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Degradation of Crude Oil Polluted Soil Using Magnetic Nano-Particles

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ABSTRACT

Magnetic nano particles, magnetic nano particles mixed with hydrogen peroxide and 20:10:10 NPK fertilizer were used to remediate two types of crude contaminated soils namely clay and loamy. Functional parameters such as the total petroleum hydrocarbon (TPH) , polycyclic aromatic hydrocarbon (PAH) and microbial count (MC) degradation were determine over a period of 28 days. An experimental investigation was carried out on the impacted soil by polluting two different soil samples namely, loamy soil and clay soil with crude oil. NPK 20:10:10 fertilizer, nano particles and nano particles mixed with hydrogen peroxide was used as treatment through each of the polluted soil sample in different reactors. Analysis of TPH and PAH at one weak interval for four weeks using gas chromatography –flame ionization detector (GCFID) revealed that nano -particle degraded the PAH and TPH faster in hydrocarbon polluted loamy soil and clay soil than NPK. The result from the gas chromatography indicates that the TPH and PAH of nanoparticle + H_2O_2 loamy is lower than NPK on loamy soil thereby reducing the hydrocarbon concentration in the impacted soils. The study showed that hydrocarbon concentration reduced. For PAH at day zero to day 28. Loamy + H_2O_2 + Nano reduced to 7402.54118, loamy + nano reduce to 10656.26817, clay + nano reduced to 15138.76319, loamy + NPK reduced to 14642.11469, clay + NPK reduced to 18676.62528, for TPH at day zero + day 14 loamy + nano + H_2O_2 reduced to 13741.66411, loamy + nano reduced to 21733.74985 clay + nano reduced to 27949.33806, loamy +NPK reduced by 31024.20846, clay + NPK reduced to 37387.60515. The physio-chemical properties of soil were analyzed and result obtained showed the properties of treated soil. The results obtained from the gas chromatography. PAH and TPH was compared using a graph and both showed a good fit. The results showed that nano particles can be used to remediate crude oil polluted soil. and also for microbial count rate for loamy soil and clay soil respectively.

Keywords: Nano, Particle, Soil, Clay, Loamy, NPK, TPH, PAH

1. Introduction

Crude oil is a complex mixture of hydrocarbons that is formed from partial decomposition of biogenic materials under high pressure and temperature. The compounds of crude oil can be grouped as resins, asphaltenes, aromatics and saturates. Saturates are those of smaller molecular weight and are reality biodegradable. Aromatics of one to four rings are also biodegradable. However, those of four and above aromatic ring's are non- biodegradable. (Jaja *et al.,* 2020).

Oil spills occur as a result of exploration and vandalism. Pollution from crude oil is carcinogenic because of the polycyclic aromatic hydrocarbon. It is also known to cause health problems like mental disorder and also negatively affect vegetation and food crops.

Crude oil is a mixture of hydrocarbon and compounds which can be harmful to living systems. The world is very much dependent on crude oil either as fuel for mechanized transportation equipment or as feed stock for the petrochemical industries (Medjor*et al*., 2011). The volume of crude oil supposed 82.3 million barrels per day in the year 2003, and this volume is estimated to increase to 94.3 million barrels per day in 2010 and 101.6 million per day in 2015. (Chororn*etal*., 2010). Crude oil exploration, transportation, storage has led to soil contamination due to storage tank leakage, oil spills etc. (Maoxin*et al*., 2019).

Crude oil contaminated soil is a major environmental issue and a hazard to people's health. The spills penetrates deep in the soil and this results in the loss of soil fertility (Rowland *et al*., 2015). This leads to environmental degradation and it renders the soil impotent. Crude oil contaminated soil needs to be remediated.

1.2 Remediation Techniques For Crude Oil Contaminated Environment

1.2.1 Natural Methods

Natural remediation is directly removing pollutants from the soil, ground water and others.

a) Bio-remediation

This is the use of micro-organisms to breakdown organic pollutants in the soil. These micro-organism perform the breakdown by using them as source of food.

Advantages of Bioremediation

Bioremediation is environmentally friendly because it allows organisms to degrade the harmful hydrocarbons into simpler compounds without posing treat to the environment (Venosa*et al*., 1996). The cost of bioremediation is less compared with other methods. (Sandra, 2011).

Disadvantages of Bioremediation

Bioremediation is a slow process and it is not easy to remediate a field due factors which can only be controlled in a laboratory but not on a field (Zhu *et al.*, 2001).

b) Phytoremediation

This process uses plants to remove contaminants in the soil.

c) Photoremediation

This is the use of light energy to clean up pollutants in an environment due to exposure to light.

d) Air Sparging

This involves the injection of air or oxygen into a polluted aquifer. The injected air transverses horizontally and vertically in channels through the soil column. Oxygen added to the contaminated ground water and vadose-zone soil can enhance biodegradation of contaminants.

1.2.2 Fenton

a) Fenton Reagent

Fenton reagent is a mixture of hydrogen peroxide and soluble iron (II) salts to produce hydroxyl radicals. These can be used to break down organic matter including recalcitrant PAH. This is possible because hydroxyl radical is a strong oxidizing agent.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^- + H^* \quad (1)$$

b) Fenton Like Reagent

Fenton like is chemically similar to fenton reagent. Fenton like uses an insoluble iron in form of magnetite while fenton reagent is a soluble iron (II) salts. Fenton like could be more effective and efficient. (Ebiana*et al*.,2014)

$$Fe_3O_4 + 2H_2O_2 \xrightarrow{UV\ Energy} 3Fe_3 + +2HO^- + 2HO^* + 2O_2(g) \quad (2)$$

c) Use of Chemicals

Chemical treatment involves the use of heavy bases like NaOH, KOH, Mg $(OH)_2$, and $Ca(OH)_2$, to neutralize acidic polluted environment to form salt and water only

1.3 Petroleum Hydrocarbon Degrading Microorganisms

Petroleum has compounds that microorganisms can feed on. There are two genes of microorganisms that break down crude oil. Bacteria such as Aciromobacter, Acinetobacter, Actinomyces, Baallus, Burkholderia, Exiguobacz'erium, Kiebsiella, Microbacterium, Nacadrdia, Psuedornonas, Spiniliwn,

Streptornyes and Vibrio and fungi and yeast such as Allescheria, Aspergillus, candida, Dabayornyces, Mucor, Penicilliurn, Saccharomyces and Trichoderna. Naturally these microorganisms may be few. However, crude oil polluted sites, the microbes increase because they use petroleum hydrocarbon as a carbon source. (Bustard,2000)

1.4 Growth Cycle of Micro-Organisms and Reproduction

The growth cycle of micro-organisms are in five phases; the lag phase, exponential or growth phase, stationary phase, declining growth and death phase. It should be noted that in any specific population, not all are in the same phase of the growth curve at anytime. Some cells may be in the growth phase while others are in the death phase, each species has its own specific growth curve, The growth curve for species will not be identical for different environmental conditions.(Ebuchi*et al*.,2005).

1.4.1 Lag phase

Bacteria adjust to growth conditions. In this period each bacteria matures but do not divide.

This period of no division is called the lag phase and can last for 1 hour to several days. (Ebuchi*et al*.,2005).

1.4.2 Exponential and Declining Growth

Sometimes called the logarithmrised by cell doubling. The number of new cells appearing per unit time. If growth is not limited, doubling will continue at a constant rate but growth cannot continue indefinitely.(Rowland *et al.*, 2015).

The exponential phase can be expressed as

$$\mu = \frac{1}{X\frac{(X)}{dt}} \quad (3)$$

Where;

μ is the specific growths rate

X is the mass of bacteria present.

dt is the difference in time.

1.4.3 The Stationary Phase

Nutrients in this phase are limited. The growth rate and death rate are equal. Mutation may happen during stationary phase.(Schwab *et al*., 1994).

1.4.4 Death Phase (decline phase)

Bacteria die due to lack of nutrients, temperature above or below the tolerance level.(Schwab *et al*., 1994).

1.5 Environmental conditions for bacteria growth

Environmental factors that can influence the growth of bacteria are temperature, p^H ,water, level of oxygen,nutrients and toxins.(Salami, 2007).

1.5.1 Temperature

Temperature affects the growth of bacteria.

(a) *Psvchrophiles*: *Psychrophiles* are bacteria that thrive in cold area with a temperature of 15°c or lower. *Psvchrophiles* are typically found in earths cold ecosystems.

(b) *Mesophiles*: *Mesophiles* thrive at moderate temperature between 200^{o}C and 45 ^{o}C, many pathogens found in human beigns are *mesophiles*.

(c) *Thermophiles*: *Thermophiles* thrive in temperatures of 45 ^{o}C - 60 ^{o}C.

(d) Acidity: Bacteria thrive around p^{H} 6.5 to 7.0.

1.6 Model of the Rate of Remediation

Maithus law gives exponential growth as;

$$\frac{dx}{dt} = \mu x \tag{4}$$

On integration gives

$$X = X_o e^{\mu t} \tag{5}$$

Pearl and Reed modified the growth equation by adding a further term to explain inhibition at increased biomass concentration.

$$\frac{dx}{dt} = \mu x - \mu \gamma X^2 \tag{6}$$

On integration it gives

$$X = \frac{X_o e^{\mu t}}{1 - \gamma X_o (1 - e^{\mu t})} \tag{7}$$

(Chukwuemeka,2016).

1.7 Nano-Particles

Nano-particles are particles between 1 and 100 nanometers(nm) in size with a surrounding interfacial layer. (Satoshi *et al.*, 2013).

1.7.1: Methods of Nano-Particle Synthesis

Nano particles can be prepared using two methods. The first method is called the breakdown method.in this method, an external force is used to breakup a solid into smaller particles. The second method is called the build-up method. In this method nanoparticles are formed from molecular condensation. (Chen,2006)

1.8: Polycyclic Aromatic Hydrocarbon

Polycyclic Aromatic Hydrocarbons (PM-is) are compounds of 2-6 rings fused together consisting of benzene with molecular mass of 128g/rnol in naphthalene to 278g/mol in denopyrene (Okparanma*et al.*, 2009). The degradation of PAH has been at the focus of research due to its carcinogenic nature and resistance to natural oxidative processes. A lot of work have been done on PAHs and its remediation of which some are reviewed below:

(Martens *et al*.,1995) used Fentons reagent to treat commercially sourced individual PAHs as well as PAH contaminated soil in an enhanced oxidative process. The authors metabolized and oxidized PAHs in a microbial environment with a surfactant, Sodium dodecylsulphate (SDS) at low concentration l0mm/mol resulting in rapid desorption of PAH from soil and sediment. It was described as chemical and biological treatment. The PAHs degradation was monitored by a high-performance liquid chromatograph. Naphthalene was the most readily degraded PAH while Fenton reagent was not effective in the degradation of fluoranthene. However, overall efficiency of Fenton recorded was 87%.

Similarly, (Moraes*etal*., 2004) applied the photo - Fenton technique in treating contaminated saline wastewater. The reaction was carried out in a photochemical reactor and monitored using the UV-Vis spectrophotometer as well as measurement of total organic carbon. The authors found the

optimum pH range for photo-Fenton reaction as pH 3-15 while at pH greater than 4, iron precipitates as hydroxides. Mineralization efficiency of 96% was reported for the same study.

(Okparauma, *et al*., 2009) analyzed polycyclic aromatic hydrocarbons (PAHs) in drill cuttings from Nigerian oil with a view of understanding their sources (petrogenic or pvrogcnic) and production origins using composting/bioremediation method monitored with a gas chromatograph. Several composites comprising of 4000g of drill cuttings were collected, mixed with topsoil, poultry droppings, saw dust, watered and packed in a container (reactor) for a 42 days composting period. It was observed that PAHs in the drill cuttings had dual origins of petroleum (petrogenic) and combustion (pyrogenic) sources. The authors found that drill cuttings contained PARs of 2-6 fused rings. The rate of degradation achieved for individual PARs over a 42-days period of composting was 98.1%.

(Zhang, *et al.,* 2011) reported the X-ray absorption line structure (XAFS) of starch-stabilized magnetite nanoparticles (SSMNPs) and its application in the removal of arsenate ions from contaminated soil and ground water. The study showed that adsorption properties and sizes of magnetite ranges between 10 - 20nm and could be manipulated or adjusted using varying concentrations of starch.

(Onojake*et al*., 2011) assessed the physico-chemical properties of hydrocarbon contaminated soil around Ebocha-8 Oil field in Niger Delta. The study focused on the pH, conductivity, moisture content, total organic carbon, total hydrocarbon content, total organic mailer etc. soil and were monitored with statistical parameters/analysis. The results showed severe alteration of soil characteristics as a result of high hydrocarbon contents and its attendant effect on the food production of the region.

(Usnian*et al.,* 2012) prepared magnetic iron reagents as a replacement for soluble iron in a Fenton reaction and tagged it, ‘Fenton - like’ for soil remediation purposes. The studs as to evaluate the

feasibility of using magnetite activatespersulfate, $S_2O_8^{2-}$ and H_2O_2 for clean-up of both weathered and fresh crude oil. The study found that the magnetite acted as catalyst in a Fenton-like and persulfate oxidation reactions. The result showed over 80% degradation of hydrocarbons by the reactants.

(Okpara*et al*., 2014) used the starch stabilized magnetic nanoparticles (SSMNPs) to remove nickel ions from crude oil. The authors synthesized SSMNPs using modified method (Zhang, et al, 2011). The process of nickel removal as monitored using UV - Vis spectrophotometer. The magnetic iron oxide particles were reported to have acted as adsorbents to nickel ions in the crude. The authors summarized that SSMNPs were more effective in the removal of nickel porphyrin complexes from crude oil than bare magnetite nanoparticles.

(Kharissova*et al.*2015) reviewed works done on magnetic adsorbents of micro- and nano materials. The review focused on xerogels, acrogels, and hydrogels based upon their applications in biomedicine and the environment. The magnetic adsorbents studied covered those of elemental, iron oxides and ferrites on organic (polysaccharides, polymers, etc.) or inorganic supports (Carbon, zeolite, etc.). The authors remarked that all the magnetic adsorbents studied have common advantage of recovery with a magnet, an attractive and promising property for environmental/clean up applications.

(Lu *et al*.,2007) reviewed research work on special features of magnetic nano-particles. The authors reported the sizes and shapes of the magnetic nanoparticles. The sizes ranged from 10 — 20Onm for the magnetite. The report also examined how functionalization, co- precipitation, thermal decomposition and micelle nucleation influenced the size, shape and the applications of the various magnetite nanoparticles. (Yun et al., 2003) carried out a study in Xiamen western sea to isolate PAH degrading bacteria. It ‘as reported that the concentration of PAH in the aquatic environment was

mainly of petrogenic origin. The authors concluded that a regular monitoring is inevitable to ensure water quality.

2. Materials and Methods

2.1. Materials

The materials used in the research were as follows:

(i) NPK 20:10:10……..School to Land Iriebe, Oyibo L.G.A Rivers state, Nigeria.

(ii) Ferric chloride anhydrous ($FeCl_3.6H_2O$)……..…..BDH Chemical LTD. Poole England

(iii) Ferrous chloride Hydrate($FeCl_2.4H_2O$)……BDH Chemical LTD. Poole England

(iv) Sodium hydroxide pellets (NaOH)……BDH Chemical LTD. Poole England

(v) Anhydrous sodium sulphate (Na_2SO_4)…….BDH Chemical LTD. Poole England

(vi) Silica gel……Vikers Laboratory, England

(vii) Dichloromethane (DCM)…….Qualikems Laboratory, India.

(viii) Crude oil……Bonny light crude

(ix) Gas chromatograph flame ionization detector……..Austino Laboratories Port Harcourt, Nigeria.

(x) Ultra violet visible spectroscopy (UV-Vis Spec.)…….Chemistry Laboratory, Rivers State University (RSU) Port Harcourt, Nigeria.

2.2. Methods

2.2.1 Preparation of MNPs

The Iron (II) solution was prepared by dissolving 4.40g of $FeCl_2.4H_2O$ in 25.0ml of de-aerated de-ionized water. Similarly, iron (III) was prepared by dissolving 1.98g of $FeCl_3.6H_2O$ in the same volume of de-aerated deionized water.thetwosolutions were mixed together and made up to 61.0ml with the same de-aerated deionized water. The mixture was stirred thoroughly,flushed with nitrogen (N2)gas for 30 minutes and then reacted with 0.44M NaOH droplets until the solution turned blackish with continuous stirring. A total of 163.0ml NaOH was used before the black magnetite precipitates were formed.

The black precipitate was separated by placing a bar magnet by the side of the test tube while decanting the clear supernatant. The magnetite precipitates were dried at 80^oC in an oven overnight before storage in capped sample bottles.

2.2.2 Experimental Procedure

The soil sample used in this study were loamy soil and clay soil. The choice of using two types of soil was to ascertain the efficiency of the process on different types of soils in Rivers State. The soil samples were collected from an agricultural farm in Rivers State University and was kept for three days in the laboratory at the Chemical/Petrochemical Laboratory, Rivers state University..

1kg of loamy soil sample were weighed into five plastic reactor labeled A (1,2,3,4,5), and 1kg of clay soil sample were weighed into four plastic reactor labeled B (1, 2,3,4), contaminated with 200mls of Bonny light crude oil each, measured using 200ml. measuring cylinder for sample A four reactor was polluted, while for sample B three reactor was polluted and stirred for 5min each.

The polluted sample A & B were collected for determination of initial condition of the physiochemical properties of the soil sample. Each of the mixture was properly mixed to ensure uniform concentration of the crude oil in the soil sample. It was left for three days to settle without any disturbance. The treatment of the soil commenced after three days by application and mixing of 15g of 20:10:10NPK fertilizer into sample A5 and B4 polluted soil, while sample A4 and B3 treatment were 10g Nano particle; sample A4 treatment were 10g of Nano particle with H_2O_2 while soil sample in A1, A2, A3 and B1, B2 had no treatment application of (nano particle and NPK) sample A5 and B4 contained crude + NPK, while sample A4 and B3 contain nano particle of 10g each + crude. Sample A3 contain only crude +Nano particle + H_2O_2. The soil sample after treatment were collected to determine the physiochemical properties using gas chromatography laboratory analysis. For MC, PAH and TPH (Usman*et al*., 2012).

2.2.3 Total Petroleum Hydrocarbon(TPH) And Polycyclic Aromatic Hydrocarbon(PAH) Content By G.C (FID)

Soil sample extraction

10 g of soil sample was added into a bottle and it was mixed with anhydrous sodium sulphate (Na_2SO_4). The sample in the beaker was stirred. The reason for adding Na_2SO_4 was to remove moisture from the soil sample. Then 300 µg/ml of 1-chlorooctadecane was added to the bottle containing the soil sample. 30 ml of dichloromethane (DCM) was added to the sample as an extracting solvent and the bottle containing the soil sample was closed very tight and transferred to a shaker.

The sample was agitated for 5 to 6 hours at room temperature using. After agitation, the sample was allowed to settle for 1 hour and then filtered through a filter paper into a clean beaker. The filtrate was allowed to concentrate to 1 ml by evaporation overnight in a fume cupboard.

Sample clean – up

The sample was cleaned-up was using a glass column. The Column was prepared by inserting glass cotton into the column. Then Silica gel was dissolved with DCM to form a slurry, then slurry was added into the column. Anhydrous Na_2SO_4 was added into the column, next was the addition of pentane. After preparing the column, the sample extract was mixed with cyclohexane in a beaker and then it was transferred into the prepared column. The sample extract was eluted using pentane as a solvent and the eluted sample collected in a beaker below the column. The sample was further eluted by adding more pentane solvent into the column. After elution the column was rinsed with DCM. The eluted sample was allowed to stand overnight at room temperature in a fume cupboard for evaporation to take place.

Sample separation and detection

The separation and detection of compounds in soil samples were carried out using Agilent 6890N Gas Chromatograph - Flame Ionization Detector (GC-FID) instrument. 3 µl of concentrated sample eluted from column was injected into GC vial. The blank DCM was injected into micro-syringe of GC to clean the syringe (3 times) before taking the sample for analysis. The micro-syringe was further rinsed with the sample. Then the sample was injected into the column for separation of compounds in the sample. After separation the compounds were passed through a flame ionization detector. FID detects the compounds in the sample. The amount of TPH and PAH was resolved at a particular chromatogram in mg/kg for soil sample.

2.2.4 Total Bacteria Count

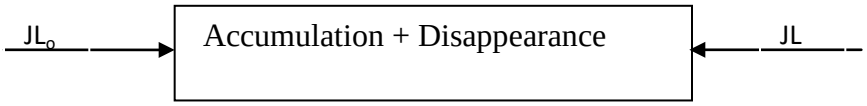
The soil sample was mixed, and a suspension of 1 g (dry weight equivalent) in 10 ml of sterile water was prepared. One ml of the soil suspension was then diluted serially (ten-fold) and used in the estimation of aerobic heterotrophic bacterial by standard spread-plate dilution

method described by (Seeley *etal*,1981), in triplicate. Nutrient agar containing 0.015% (w/v) nystatin (to inhibit fungi growth) was used for bacteria isolation and incubation was at 35 ^{o}C for five days.

2.2.5 Model Derivation and Validation

Model Derivation

The model for the rate degradation of concentration of total hydrocarbon which is represented by L ^{o}Sgiven by: constant stirred tank reactor equation from first stirred tank reactor equation from first principle



Input of total hydrocarbon to soil = output rate + disappearance due to biochemical reaction + accumulation (8)

Input = JL_o (9)

Rate of disappearance due to biochemical reaction = R_yV (10)

Rate of accumulation = $V\frac{dL}{dt}$ (11)

Substitute 9,10,11 into equation (8) gives

$$JL_o = JL + RyV + V\frac{dL}{dt} \quad (12)$$

Dividing equation (12) by V

$$\Rightarrow \frac{JL_o}{V} = \frac{JL}{V} + Ry + \frac{dL}{dt} \quad (13)$$

At steady state meaning that t = 0, $L_o = L$ using the above condition into (13)

$$\frac{dL}{dt} = \frac{J}{V}(L_o - L_o) - Ry \tag{14}$$

$$\frac{dL}{dt} = -Ry \tag{15}$$

Where $Ry = K_sL$ (16)

Equation (15) is the mathematical model representing the process, the above model can be solved using the appropriate method to be specific using separation of variable.

$$\frac{dL}{dt} = K_sL \tag{17}$$

$$\frac{dL}{dt} \cdot \frac{dt}{L} = -k_sL \cdot \frac{dt}{L} \tag{18}$$

$$\frac{dL}{L} = -K_s dt \tag{19}$$

Integrating both side of equation (E), we have

$$\int_{Lo}^{L} \frac{dL}{L} = -K_s \int_o^1 dt \tag{20}$$

$$\text{In } L\int_{Lo}^{L} = -K_s{}^t \int_o^t dt \tag{21}$$

$$\text{In } L - InL_o = -K_s(t - o) \tag{22}$$

$$In \frac{L}{L_o} = -K_s t \quad (23)$$

$$In \frac{L}{L_o} = -K_s t \quad (24)$$

Taking exponential on both sides of equation

$$\frac{L}{L_o} = e^{-kst} \quad (25)$$

$$L = L_o e^{-kst} \quad (26)$$

Determining the rate of biodegradation of the concentration of total hydrocarbon (TPH)

Lo = Initial concentration of TPH

L = Final concentration of TPH

K = Rate of degradation of TPH

t = time in days/weeks

3. Results and Discursion

Table 1: Physiochemical Characteristics Crude Polluted Loamy Soil

Parameters	Day Zero	Day 7	Day 14	Day 21
TPH(mg/l)	51619	50505	49298	47967
MC(cfu/g))	183	242	283	394
PAH(mg/l)	25827	25593	25077	24508

Table 1 shows that the concentration of TPH on loamy soil contaminated with crude oil is decreasing as the number of days is increased from zero to 21 days, this shows a slow rate of self remediation. Microbial count is also increasing as the number of days is increased, while the concentration of PAH decreases with an increase in the number of days.

Table 2: Physiochemical Characteristics Crude Polluted Clay Soil

Parameters	Day Zero	Day 7	Day 14	Day 21
TPH(mg/l)	52539	51885	51016	49844
MC(cfu/g))	136	198	215	342
PAH(mg/l)	20106	25875	25521	24790

Table 2 indicates that as the number of days is increased from zero to 21 microbial count increases but at a much slower rate owing to the contamination of the soil by crude while the concentration of PAH increases slightly after 7 days but the concentration of TPH decreases continuously throughout the 21 days period

Table 3: Physiochemical Characteristics Crude Polluted ClaySoil Treated with Nano Particle

Parameters	Day Zero	Day 7	Day 14	Day 21
TPH(mg/l)	48418	39453	27949	19496
MC(cfu/g))	205	2840	16200	218000
PAH(mg/l)	23934	23936	15139	9222

Table 3 shows the effect of TPH, MC,and PAH after the clay soil contaminated with crude was treated with Nano particle. The concentration of both TPH and PAH decreased continuously throughout the 21 day period. Microbial count increased slowly for the same period of time.

Table 4: Physiochemical Characteristics Crude Polluted Loamy Soil Treated with Nano Particle

Parameters	Day Zero	Day 7	Day 14	Day 21
TPH(mg/l)	46284	35618	21734	12513

MC(cfu/g))	274	7080	47200	831000
PAH(mg/l)	2252	2251	10656	3815

Table 4 shows the effect of TPH, MC, and PAH after loamy soil contaminated with crude was treated with nano particles only. The concentration of TPH and PAH decreased greatly over a 21 day period while microbial count increased tremendously. Hence treatment of crude polluted loamy soil with nano particles has shown to be an effective method of remediation.

Table 5: Physiochemical Characteristics Crude Polluted Loamy Soil Treated with Nano Particle and Hydrogen Peroxide

Parameters	Day Zero	Day 7	Day 14	Day 21
TPH(mg/l)	43645	30376	13742	5623
MC(cfu/g))	428	708	47200	24800000
PAH(mg/l)	21616	21615	7453	7452

Table 5 shows the effect of TPH, MC and PAH after loamy soil contaminated by crude was treated with nano particle and hydrogen peroxide acting as the catalyst. The concentration of TPH and PAH decreases exponentially as the number of days increases from zero to 21 days. Microbial count also increases exponentially showing the efficacy of method applied to remediate the contaminated soil.

Table 6: Physiochemical Characteristics Crude Polluted ClaySoil Treated with NPK

Parameters	Day Zero	Day 7	Day 14	Day 21
TPH(mg/l)	50774	45218	37388	31670
MC(cfu/g))	194	213	9280	5740
PAH(mg/l)	25070	25070	18677	13029

Table 6 shows the effect of TPH,MC, and PAH after clay soil polluted with crude oil was treated with NPK. The concentration of TPH and PAH decreased as the number of days increased while microbial count increased as well. This method of treatment is less effective when compared to the one in table 6

Table 7: Physiochemical Characteristics Crude Polluted Loamy Soil Treated with NPK

Parameters	Day Zero	Day 7	Day 14	Day 21
TPH(mg/l)	51619	50505	49298	47967
MC(cfu/g))	183	242	283	394
PAH(mg/l)	25827	25593	25077	24508

Table 7 shows the effect of TPH, PAH and MC after loamy soil contaminated with crude oil was treated with NPK, the concentration of TPH and PAH both decreases as the number of days increases while Microbial count increases as the number of days is increased but this is less effective when compared to crude polluted clay soil treated with NPK.

4.2 Total Petroleum Hydrocarbon Results

4.2.1 Effect of TPH on Polluted Loamy Soil

Figure 1 shows how Total petroleum hydrocarbon is changing with the number of days. As the number of days increases the concentration of total petroleum hydrocarbon decreases slowly due to self remediation taking place.

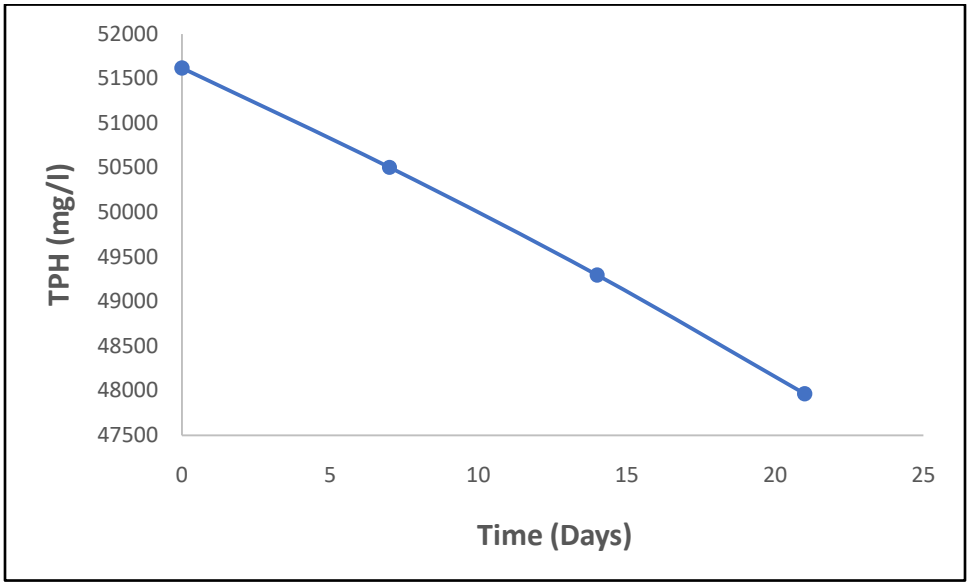


Figure 1: Variation of TPH with Time on Crude Polluted Loamy Soil

4.2.2: Effect of Total Petroleum Hydrocarbon on Crude Polluted Clay Soil

Figure 2shows how Total petroleum hydrocarbon is changing with the number of days. As the number of days increases the concentration of total petroleum hydrocarbon decreases slowly due to self remediation taking place.

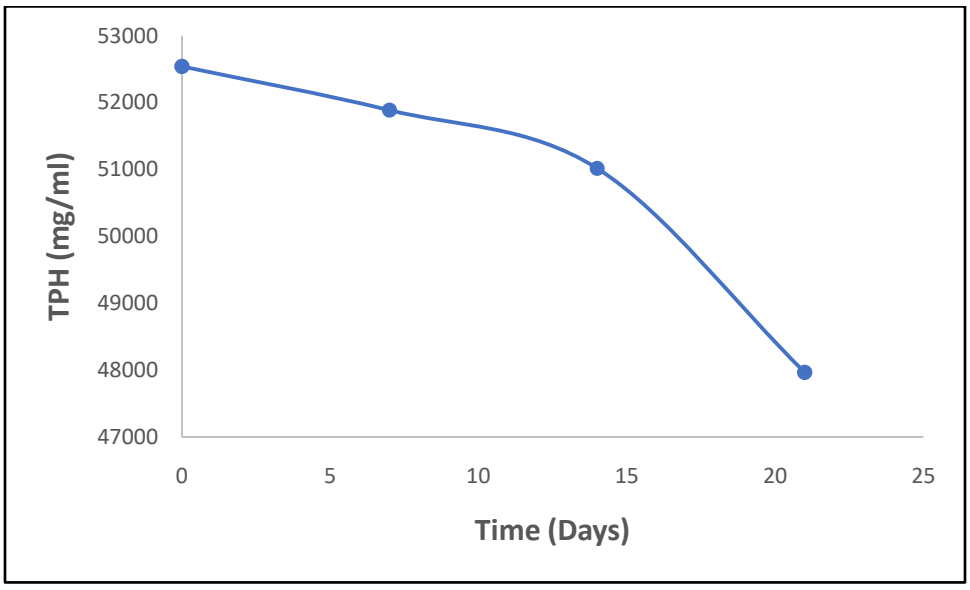


Figure 2: Variation of TPH with Time on Crude Polluted Clay Soil

4.2.3: Effect of Total Petroleum Hydrocarbon on Crude Polluted Loamy Soil Treated With Nano Particle only

Figure 3 shows how the concentration of total petroleum hydrocarbon is changing with the numbers of days. After the treatment of the soil with nano particle, the concentration of TPH decreased greatly from day zero to day 21 due to the remediating capability of the nano particle used for the treatment of the soil.

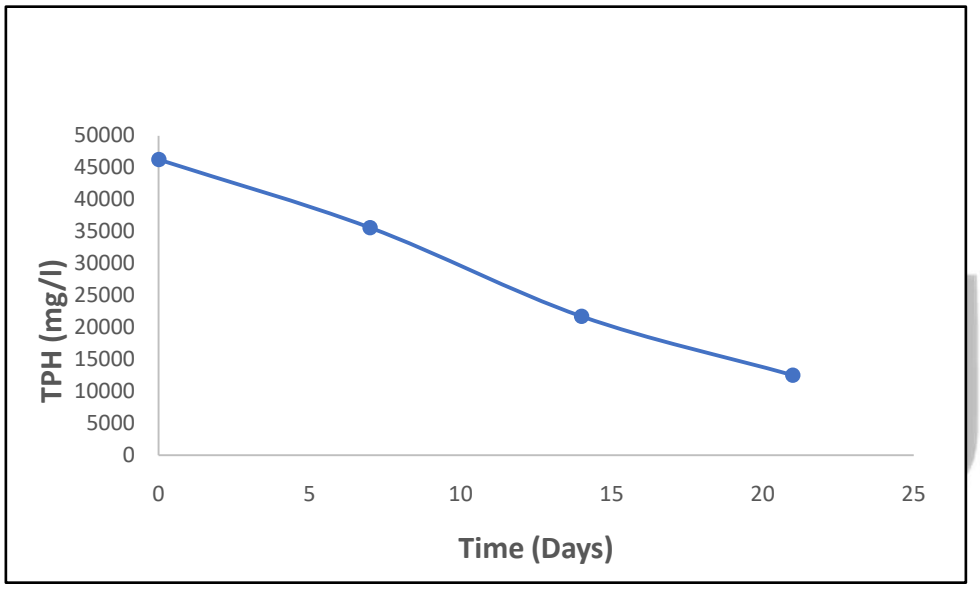


Figure 3 Variation of TPH with Time on Crude Polluted Loamy Soil Treated with Nano Particle only

4.2.4: Effect of TPH on Crude Polluted Clay Soil Treated With Nano Particle Only

Figure 4 shows how the concentration of total petroleum hydrocarbon is changing with the numbers of days. After the treatment of the soil with nano particle, the concentration of TPH decreased greatly from day zero to day 21 due to the remediating capability of the nano particle used for the treatment of the soil. Careful examination of TPH on both clay and loamy soil treated with nano particle shows that remediation was more effective in the case of the loamy soil than the clay soil.

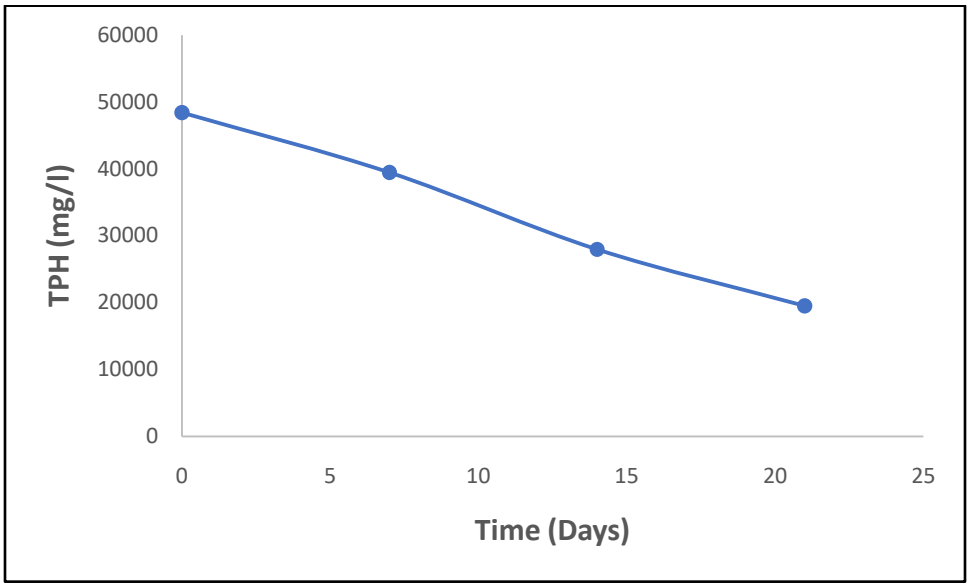


Figure 4: Variation of TPH with Time on Crude Polluted Clay Soil Treated with Nano Particle only

4.2.5: Effect of TPH on Crude Polluted Loamy Soil Treated With Nano Particle and Hydrogen Peroxide

Figure 5 shows how the concentration of total petroleum hydrocarbon is changing with the numbers of days. After the treatment of the soil with nano particle, the concentration of TPH decreased greatly from day zero to day 21 due to the remediating capability of the nano particle and hydrogen peroxide used for the treatment of crude polluted loamy soil. The addition of hydrogen peroxide to nano particle improved the remediation process more than when only nano particle was used because the hydrogen peroxide acts as a catalyst to the nano particle.

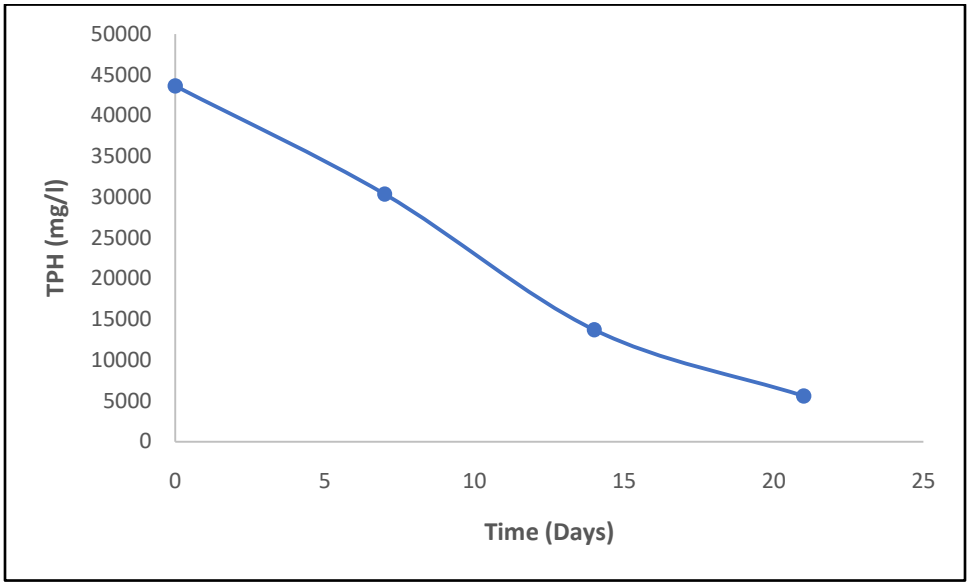


Figure 5: Variation of TPH with time on Crude Polluted Loamy Soil

4.2.6: Effect of TPH on Crude Polluted Clay Soil Treated With NPK

Figure 6 shows how the concentration of TPH is decreasing with the number of days. The remediation rate is low when NPK is used for treating crude polluted clay soil than the case of treating with nano particle and hydrogen peroxide.

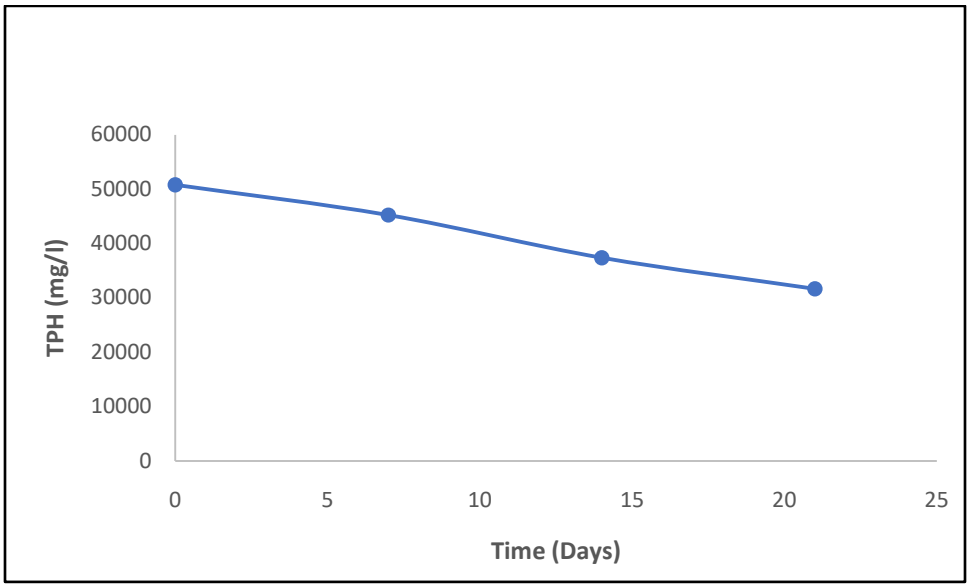


Figure 6: Variation of TPH on Crude Polluted Clay Soil Treated with NPK

4.2.7: Effect of TPH on Crude Polluted Loamy Soil Treated With NPK

Figure 7 shows how the concentration of TPH is decreasing with the number of days. The remediation rate is higher when NPK is used for treating crude polluted loamy soil than crude polluted clay soil for the same period of time.

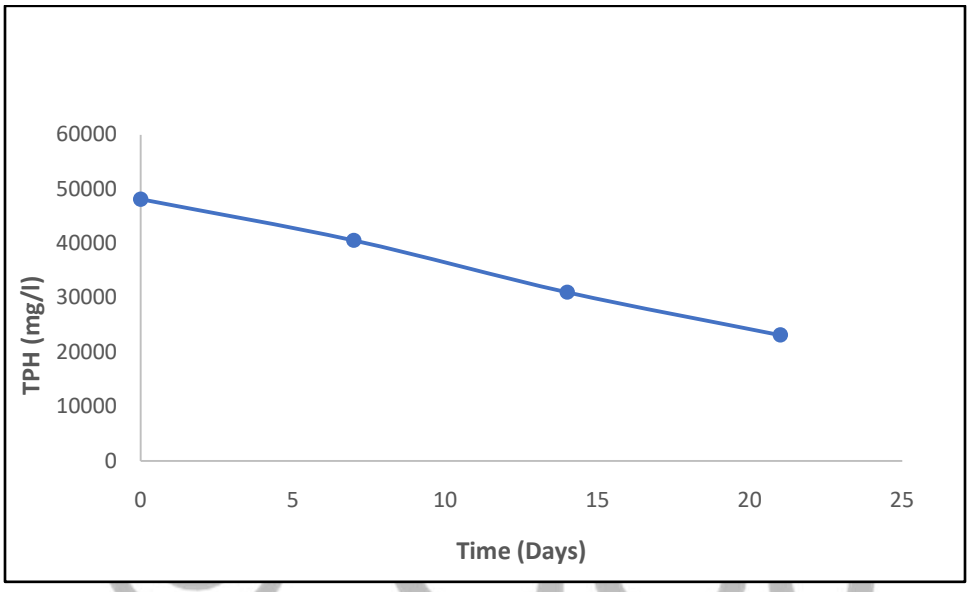


Figure 7: Variation of TPH on Crude Polluted LoamySoil Treated with NPK

4.3: Microbial Count Results

4.3.1: Effect of Microbial Count on Crude Polluted Loamy Soil

Figure 8 shows that microbial count increases with the number of days on crude polluted loamy soil without treatment, hence self-remediation occurred and has increased above 200000cfu/g after the end of 21days.

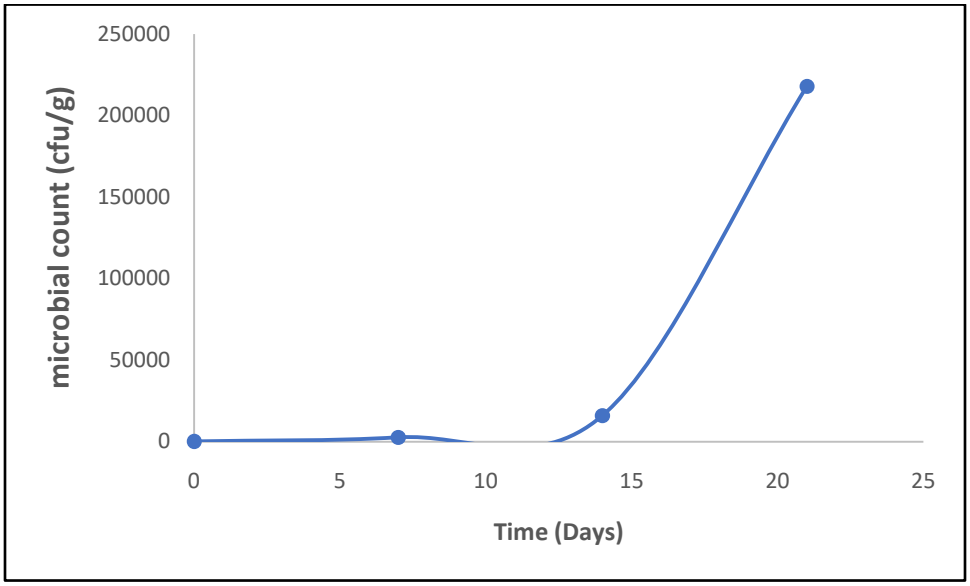


Figure 8: Variation of Microbial Count on Crude Polluted Loamy Soil with Number of Days

4.3.2: Effect of Microbial Count on Crude Polluted Clay Soil

Figure 9 shows how microbial count is changing as the number of days increases from day zero to day 21, it slowly increases from zero to a maximum of 9000cfu/g then decreases again up to about 6000cfu/g due to the fact that no treatment has been done on the soil so it is increasing and decreasing as the contamination of the soil increases or decreases with the number of days. The remediation rate of crude polluted clay soil is lower than that of crude polluted loamy soil when compared over the same time interval.

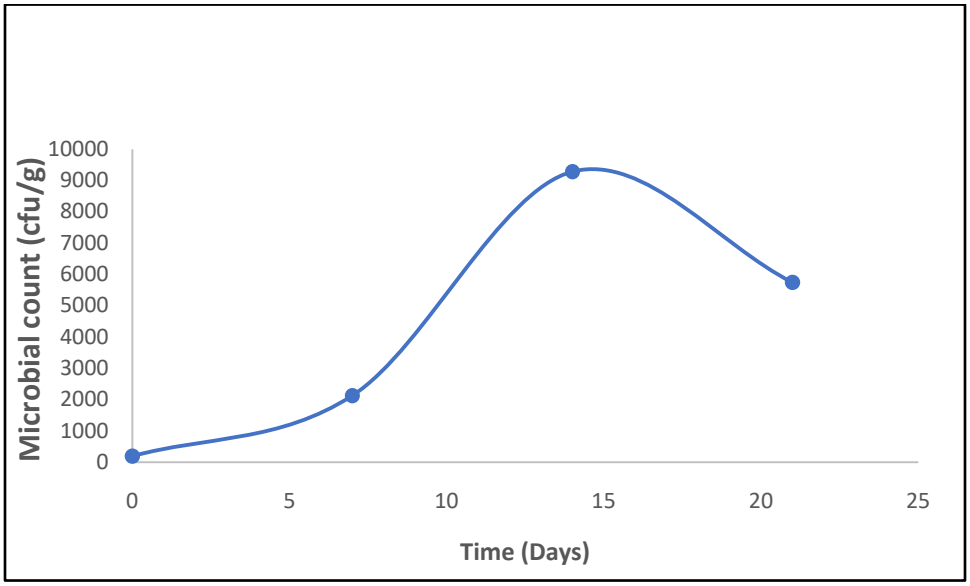


Figure 9: Variation of Microbial Count on Crude Polluted Clay Soil with Number of Days

4.3.3: Effect of Microbial Count on Crude Polluted Clay Soil Treated with Nano Particle Alone

Figure 10 shows how microbial count is changing as the number of days increases from day zero to day 21, After treatment with nano particle it increased from 100cfu/g to a maximum of 2500100cfu/g then decreases again up to about 500100cfu/g due to the fact that after treatment the contamination of the soil still increases with the number of days. remediation rate of crude polluted clay soil treated with nano particle alone has proven to be ineffective.

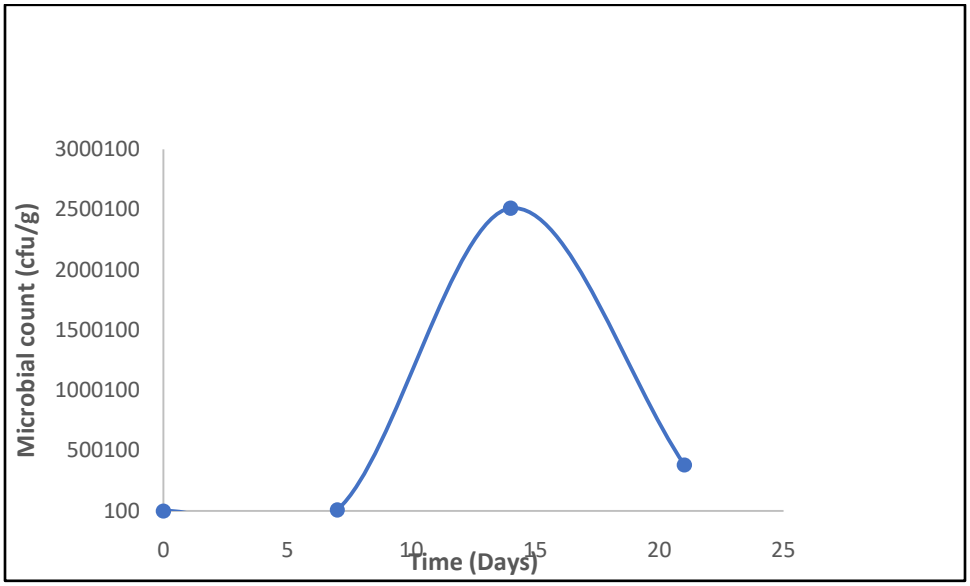


Figure 10: Variation of Microbial Count on Crude Polluted Clay Soil Treated with Nano Particle Alone with Number of Days

4.3.4: Effect of Microbial Count on Crude Polluted Loamy Soil Treated with Nano Particle Only

In figure 11 microbial count increases greatly from day zero to day 21, it stated at 100cfu/g and increased to a maximum of 800100cfu/g. remediation of crude polluted loamy soil treated with nano particle proves to be more effective when compared with that of clay soil for the same period of time.

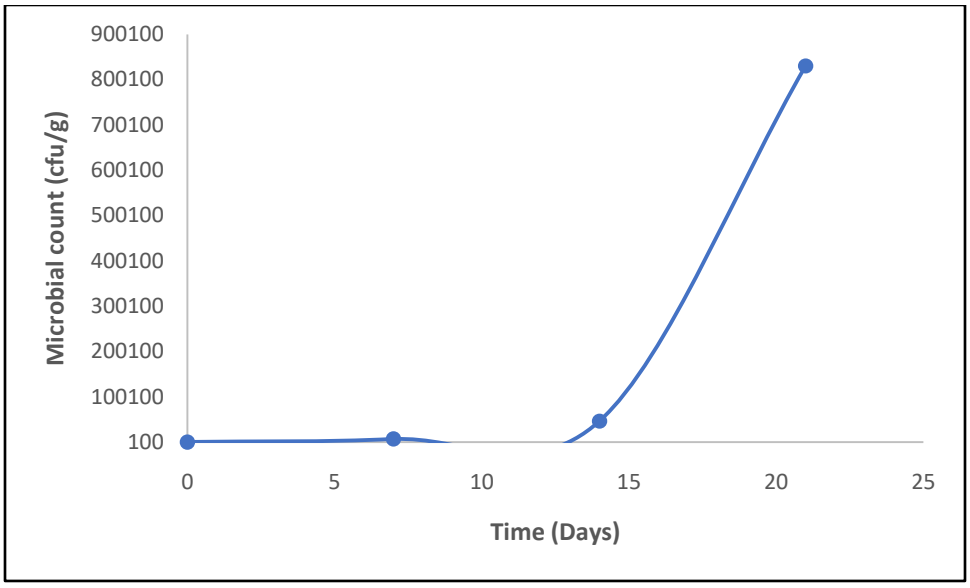


Figure 11: Variation of Microbial Count on Crude Polluted Loamy Soil Treated with Nano Particle Only

If figure 12 Microbial count increases with treatment of NPK to maximum of 9000cfu/g before dropping to 600cfu/g when its maximum remediating capacity has been exceeded. Treatment of crude polluted soil using NPK is ineffective.

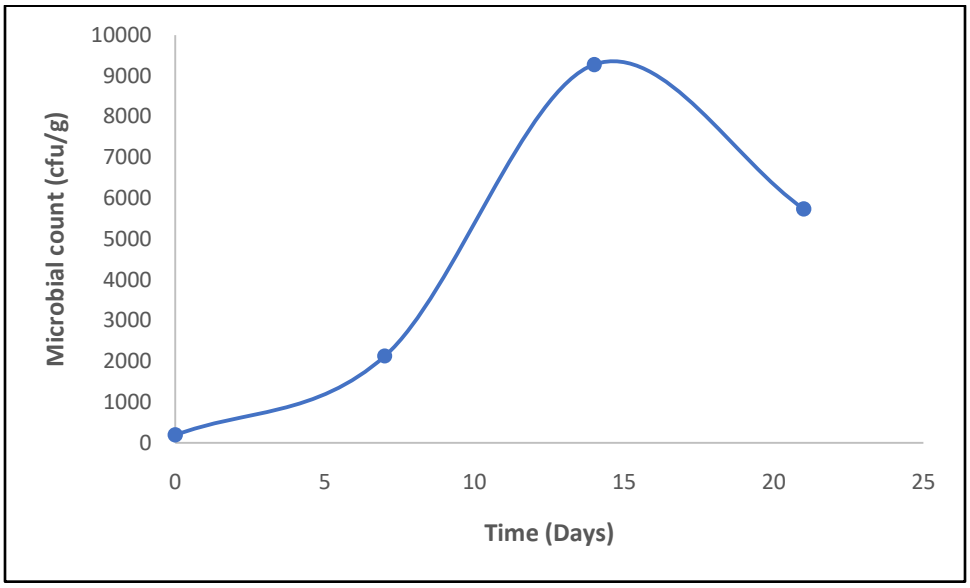


Figure 12: Variation of Microbial Count with Number of Days on Crude Polluted Clay Soil Using NPK

In figure 13 microbial count remained at a steady value of 300cfu/g from day zero to day 14 before rising exponentially to a maximum value of 25000300cfu/g at the end of 21 days. The exponential increase is as a result of the hydrogen peroxide catalyst added to the nano particle.

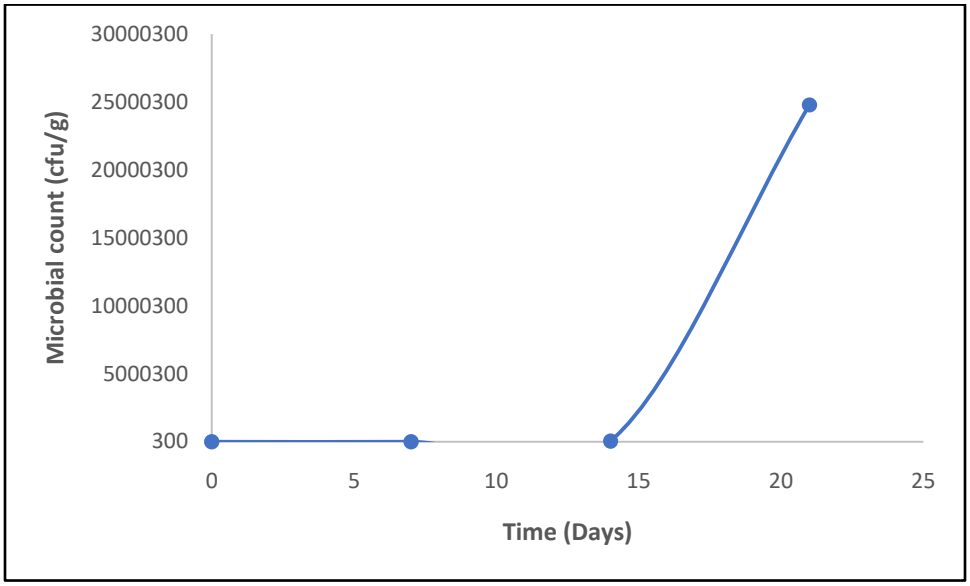


Figure 13: Variation of Microbials Count on Crude Polluted Loamy Soil Treated with Nano Particle and Hydrogen Peroxide

In figure 14 microbial count remained at a steady value of 300cfu/g from day zero to day 7 then rises to a maximum value of 200200cfu/g on day 14 before dropping to 500200cfu/g on day 21. The decrease is caused by the fact that the remediating ability of the NPK has reached its maximum capacity and no further remediation can occur above this value. Treatment of crude polluted loamy soil with NPK is ineffective.

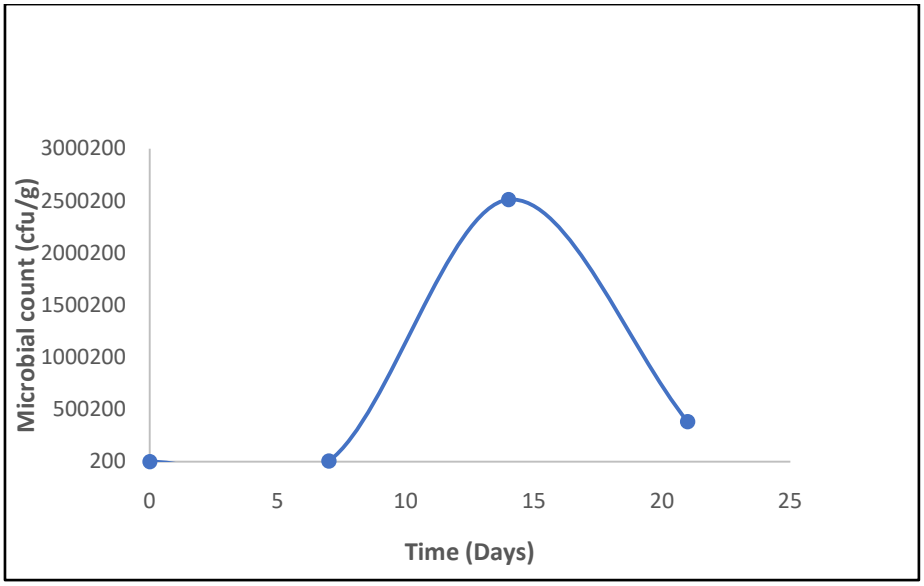


Figure 14: Variation of Microbial Count on Crude Polluted Loamy Soil Treated with NPK

In figure 15 the concentration of PAH increased slowly to 50000mg/ml from day zero to day 14 before increasing to a maximum value of 200000mg/ml at the end of day 21, hence the rate of contamination of the soil is increasing rapidly with the number of days and remediation is yet to take place.

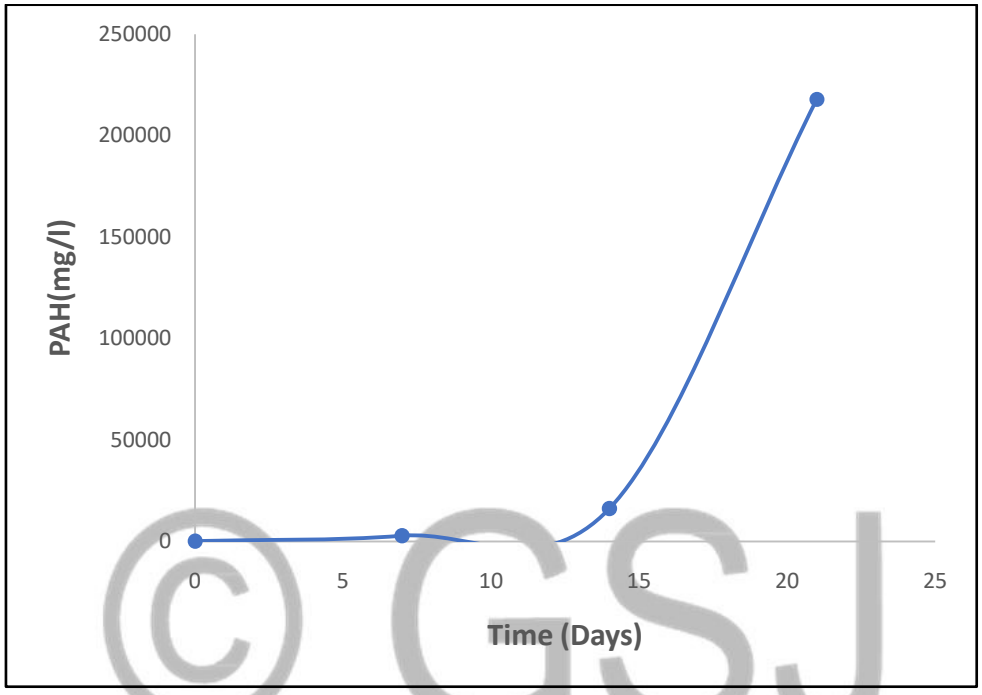


Figure 15: Variation of PAH on Crude Polluted Loamy Soil

In figure 16 the concentration of PAH increased from zero to 8000mg/ml from day zero to day 14 before dropping to 6000mg/ml at the end of 21 days, hence self remediation gradually takes place on crude polluted clay soil without treatment.

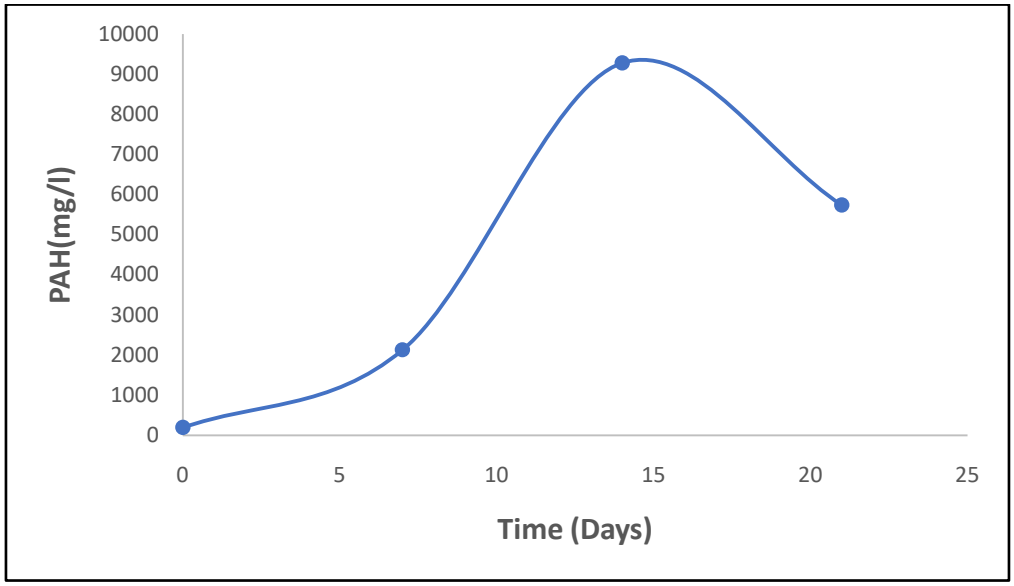


Figure 16: Variation of PAH Crude Polluted Clay Soil

In figure 17 the concentration of PAH starts dropping 22500mg/ml to 4000mg/ml at the end of the 21 day treatment period, hence treatment of crude polluted loamy soil using nano particle alone was effective.

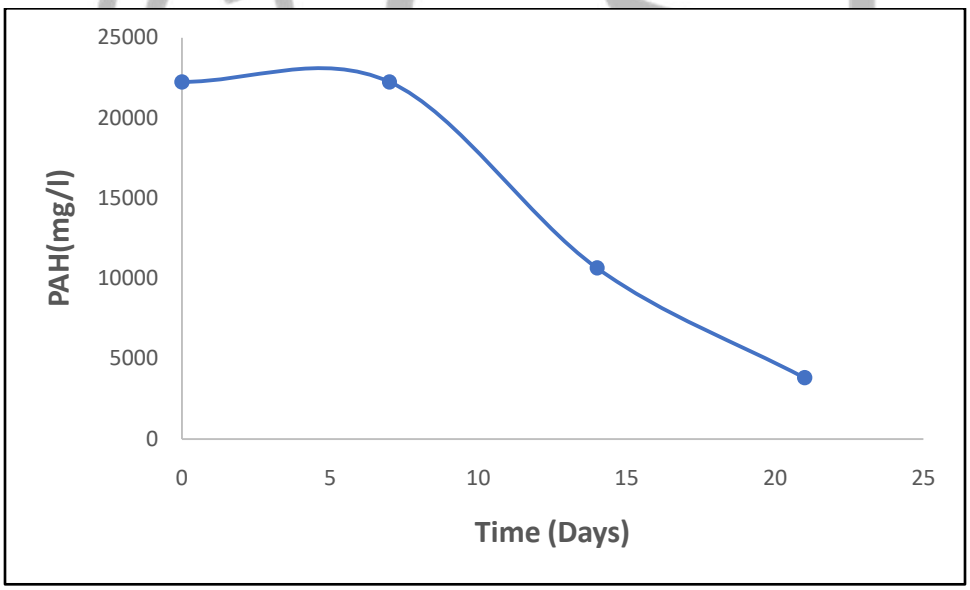


Figure 17: Variation Of PAH on Crude Polluted Loamy Soil Treated with Nano Particle only

In figure 17 the concentration of PAH increased from zero to a maximum of 2500000mg/ml from day zero to day 14 then drop again to 500000mg/ml on day 21, this shows that nano particle is ineffective for treatment crude polluted clay soil.

In figure 18 the concentration of PAH increased from zero to a maximum of 2500000mg/ml from day zero to day 14 before finally dropping to 500000mg/ml at the end of day 21. Hence treatment of crude polluted clay soil using nano particle greatly reduced the rate of contamination of the soil.

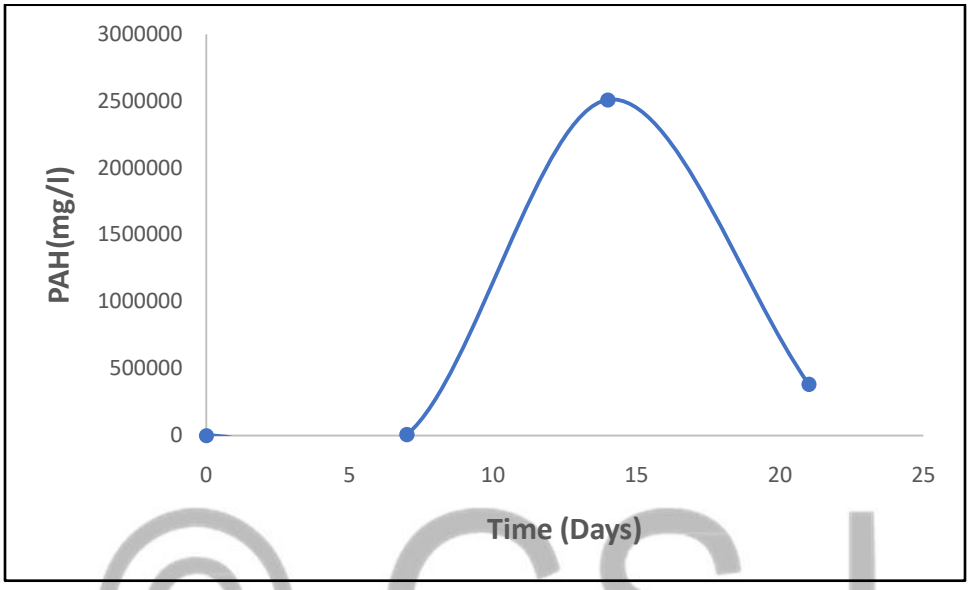


Figure 18: Variation of PAH on Crude Polluted Clay Soil Treated with Nano Particle only

In Figure 19 the concentration of PAH decreased from 22500mg/ml to 5000mg/ml over a period of 21 days. This shows that treatment of crude polluted loamy soil using nano particle and hydrogen peroxide is very effective as a result of the addition of the catalyst to speed up the remediation rate.

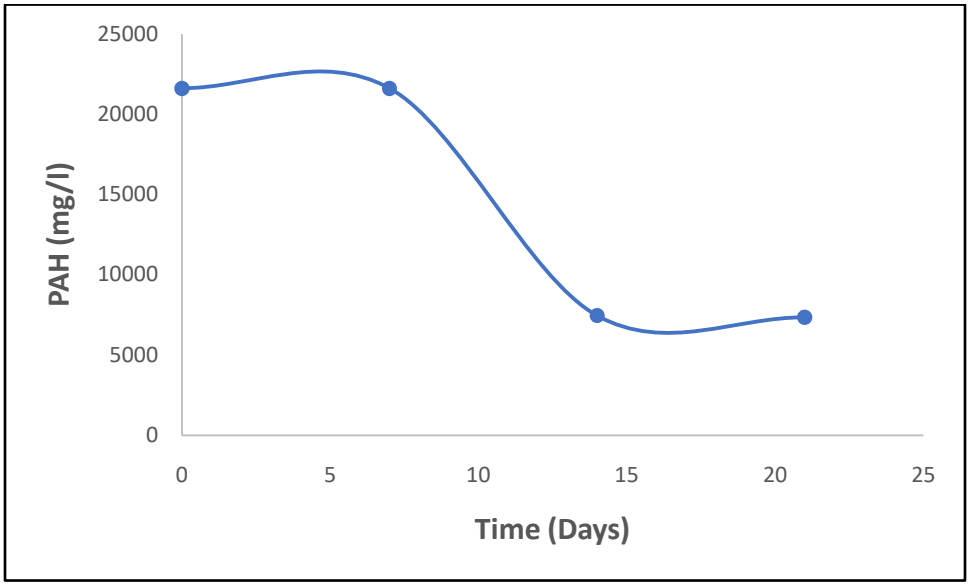


Figure 19: Variation of PAH on Crude Polluted Loamy Soil Treated with Nano Particle and Hydrogen Peroxide

In figure 20 the concentration of PAH reduced from 25000mg/ml to 1000mg/ml. Hence remediation of crude polluted clay soil using NPK is less ineffective when compared to nano particle and hydrogen peroxide catalyst.

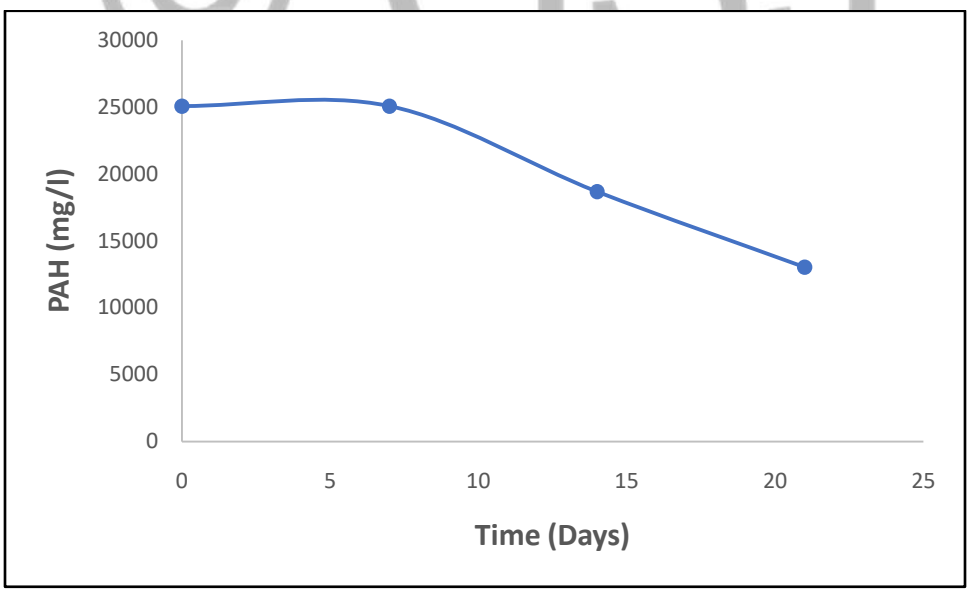


Figure 20: Variation of PAH on Crude Polluted Clay Soil Treated with NPK

In figure 21 the concentration of PAH decreased from 250000mg/ml to about 1000mg/ml over the 21 day period of the experiment. Hence remediation of crude polluted loamy soil using NPK is far more effective than that of clay soil.

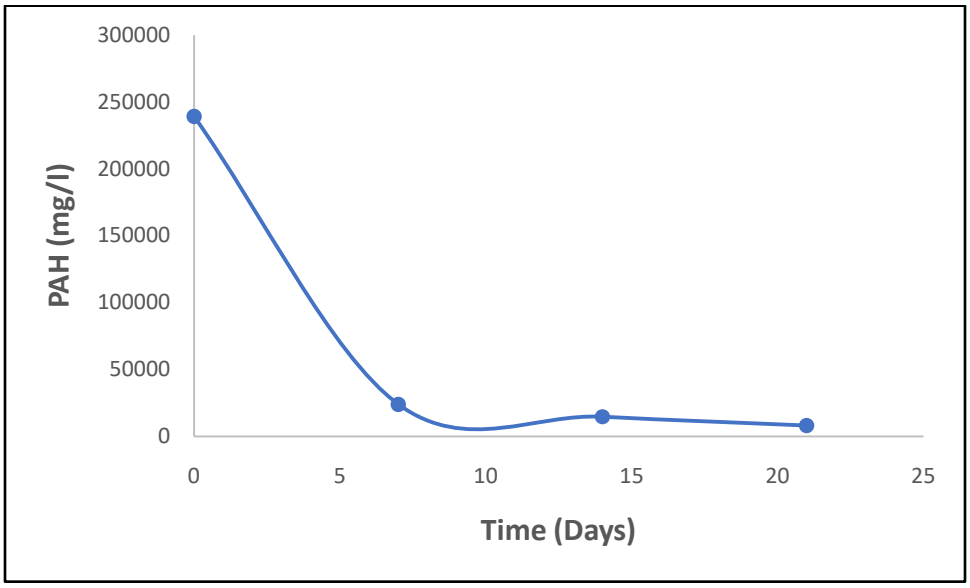


Figure 21: Variation Of PAH on Crude Polluted Loamy Soil Treated With NPK

In figure 22 both the concentrations of TPH and PAH on crude polluted loamy soil was compared and it was observed that the concentration of PAH is lower than that of TPH over the same 21 day time interval, hence self remediation of PAH on crude polluted loamy soil is more than TPH.

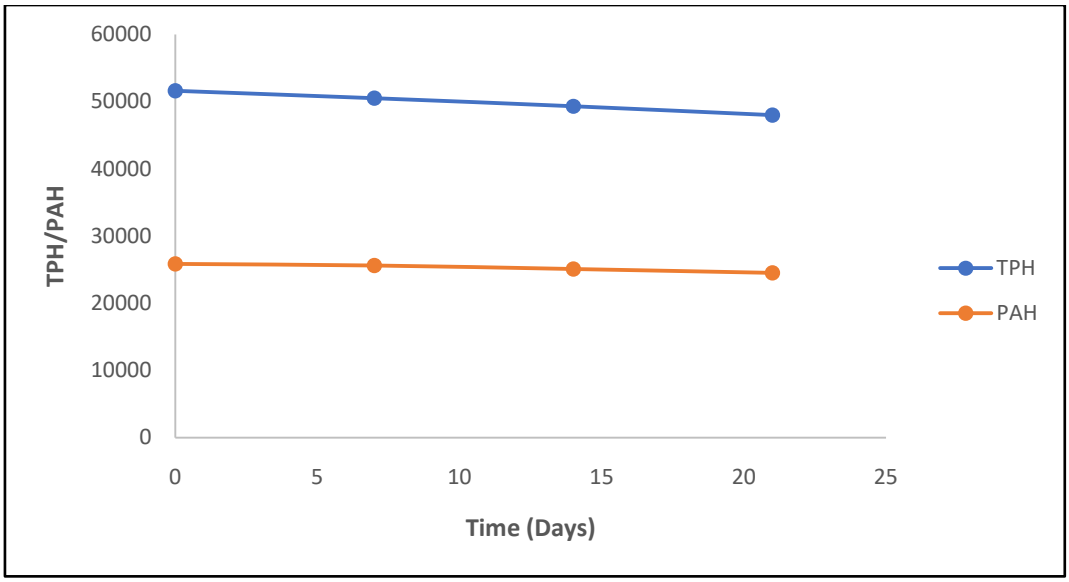


Figure 22: Variation of TPH/PAH on Crude Polluted Loamy Soil.

In figure 23 both the concentrations of TPH and PAH on crude polluted clay soil was compared and it was observed that the concentration of PAH is lower than that of TPH over the same 21 day time interval, hence self-remediation of PAH on crude polluted clay soil is more than TPH.

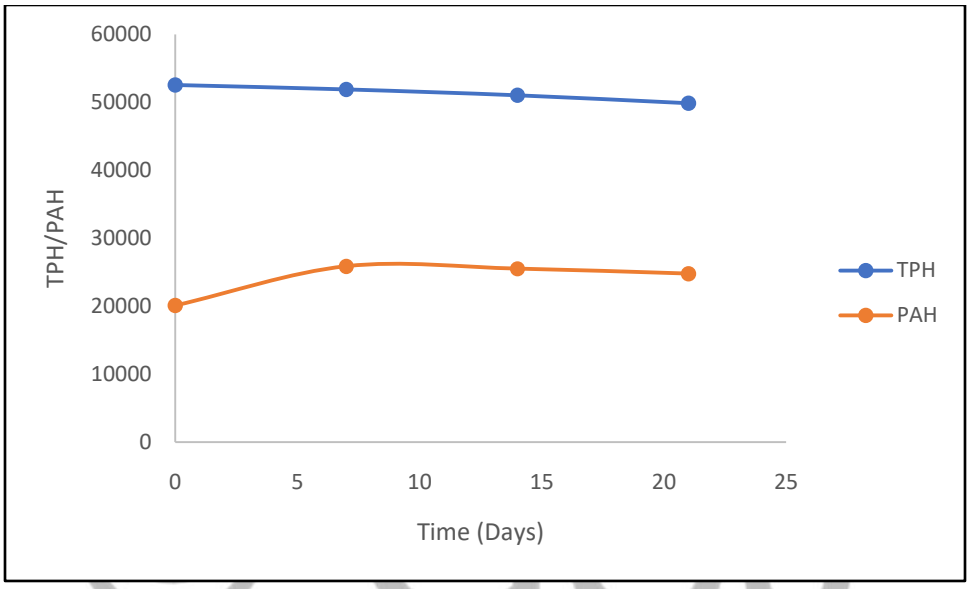


Figure 23: Variation of TPH and PAH on Crude Polluted Clay Soil

In figure 24 the concentrations of both TPH and PAH were compared for crude polluted clay soil treated with nano particle and it was observed that the concentration of PAH is less than that of TPH hence the soil still has more of TPH than PAH.

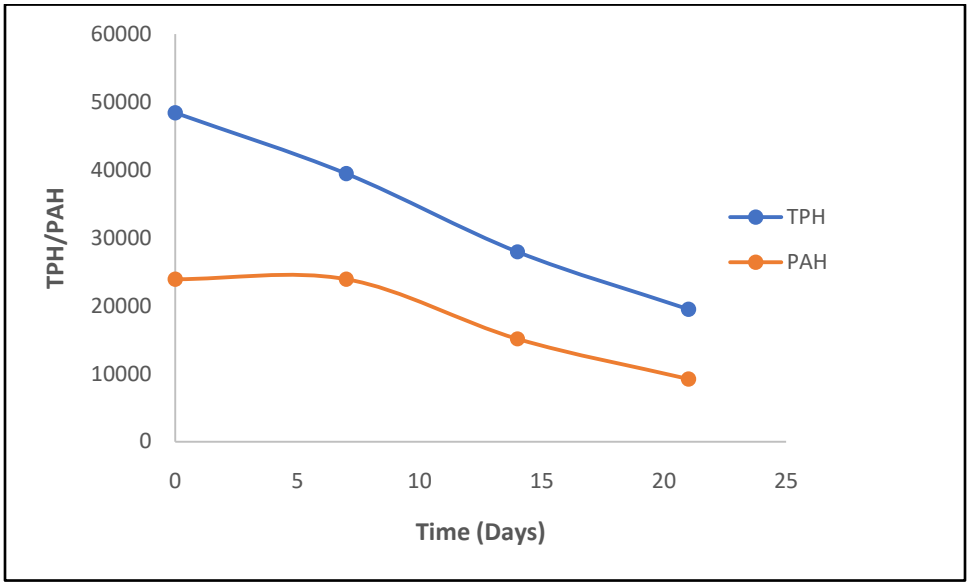


Figure 24: Variation of TPH and PAH on Crude Polluted Clay Soil Treated with Nano Particle

In figure 25 the concentration of TPH and PAH on crude polluted loamy soil treated with nanoparticle were compared and it was observed that the concentration of PAH in the soil after treatment is far less than the concentration of TPH.

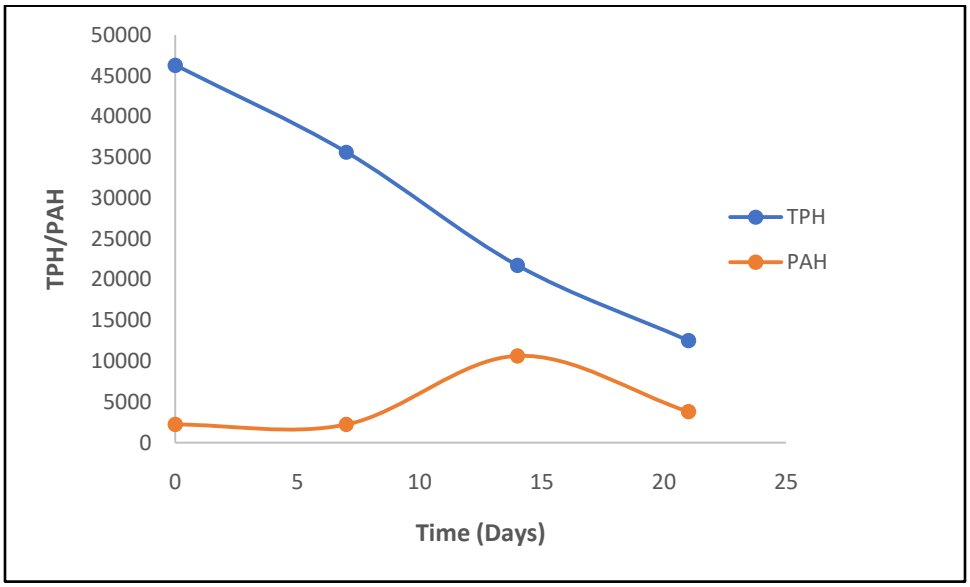


Figure 25: Variation of TPH and PAH with Time on Crude Polluted Loamy Soil Treated with Nano Particle.

In figure 26 the concentrations of TPH and PAH for crude polluted loamy soil treated with nano particle and hydrogen peroxide were compared and it was observed that the concentration of TPH in the soil is lower than that of PAH over the same interval of time.

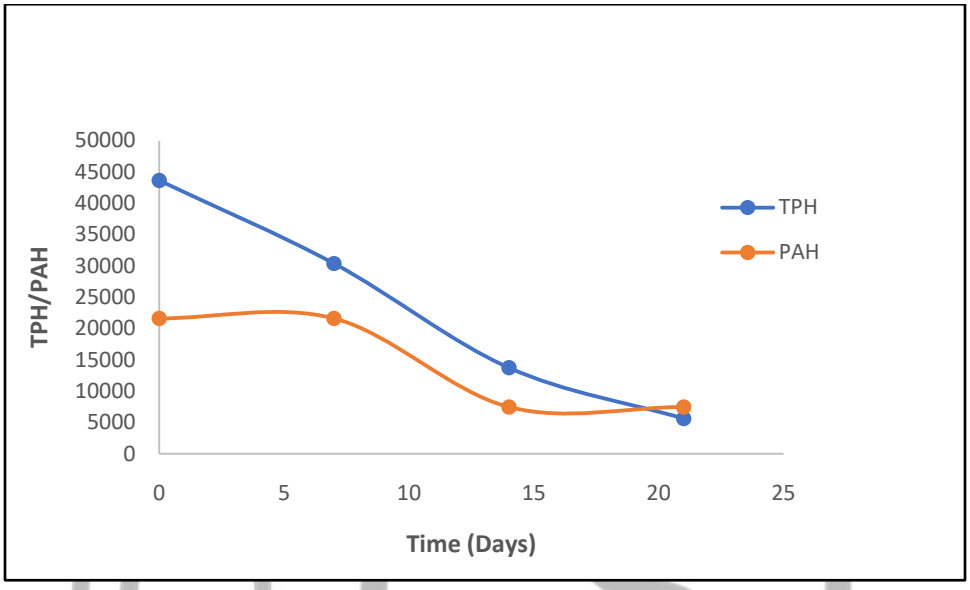


Figure 26: Variation of TPH and PAH with Time on Crude Polluted Loamy Soil Treated with Nano and H_2O_2

In figure 27 the concentrations of TPH and PAH on crude polluted clay soil treated with NPK were compared and careful examination reveals that the concentrations of TPH in the soil is far greater than that of PAH.

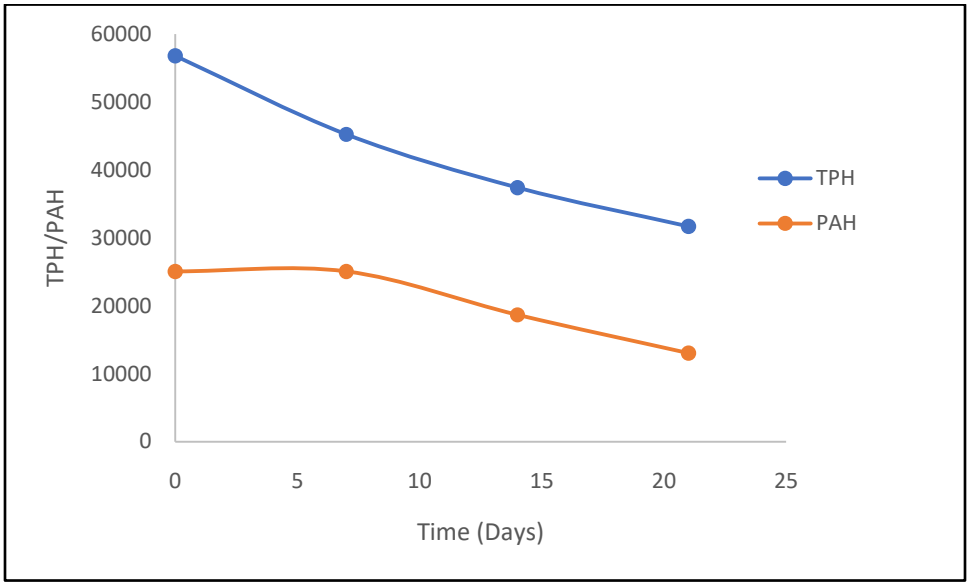


Figure 27: Variation of TPH and PAH on Crude Polluted Clay Soil Treated with NPK

In figure 28 the concentrations of TPH and PAH on crude polluted clay soil treated with NPK were compared and careful examination reveals that the concentrations of TPH in the soil is far greater than that of PAH.

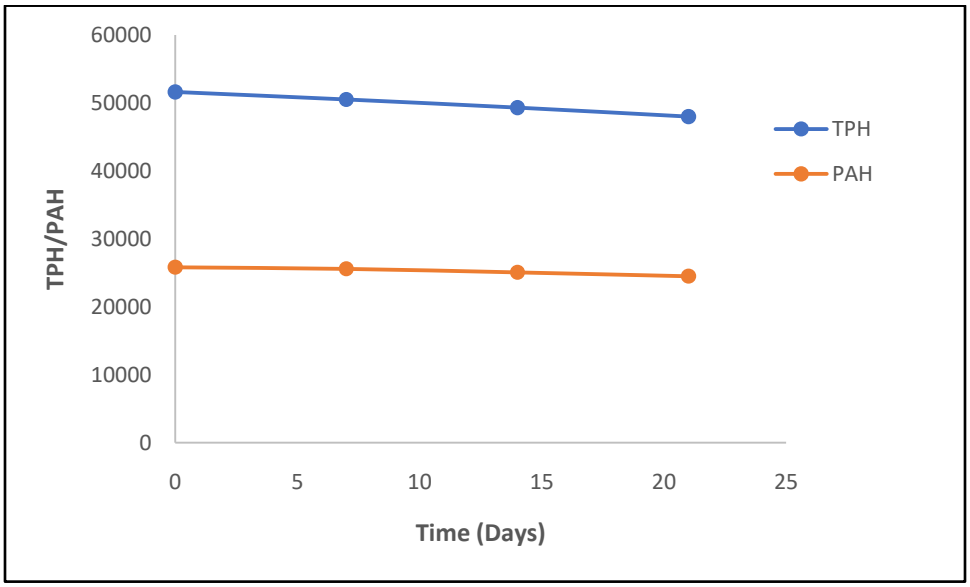


Figure 28: Variation of TPH and PAH on Crude Polluted Loamy Soil Treated With NPK

In figure 29 microbial count for different soil type were compared and it was observed that crude polluted loamy soil treated with nano particle and hydrogen peroxide gave maximum microbial count of 25000100cfu/g showing the effectiveness of the treatment method.

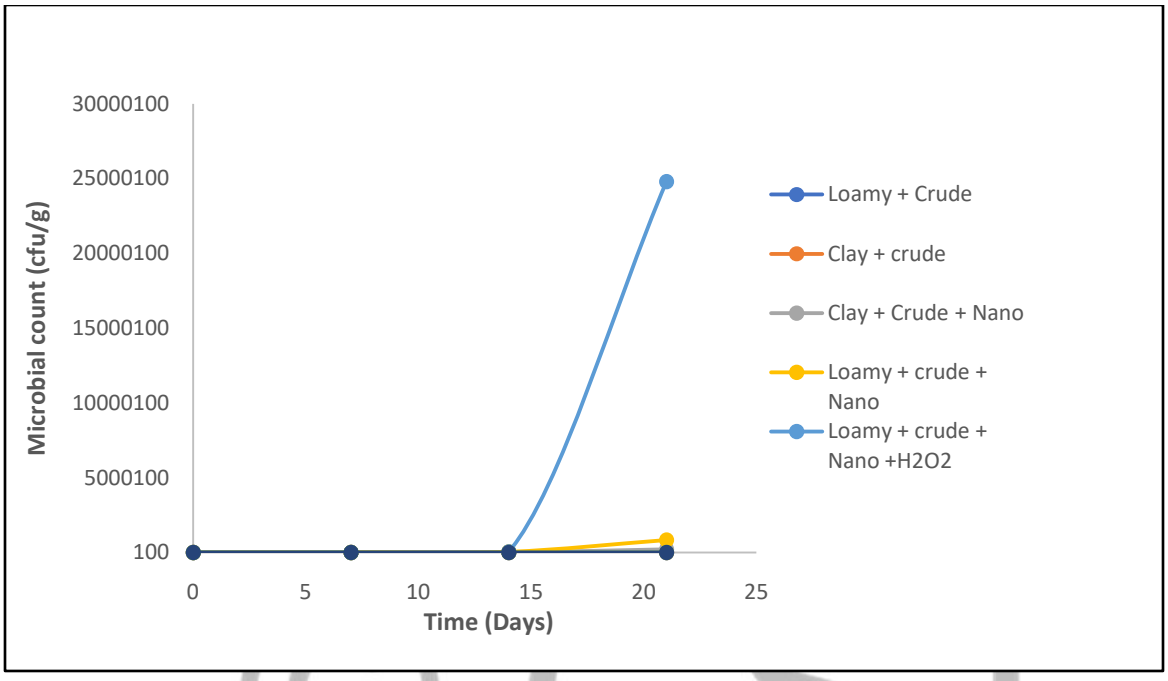


Figure 29: Variation of Microbial Count with Time for Different Soil Type

In figure 30 the concentrations of PAH variation with time for different soil type were compared and it was observed that the best result was crude polluted loamy soil treated with nano particle because it reduced the concentration of crude contaminants in the soil to the least minimum.

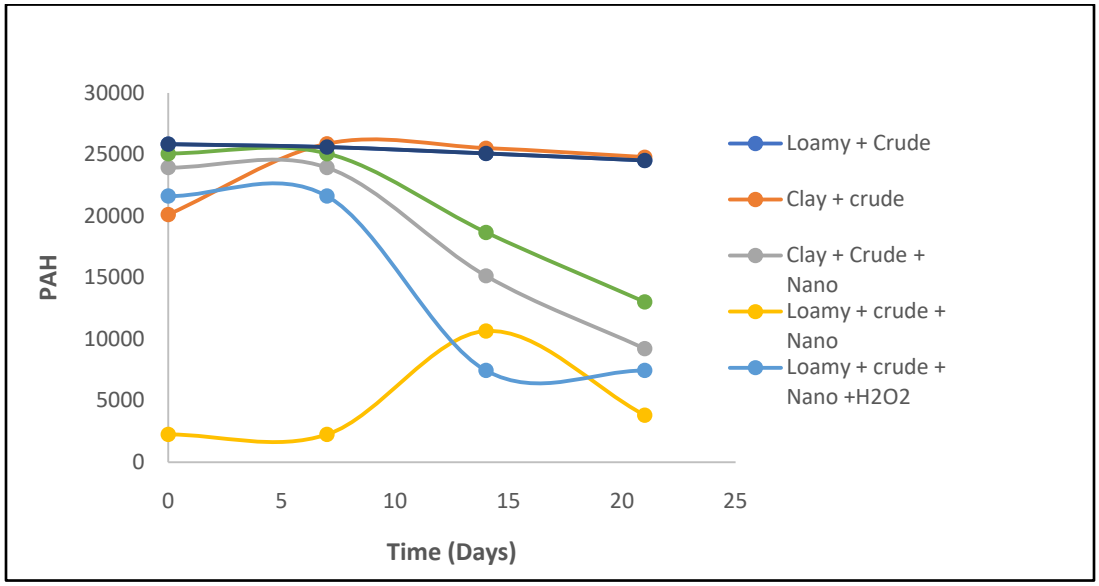


Figure 30: Comparison of PAH for Different Soil Type

In figure 31 the concentrations of TPH variation with time for different soil type were compared and it was observed that the best result was crude polluted loamy soil treated with nano particle and hydrogen peroxide because it reduced the concentration of crude contaminants in the soil to the least minimum.

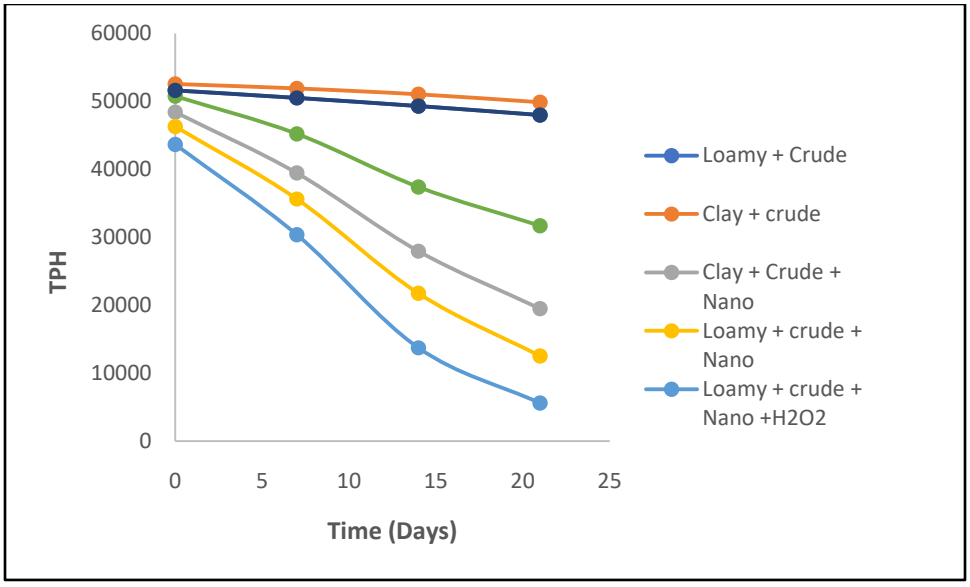


Figure 31: Comparison of TPH with Time for Different Soil Type

4. Conclusion

The use of Nano particle, H_2O_2 and NPK as a method to enhance remediation of petroleum contaminated loamy soil and clay soil was investigated using the effects of Nanoparticle, H_2O_2 and NPK on the physicochemical properties of the impacted soil as a determining TPH & PAH concentration in loamy soil and clay soil through petroleum contaminated soil. The laboratory analysis was carried out using gas chromatography. The result showed that the physicochemical properties of treated soil and untreated soil loamy and clay. The best result for all three functional parameters namely PAH, TPH and MC was Nano particle mixed with hydrogen peroxide as a catalyst. NPK treatment was found to be ineffective because its remediation rate was overcome by the high contamination of the soil by crude.

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