of nanoremediation

Significance of the Study

This study will enable us establish a relative cost effective and fast remediation technique that can achieve a higher efficiency amongst other remedial technologies. This study will help to support programs aimed at reducing land pollution, enhance good water quality and promote the general well-being of the inhabitants of oil producing communities. It is also significant because it will help to bring an enduring solution to community crises emanating from oil spill problems within the Niger Delta region.

Scope of the study

This investigation encompassed the sampling of ground and surface water from selected areas within the coastal region of Niger Delta. Soil samples were collected within the study location for analysis using zinc oxide and iron oxide nanoparticles to enhance effective remediation. Characterization of the nanoparticles was limited to the use of scanning electron microscopy (SEM), XRD and FTIR.

Materials and Method

Study Area Description

The study area is the Ogoni land, within the coastal region of Niger Delta. The area which is an oil producing state in Nigeria is situated at the Gulf of Guinea between 5^0 - 8^0 E and 3^0 - 6^0 N. Ogoni territory lies on 404 square miles of the coastal plains terraces to the north-east of the Niger River Delta. Inhabited by about a million people, its population density is among the highest in any rural area of the world. It is a rain forest zone with relative high temperature and high humidity.

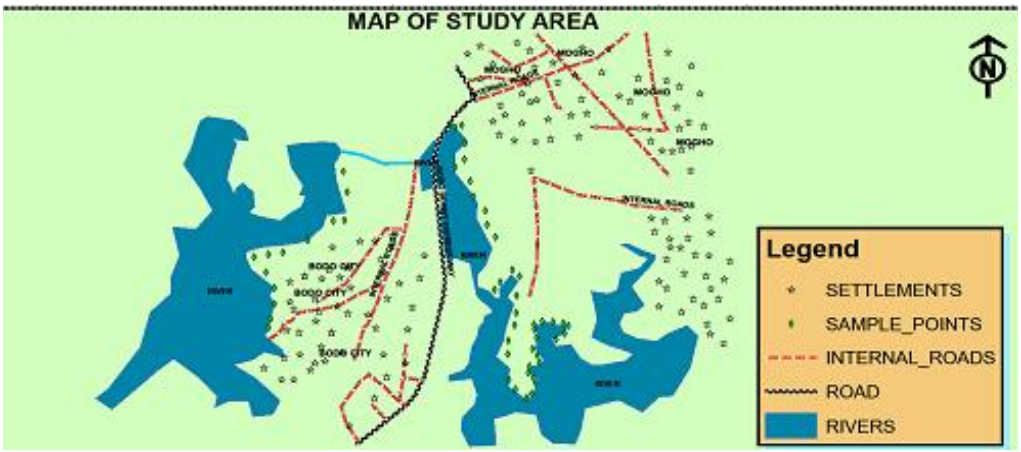


Fig 1: Map of the Study

Sample Collection

Collection of Soil and Water samples

Surface soil (0-15cm) and subsurface soil (15-30cm) were collected from two locations within the contaminated sites using the grab sampling method.

Collection and preparation of plantain peel extract

Plantain peel (*Musa paradisiacal*) was obtained from Ogbogonogo market in Asaba, Delta State of Nigeria. The peel was removed from the main plantain bunch, washed with clean water to remove impurities, chopped into bits, sun dried for 7 days and ground with a clean blender into a smooth powder. 200 ml of distilled water was then added to 150g of the plantain peel powder, stirred thoroughly and filtered using Whatman No 1 filter paper with a pore size of 25 µm. The extract obtained (MPE) was carefully stored in a refrigerator for further analysis.

Analysis of Physicochemical parameters

Physicochemical parameters of the water samples were evaluated to ascertain the extent of contamination prior to and after remediation. Soil samples were also collected from oil spilled petroleum contaminated sites in Mogho Khana and Bodo City Local Government Area in Rivers State, Nigeria from two depths viz; 0-15cm and 15-30 cm while another soil sample was collected from an uncontaminated area which served as control. The soil samples were stored in clean sterile polythene bags and thereafter, sent to the laboratory for physicochemical analyses maintaining all laboratory conditions. The physicochemical parameters analyzed were:

pH measurement

This was carried out using the APHA 4500-H^+B method. The electrode was dipped in buffer 4 solution and the meter was calibrated using the appropriate knob after the pH meter was switched on for ten minutes stabilization. The electrode was transferred into buffer 9 solution and was calibrated to same pH, the electrode was rinsed with distilled water jet from the wash bottle and dipped finally to the soil solution in the beaker after stirring several minutes to homogenized properly. The pH value displayed on the pH meter screen that remained constant for 30 seconds was recorded as the pH value of the solution.

Total organic carbon (TOC)

TOC was determined using the Walkley-Black method. About 0.2 g of air-dried soil samples was sieved and weighed into a clean 500 ml conical flask. 5 ml $K_2Cr_2O_7$ and 7.5 ml H_2SO_4 solution were measured and added to the flask accordingly. Another 5 ml of K_2CrO_4 and 7.5 ml H_2SO_4 were introduced into another clean conical flask and was labeled blank

test. The conical flasks were subjected to constant heating on an electro-thermal heater for 10-15 minutes. When the oxidation/reduction process was accomplished by the appearance of greenish-yellow solution of the digest then, digest was cooled to room temperature and was diluted to 100 ml with distilled water. 25 ml of this solution was withdrawn into a clean conical flask using a pipette and was titrated with Ferrous Ammonium sulphate to reddish solution using ferroin solution as indicator. Blank test was titrated and the respective titres were recorded

The chemistry of this procedure is as follows:

$$2Cr_2O_7^{2-} + 3C + 16H^+ \longrightarrow 4Cr^{3+} + 3CO_2 + 8H_2O$$

$$\%TOC = \frac{\boldsymbol{Blanck\ titre - Sample\ titre\ x\ 0.3\ x\ 0.2}}{\boldsymbol{Weight\ of\ Sample}}$$

Nitrate – Nitrogen

Determination of nitrate was also based on APHA method (APHA 4500-NO^{3-}). One gram of soil sample was weighed into a clean conical flask using weighing balance. 100 ml distilled water was added and content was stirred for 5 minutes with magnetic stirrer. This solution was filtered through Whatman filter paper into a 100 ml volumetric flask.

One millilitre of filtrate was pipette into a clean test tube then 0.5 ml brucine reagent was added and 2 mls concentrated sulphuric acid. A blank was prepared using distilled water. The yellowish colour developed by sample filtrate was read at 420 nm wavelength in a spectrophotometer using blank test to zero the spectrophotometer. Standard NO^{3-} solution was prepared and was treated as was described above in the sample test. The colour was read at same wavelength using blank test to zero the spectrophotometer. A calibration graph was plotted using the standard values. The concentration of the NO^{3-} (Nitrate-Nitrogen) ion in the soil solution was interpolated from the standard graph.

Phosphate – Phosphorus

The determination of phosphate was based on standard method (APHA 4500-PD).One gram of soil sample was weighed into 250 ml conical flask. 50 ml solution of glacial acetic acid was added and was stirred for 5 minutes. The mixture was filtered into a clean volumetric flask through Whatman filter paper.

Standard Phosphate Phosphorus

Standard Phosphate Phosphorus was analyzed according to the method described by APHA 4500-PD (Uzor *et al.,* 2020). This was prepared, from where lesser concentration ranges were further prepared. 50 ml of the test sample was measured into 100 ml volumetric flask after which distilled water and standard phosphate phosphorus solution were added and labeled accordingly. 8.0 ml of combined ascorbic acid reagent was then added to the flask made and up to 100 ml with distilled water. This was allowed to stand for 20 minutes for proper colour development and was off read at 880nm wavelength in the UV Visible

spectrophotometer using distilled water as blank. The absorbance of the standard phosphate concentration ranges was recorded from which standard graph of absorbance against concentration was plotted to obtain a straight line graph. The concentration of the PO_4^{3-} in the sample was interpolated from the graph.

Total Hydrocarbon Content

1 g of sieved sample was extracted with 15ml of ethyl ether, in a glass test tube. The extraction was partitioned, between distilled water in a separatory flask. The organic layer (lower phase) was taken with a clear test tube and was dehydrated by adding a spoonful of anhydrous sodium sulphate. The clear extracted solution was absorbed at 460nm wavelength with UV Visible Spectrophotometer.

Biosynthesis of ZnO Nanoparticles (ZnONPs) using MPE

The synthesis of the ZnONPs was carried out according to the method described by Sutrahar & Saha, (2016). 5g of zinc acetate ($ZnC_4H_6O_4$) was mixed with distilled water and the solution added to 15 ml of PEx in a 250 ml Erlymeyer flask. The solution was subjected to continuous stiring and heating at 100 rpm for 4 hours. The resultant nanoparticle solution was purified by centrifugation at 10,000 g for 20 minutes. The supernatants were discarded and the nanoparticles pellets collected, washed with distilled water dried and stored at -80^{o}C.

Scanning Electron Microscope (SEM)

Prior to analysis, the synthesized ZnO particles were mounted on aluminium studs and coated with gold film. Visualization of ZnO morphology was performed using a SEM. The size of particles was then analyzed using the Image J Program according to the method of Rueden *et al.*, 2017.

X-ray Diffraction (XRD)

The dried P-ZnNPs were characterized using PAN analytical Xpert Pro θ-2θ powder X-ray diffractometer. The instrument used a Cu Kα radiation of wavelength = 0.1541nm at 45 kV with a monochromatic filter of ^{o}2 in a scan range of 20-80^o with a scanning speed of 6o/min. The estimation of the sizes of particles was performed by Debye-Scherrer's formula.

Fourier Transform Infra-red Spectroscopy (FT-IR)

The Spectra properties of ZnO-nanoparticles were observed by Fourier Transform Infra-red Spectroscopy (FT-IR) using the dried powdered synthesized ZnO nanoparticles by FTIR spectrometer vector 22, Bruker, Germany. The pellets were scanned at 4 cm-1 resolution in the spectra range of 400-400 cm-1 at room temperature.

Application of plantain-MNPs for Oil Spill Contaminated Soil Samples

2 g was put in a 500 ml beaker and then 250 ml of distilled water was added. Various ratios of MPE/ZnONPs to contaminated oil spilled soil samples, ranging from 1:1 to 1:50, were added and mixed using a glass rod. Oil in the soil samples were extracted using hexane and determined by UV/Visible spectrophotometer at wavelength of 460nm every 20 minutes. The remaining oil was extracted from the medium, using n-hexane. The efficiency of the MPE-ZnONPs on the sample was calculated using the equation below:

$$XE\ (\%) = \frac{V0}{V1} \mathbf{X\ 100}$$

where V0 and V1 are the volume of the removed TPH, respectively. The used MPE/ZnONPs were recycled after washing them severally with n-hexane and another sample was prepared.

Kinetics of Nanoremediation of the Water samples

The kinetics of nanoremediation of the soil samples was monitored at fifteen minutes intervals to observe the relative changes that occurred and ascertain the efficacy of the method. This was achieved by monitoring the changes in the physicochemical parameters of the samples. The remediation experiment was carried out according to the methods of Elias *et al.*, 2015.

Results and Discussion

Table 1: Physicochemical parameters of Soil samples prior and after Nanoremediation

S/N	Sample ID	pH	TOC%	THC Mg/kg	CEC (Mg/kg)				$NO3^-$ Mg/g	P Mg/kg
1.					Na	K	Ca	Mg		
	Control	6.70	2.88	218.51	0.674	0.012	3.760	0.342	14.323	4.52
	$CSOA_1$	6.30	4.24	580.62	0.292+ 0.02	0.006	1.410	0.203	1.720	14.774
	$CSOA_2$	5.78	4.73	450.70	0.212	0.002	1.194	0.185	6.424	32.021
	$NRemOA_1$	6.60	3.02	289.12	0.453	0.004	2.890	0.280	10.485	6.40
	$NRemOA_2$	6.50	2.92	220.85	0.404	0.003	2.875	0.267	11.564	6.80
2.	Control	6.66	2.67	250.50	0.820	0.018	3.550	0.377	13.570	4.77
	$CSPB_1$	9.02	4.29	630.14	0.341	0.006	1.332	0.182	2.200	12.544
	$CSPB_2$	8.64	3.89	536.27	0.238	0.005	1.115	0.167	6.871	28.922
	$NRemPB_1$	6.80	2.95	310.25	0.675	0.009	1.835	0.255	11.300	5.90
	$NRemPB_2$	6.60	2.75	270.42	0.430	0.004	2.347	0.391	11.980	7.65

Sample Code: $CSOA_1$ Contaminated Soil sample (Mogho Khana) 0-15cm depth; $CSOA_2$ Contaminated Soil sample (Mogho Khana) 15-30cm depth
$NRemOA_1$ Remediated Soil sample (Mogho Khana) 0-15cm depth; $NRemOA_2$ Remediated Soil sample (Mogho Khana)15-30cm depth
$CSPB_1$ Contaminated Soil sample (Bodo city) 0-15cm depth; $CSPB_2$ Contaminated Soil sample (Bodo city) 15-30cm depth
$NRemPB_1$ Remediated Soil sample (Bodo city) 0-15cm depth; $NRemPB_1$ Remediated Soil sample (Bodo city) 15-30cm depth

pH of Soil samples

The pH of the control samples were close to neutral while samples obtained from the two sites at various depths tended towards alkaline. After remediation, the soil samples pH ranged between 6.50- 8.20. The pH range of the contaminated samples is in line with most studies revealing optimal pH range for effective degradation of soil microbes to be between 6-7 [Aparna *et al.,* 2010; Oko-Oboh *et al.,* 2016]. The nanoremediated samples accrued pH ranges close to neutral indicating efficient remediation with the plantain magnetite nanomaterials. The soil samples however had high values of total hydrocarbon content (THC) indicating high level of hydrocarbon contamination prior to remediation.

Exchangeable Cations

Cation exchange capacity (CEC) is a measure of the soil's ability to hold positively charged ions. It is an inherent soil characteristic that has the total capacity to hold exchangeable cations and retains essential nutrients thereby providing a buffer against soil acidification. It is a very important soil property influencing soil structure stability and nutrient availability.

The CEC of the top surface soil samples (0-15cm) were relatively higher than those of the sub surface samples. At 15-30 cm depth, the organic content of the sand is very low, hence the low CEC. The CEC of the subsoil layers are usually influenced by the clay content of the soil. A percentage decrease of 27.6, 66.6, 15.3 and 10.0 was observed for Na, K, Ca and Mg respectively on comparing the topsoil and subsurface soil samples of CSOA1 and CSOA2. This trend was also recorded for CSPB1 and CSPB2. However, 40%, 50%, 30% and 25% increase was observed after remediation of the topsoil and subsurface soil samples of CSOA1 and CSOA2 respectively. CSPB1 and CSPB2 took a similar trend indicating that remediation was effective in the soil samples.

The CEC of the nanoremediated soil samples were considerably higher when compared to the soil samples before remediation. The low CEC of 0.212, 0.002 and 1.194 mg/kg for Na, Mg and K respectively recorded in $CSOA_2$ is as a result of the lower depth (15-30 cm) as seen in table 1. A depth of 10 - 30 or above could result in organic content depletion and a lower CEC values as noted by Rengasamy & Churchman (1999) and this could be the reason for the low CEC within these depths as seen in t**ab**le 1.

Total Organic Carbon

TOC values ranged between 3.89 - 4.73% for all contaminated soil samples within the study sites while in the remediated soil samples, TOC% improved considerably ranging from 2.75-3.02% (Table1).

Phosphate Content

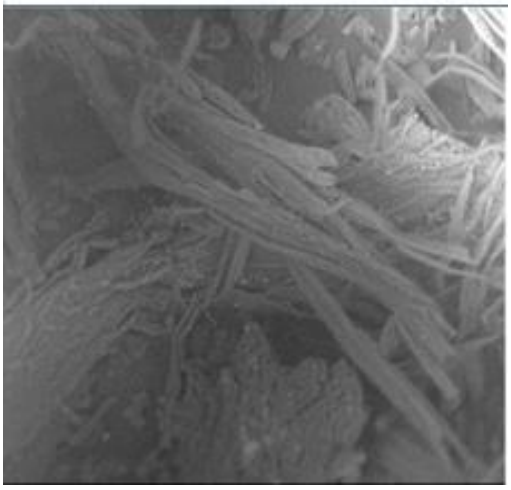
The phosphate $PO3^{-4}$ content in each contaminated soil samples had higher values than in the control and nanoremediated soil samples but were all within the World Health Organization's permissible values of 25-50 mg/kg for the protection of humans and environment.

Total Hydrocarbon

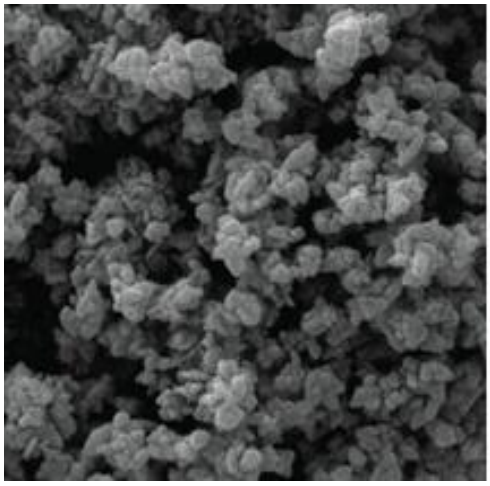
The residual THC content of each nanoremediated soil sample was above the recommended FMEnv of THC value of 50 mg/kg but below the intervention level of 5,000 mg/kg. The THC contents in nanoremediated soil samples ranged between 220.85-289.12mg/kg (NRemOAI and NRemOA2), 270.42-310.85mg/kg (NRemPBI and NRemPB2). However, some metabolites known as carcinogens which are hazardous to plant growth were identified indicating the unhealthy status of the contaminated soils prior to remediation.

Scan Electron Microscope (SEM)

Image of the SEM image of the raw plantain peels and that of the biosynthesized plantain (*Musa paradiascal)* peels/ZnO is shown in figure 1a and 1b respectively.



(a) Raw plantain peelings



(b) Synthesized plantain peelings with ZnO

Figure 1a and 1b: SEM of plantain peels

Figure 1 shows the SEM images of unripe plantain peels and that of biosynthesized plantain (*Musa paradiascal)* peels/ZnO (figures 1a and 1b). The figures show that the structures have irregular morphology and a porous surface which can enable a large contact area between the absorbent surface for sorption purposes and oil droplets and as well give room for oil retention (Du *et al.,* 2018).

X-Ray Diffraction (XRD) diffratogram of MPE/ZnONPs

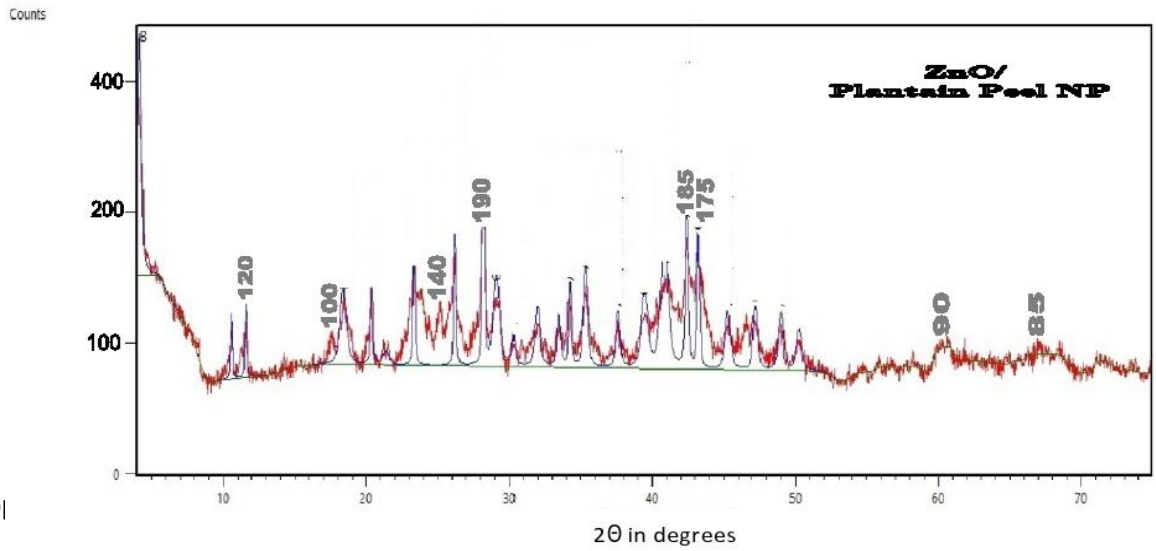


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Fig 2: XRD diffratogram of biosynthesized plantain peels extract/ZnONPs

The XRD diffratogram is shown in figure 2. This is recorded at the range of 2θ with values at 120^{O}, 175^{O}, 185^{O}, 190^{O}. These peaks are indexed at the Zinc oxide wurtzite structure crystallizing in two main forms as cubic zinc blend and hexagonal wurtzite. Other peaks are indexed at 100^{O}, 140^{O}, 85^{O} and 90^{O} for the MPE. All peaks recorded reveals that the synthesized nanopowder was free of interfering impurities devoid of any other characteristic XRD peaks other than that of zinc oxide and plantain peel extract peaks.

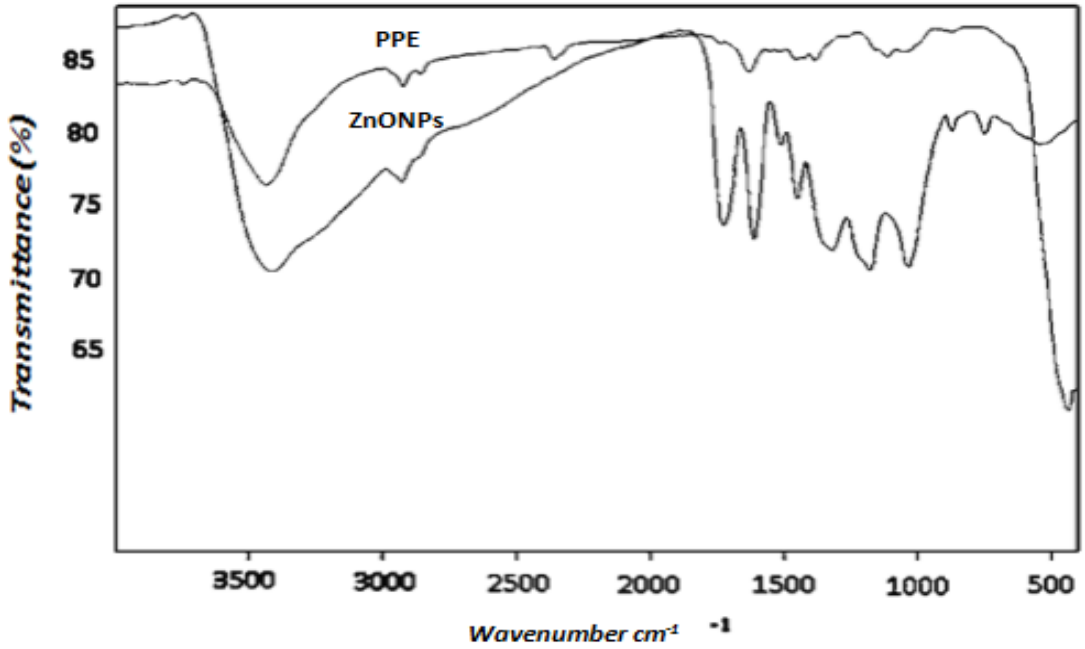


Fig 3: FTIR Spectrum of MPE/ZnONPs

Figure 3 shows the FTIR of the PPE and the ZnONPs samples reveals bands at different ranges. The peaks for PPE are at 3,350, 2,890, 2,430, 1620, 1,336 and 1,011 cm^{-1}. The peaks for ZnONPS are at 3,330, 2,942, 1,594, 1,366 and 1,030 cm^{-1}. The band stretching below 500 cm-1 (432 cm^{-1}) correspond to the Zn-O stretching mode, The band at 1,594 cm^{-1} correspond to the C-O stretching for esters and alcohols recorded within a range of 1000cm^{1} – 1300 cm^{-1}. The absorption peak at 2,942 is ascribed to the C-H stretch/bending vibrations in alkanes and the peak at 1594 is the C=C stretch of aromatic rings. These data are in line with the results observed by Srinivasa & Rao, (2015)

Mechanism of reaction proposed for MPE synthesis with Zinc oxide nanoparticles

Musa Paradisiaca extract (MPE), synthesized to ZnO nanoparticles is shown in mechanism MPE is made up of organic constituents such as sugars and alcohols (Hassan *et al.*, 2011). These acts as a reducing and stabilizing factor (Jiang *et al.*, 2005) with the ability of binding to the metal to form metal oxide nanoparticles. The formation of the ZnO nanoparticles proceed via a two step process involving the formation of the hydroxyl group by the interaction of the zinc acetate and the MPE followed by oxidation at 350^{O}C yielding the ZnO product (Imade *et al.*, 2022). As a result of zinc metal attachment to the acetate anion in the salt, there is a high reduction potential and tendency to donate electrons and create available sites for pollutants adsorption as seen in the following mechanism (figure 4):

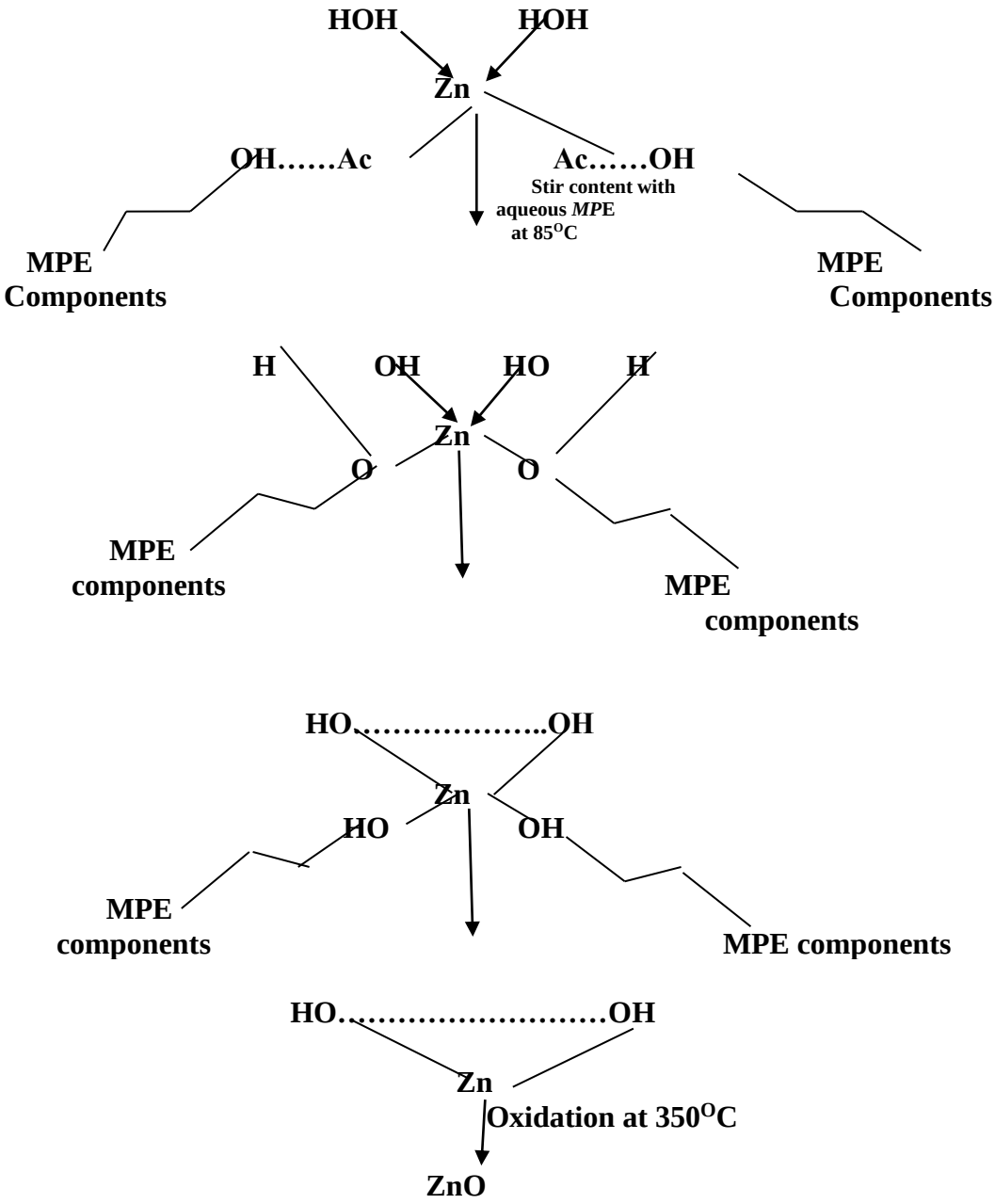


Fig 4: Mechanism proposed for MPE synthesis with Zinc oxide nanoparticles

Trends of Oil spill removal per time in soil samples

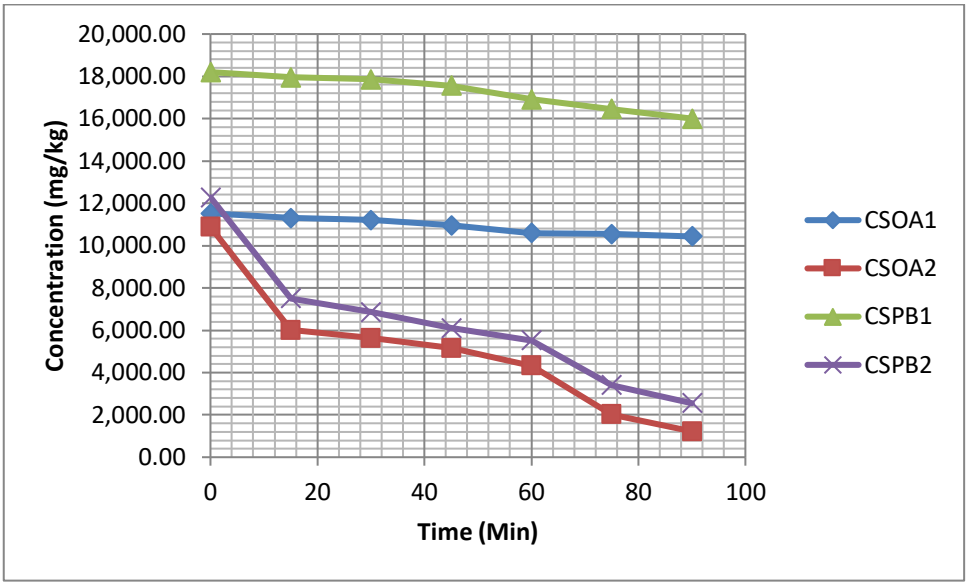


Fig 5: Trends of Oil spill removal per time in soil samples

Results for the removal trend of TPH from Mogho Khana and Bodo- City soil samples are indicated in figure 5. Soil samples obtained from 0-15cm depths soil (CSOA1 and CSPB1) in both sites had TPH concentration of 11,525.50 mg/kg ±0.40 and 18,200.50±0.10 mg/kg respectively before the commencement of analysis. TPH reduction was observed to be minimal and followed the same trend with CSOA1 recording 9.48% reduction after 90 minutes while TPH reduction in CSOA2) was 12.06% after 90 minutes of analysis. High concentration and high molecular weight of poly aromatic hydrocarbons probably difficult to degrade may be the reason for the low TPH percentage reduction (Rons and Rosenberg, 2014). More also, the samples may contain high activity of bacterial ensembles within the saturated oil spilled samples. This finding is in line with the works of El-Dars *et al.*, (2016) who recorded a high TPH reduction rate of 53.21% in contaminated soil samples amended with Sugarcane Bagasse.

Soil samples from 15-30cm depths (CSOA2 and CSPB2) from Mogho Khana and Bodo-City respectively recorded initial concentrations of 10,885.00±2.50 mg/kg and 12,285.00±1.30 mg/kg by the commencement of analysis. TPH percentage reduction was promiscuous in both depths (88.78% and 79.24%) respectively. This may be probably due to temperature difference, soil moisture and soil structure of the samples. Due to the depth of the subsoil light and heat penetration is retarded and oil percolation down to lower depths

may have resulted in volatility of oil content, low weight hydrocarbon and low TPH concentration, hence the lighter weight hydrocarbons are easily degraded resulting in high percentage TPH reduction. Though there was significant decrease in Total petroleum Hydrocarbon (TPH) observed in all the samples after analysis, the values were still above the permissible limits of FMEnv standards. Higher levels of TPH observed for CSOA1 and CSPB1 after analysis and may be accrued to the degree of oil saturation of the topsoil. Statistical analysis showed that there was no significant differences in the diminishing trend of samples obtained from 0-15 cm and 15-30 cm depths from both sites, (ANOVA, p = 0.05), there was significant difference in the diminishing trend in samples obtained from 0-15 cm and 15-30 cm depths within the same site. ANOVA, $P \geq 0.05$ at 95% confidence limit

Percentage Remediation of soil samples

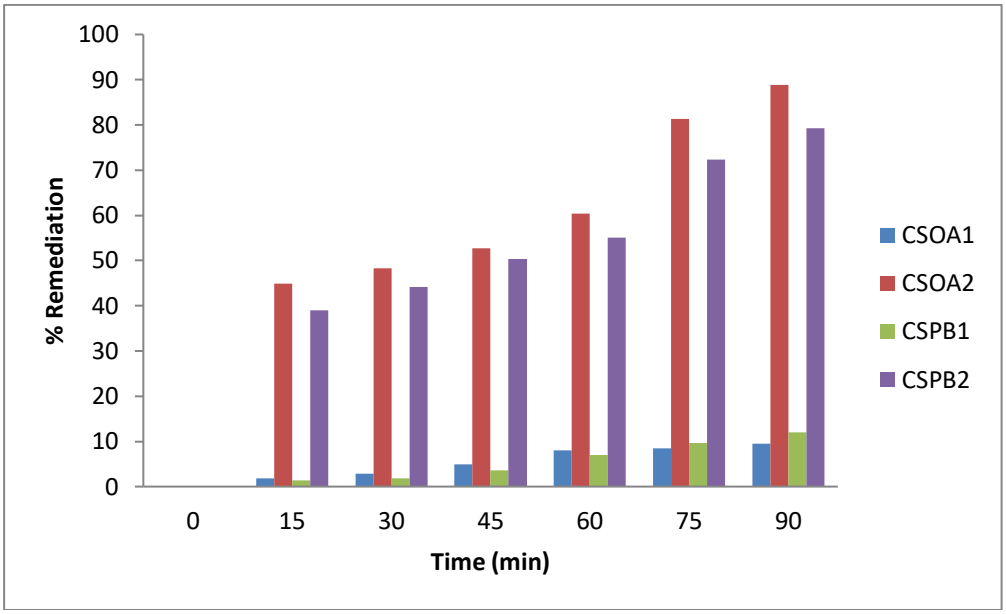


Fig 6: showing percentage remediation of soil samples

A plot of percentage remediation against time indicates that remediation was minimal 9.48% and 12.06% for CSOA1 and CSPB1 respectively at the end of analysis as shown in figure 6. Oil saturation within these topsoil and heavy molecular weight hydrocarbons may have resulted slow degradation rate of TPH in the samples. CSOA2 and CSPB2 had percentage remediation of 88.79 and 79.24 respectively after analysis and could be accrued to soil nature and temperature difference.

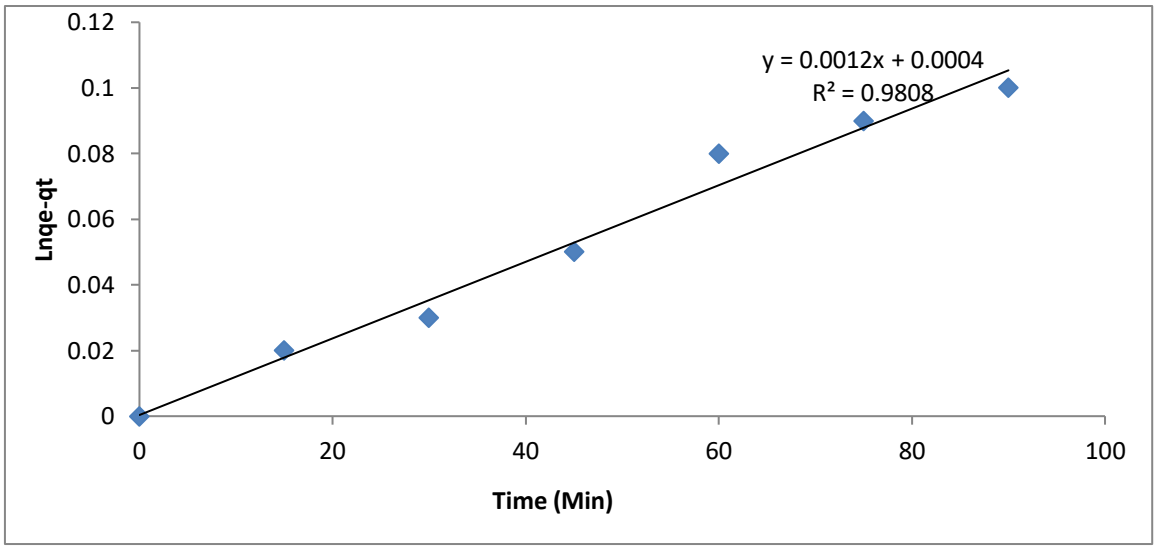
Kinetic model of nanoremediation of Soil samples

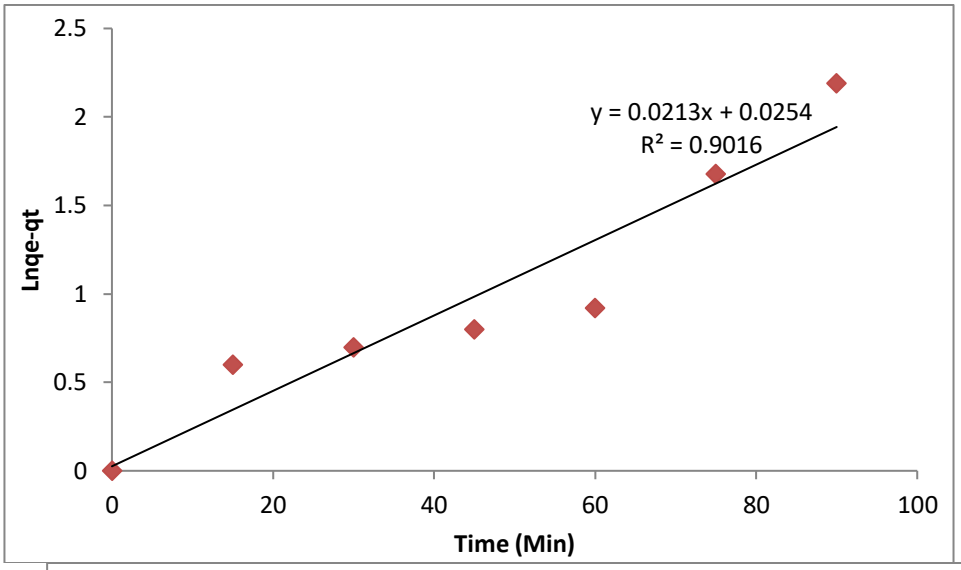
The reaction pathways of the contact between the oil samples and MPE synthesized ZnO nanoparticles took a pseudo-first order which is based on the assumption that the rate limiting step is a chemical sorption. The adsorption rate is dependent on the adsorption

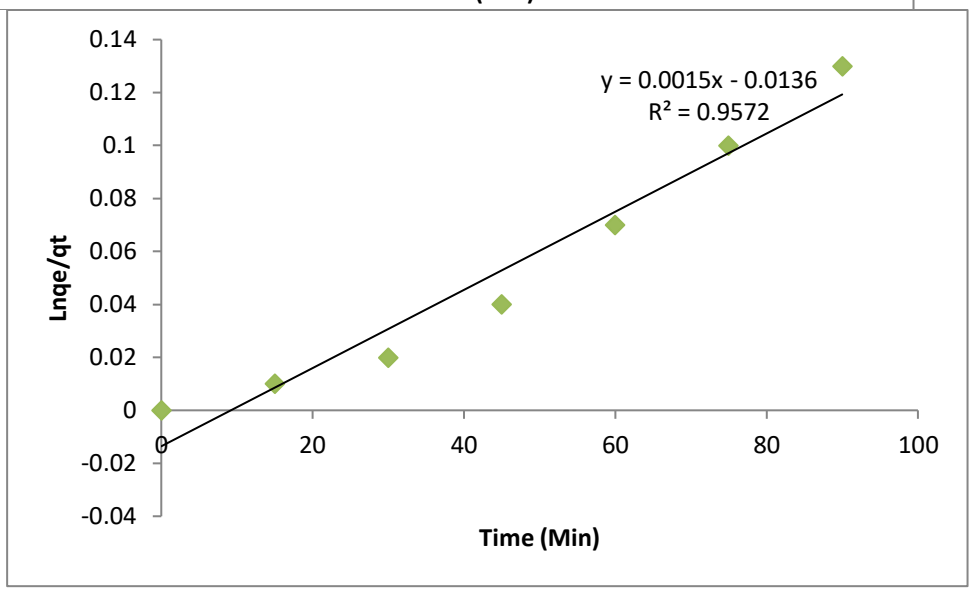
capacity and not on the concentration of the adsorbate as symbolized in the following linear equations

The expression given by Lagergren kinetic model for the Pseudo- first order is given as:
Log10qe-qt = log10qe-kt/2.303……(1)
lnqe/qt = ln (qe – qt)……(2)
ln (qe – qt) = ln (qe – k1t)……(3)

Where qe and qt (mg/kg) are oil spill retention capacity at equilibrium and time t (min), k1 (min-1) is the constant rate parameters of the Lagergren pseudo-first order model based on the adsorption that the rate of change of solute uptake with time is directly proportional to the difference in saturation concentration and the amount of solid uptake with time which is generally applicable over the initial stage of adsorption process (Prabhakaran *et al.,* 2014). The values of k1 as well as the adsorption capacity (qt) were determined from the slope and intercept of the plotted curves (Figures 7a-d). Correlation coefficient R^2 were close to 1 in all samples. This observation is constant with findings of Omer *et al.,* (2020)who studied the kinetics and thermodynamics for the sorptive removal of crude oil spills using a low-cost chitosan-poly (butyl acrylate) grafted copolymer. The Elovich kinetic model employed in their study revealed a linear graph with R^2 close to 1







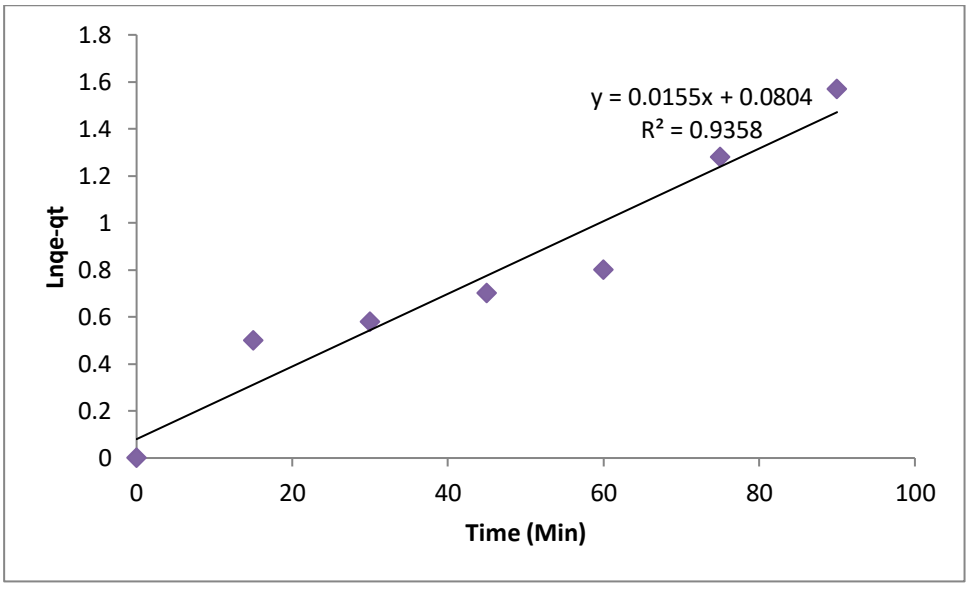


Fig 7a-d: Pseudo – first order plot for the diminishing trend of TPH in soil samples on application of synthesized MPE/ZnO nanoparticles

Conclusion

Inefficiencies and environmental hazards often attained in the attempt to remediate oil contaminated soils and other affected media has kept the remediation industry in a dilemma of recent. In other to overcome this challenge, green synthesis using *Musa Paradisiaca* extract, a cost effective waste material synthesized with ZnO for the remediation of oil contaminated soil medium has proven to be efficient amongst other remediation technologies. The synthesized MPE/ZnONPs employed in this study exhibited adsorption properties when used on the oil spill contaminated soil samples and the degradation efficiencies were found to range between 1.87 – 9.48%(CSOA1); 1.38 – 12.06% (CSPB1); 44.87 – 88.79% (CSOA2) and 38.95 – 79.24% (CSPB2) for the oil contaminated samples suggesting that the synthesized MPE/ZnONPs had good efficacy for oil spill removal in the contaminated soil samples. Kinetic of remediation gave a linear graph and took a pseudo-first order reaction with R^2 values close to 1 (R^2 = 0.980, 0.901, 0.957 and 0.935).

Recommendation

It is therefore recommended that for optimum remediation efficacy, most especially in oil saturated soil medium, surfactant enhanced ex situ soil washing may be employed

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