

Surfactant Enhanced Soil Washing Technique and its Kinetics on the Remediation of Crude Oil Contaminated Soil.

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ABSTRACT

Hydrocarbons are considered as global environmental threats because of their toxic and mutagenic effects, therefore the removal of this contaminant from the environment becomes increasingly important. Surfactants aid in the removal of organic contaminants from the soil, but the choice of surfactant, suitability, its environmental friendliness, toxicity, and effectiveness must be of paramount concern. The primary objective of this study was to evaluate the efficiency and effectiveness of using sodium dodecyl sulphate (SDS) surfactant in remediating crude oil contaminated soil through surfactant enhanced soil washing technique at established optimum conditions; kinetic evaluation of the process as well as the surfactant treatment effect on soil quality.

Soil was artificially contaminated with 10% crude oil by laboratory simulation. Crude oil contamination adversely affected soil properties such as pH, conductivity, and total phosphorus as there was statistical significance at $p < 0.05$. Optimum concentration established for SDS was found to be 40,000ppm at ambient temperature for the surfactant treatment. The surfactant method was found to be very rapid and effective with 88.32% remediation efficiency achieved at the end of seven hours as there was significant difference statistically at $p < 0.05$ in the TPH removal rate or treatment efficiency. The kinetics

of the process followed first order with a rate constant of 0.291 hour^{-1} and calculated half life of 2 hours 24 minutes. A computation of the TPH degradation isotherm (K_d) gave negative value of unity showing the opposing trend between the concentration of the contaminant in the soil (C_s) and the concentration removed by the surfactant (C_d); which explains that as C_s is decreasing with time, C_d is increasing.

The surfactant method was found to improve the physicochemical quality of the contaminated soil at the end of the treatment process as evident in the reduction of heavy metals concentration as well as improvement in pH and conductivity property. The mechanism of hydrocarbon removal was by solubilization and mobilization of the contaminant which is usually achieved by reducing the surface and interfacial tension between air/water, oil/water and soil/water systems. SDS surfactant is biodegradable and non-toxic, thus reducing the risk of future environmental problems after the remediation process, making it an environmental friendly technique. This technique was found to be very promising because it is capable of reducing both hydrocarbon and heavy metals concentration as well improving the deteriorated properties of the soil which are essential for soil quality and productivity.

(Keywords: sodium dodecyl sulphate, SDS, surfactant, optimization study, degradation isotherm, kinetics, total petroleum hydrocarbon)

INTRODUCTION

Total petroleum hydrocarbons are persistent organic pollutants present at hydrocarbon contaminated soils and are known to threaten plant, aquatic, animal, and human lives because of their toxic and mutagenic effects. Hydrocarbons are considered as global environmental threats because they do not only affect the soil in which they find their way as a result of spill but are also leached into ground and surface water further increasing the level of environmental contamination. The contamination of soils and groundwater by total petroleum hydrocarbon as crude oil or its derivatives is an environmental concern in industrial and oil producing areas. Therefore, the removal of this contaminant from soils and groundwater becomes increasingly important. Because of the deleterious effect of hydrocarbon pollution in the environment, remediation techniques to combat the ever confronting challenges of global oil spills has remain a major concern for researchers and environmental experts.

Some chemical remediation techniques might only be efficient in hydrocarbon contaminant removal but with serious effect on essential soil properties because of the chemical substances used for the remediation process. Hence it is important to assess the effectiveness and efficiency on both contaminant removal and soil quality, thus making it imperative in this study to x-ray the physicochemical quality of the soil before and after the remediation process in order to determine the effectiveness of the remediation technique under consideration in improving soil quality or otherwise.

Optimum conditions such as appropriate concentration of surfactant and pH must be satisfied to achieve very effective remediation. On the contrary, known literatures are devoid of optimization studies aimed at establishing optimum conditions for soil remediation using chemical methods especially in the case of surfactant enhanced soil washing technique. Researchers use arbitrary chosen concentrations of surfactants for their remediation studies which will definitely not yield optimal results because the process was not carried out under optimum conditions. This has been a major concern and challenge to the authors, instigating the reason and prompting the need for proper optimization studies to define optimum conditions prior to the remediation process.

Surfactants (surface active agents) may aid in remediation of soil and groundwater contaminated with hydrophobic organic contaminants (HOC) (Edwards et al., 1994, Cases et al., 2002, and Lee et al., 2002). These studies showed that aqueous surfactant solutions significantly enhanced the removal of HOC from soil and groundwater. Extractive efficiencies of surfactant solution for HOC were seven to ten times greater than those which could be obtained by flushing with water alone.

Surfactants can be used to vastly increase the solubility of the HOC in water and also lower the interfacial tension at the water-HOC interface (Rosen, 1989., Fountain et al., 1991, Cort et al., 2002, and Lee et al., 2002). More than 13,000 surfactants are commercially available (Rosen, 1989), but many are not suitable for HOC-contaminated soil and groundwater remediation. Some could become potential contaminants in soil or groundwater and might also be expected to influence the behavior of other pollutants. Unsuitable surfactant may cause soil pore clogging because they can hydrolyze to form flocs, combine to form micelles, and disperse soil colloids (Rosen, 1989., Lee et al., 2001, and Chu and Kwan, 2003). Suitable surfactants must also be commercially available, inexpensive, and nontoxic (Abdul et al., 1990).

The surfactants used in this study was selected based on its proven ability to solubilize organic contaminants in previous studies, environmental compatibility, commercial availability, biodegradability, and non-toxicity as this are very important properties a good surfactant to be used for environmental purposes should posses.

There is a high tendency that some residual or adsorbed surfactant solution will be left in the soil after the remediation process is completed, hence it is very important to choose a surfactant that is biodegradable and non-toxic so that further environmental problems will not be created after the remediation process.

In carrying out surfactant enhanced soil washing technique, it is desirable to select surfactants that will not adsorb to the soil particles, because surfactant adsorption could reduce the micellization and solubilization capacity of the surfactant, and it could result in the contaminant partitioning to the adsorbed surfactant molecules (Edwards et al., 1994 and Ko et al., 1998). Clearly, if a substantial amount of surfactant

molecules are adsorbed to the soil surface, less of them will be available for micelle formation and for total petroleum hydrocarbon solubilization.

The primary objective of this paper was to evaluate the efficiency and effectiveness of using sodium dodecyl sulphate (SDS) surfactant in remediating crude oil contaminated soil through surfactant enhanced soil washing technique at established optimum conditions; kinetic evaluation of the process as well as the surfactant treatment effect on soil quality.

MATERIAL AND METHODS

Study Area

Soil samples were collected from Agbor in Delta State of Nigeria. Agbor which is the administrative headquarters of Ika South Local Government Area is located in the northern part of Delta State, South- South Nigeria'. It lies within the coordinates of longitude $6^{\circ}05'N$ to $6^{\circ}16'N$ and latitude $6^{\circ}07'E$ to $6^{\circ}12'E$ of the equator. The mean annual rainfall ranges between 2540-3500mm and the temperature varies between $28^{\circ}C-33^{\circ}C$ around March and $23^{\circ}C-30^{\circ}C$ around August. The relative humidity of the area is highest in August and ranges between 79-86%.

Samples Collection

Soil samples were collected with a soil auger at surface depth (0-15cm) from a virgin fallow land in the forest area of Agbor, Delta State in southern Nigeria, having no pollution history and devoid of hydrocarbon contamination. The soil samples were bulked, thoroughly mixed and stored in clean polythene bags. Crude oil with specific gravity of $0.818g/cm^3$ was obtained from shell petroleum development company (SPDC) flow station in Kokori, Ethiope East Local Government Area of Delta state.

Sample Preparation, Simulation and Amendment

Soil was air dried for a period of one week in a clean well ventilated laboratory, homogenized by grinding, and filtered by passing through a 2mm mesh sieve. 1kg of soil was each measured into two clean dry plastic containers and moistened to

20% water holding capacity with distilled water to ensure proper mixing with the contaminant. Simulation of the soil samples was done by measuring 100g of crude oil corresponding to 122.25ml from gravimetric measurement into the two containers containing 1kg of soil each. The individual mixtures were thoroughly mixed to achieve a 10% artificial contamination. 10% spiking was adopted to achieve severe contamination because beyond 3% concentration, oil has been reported to be increasingly deleterious to soil biota and crop growth (Osuji et al., 2005).

Soil Characterization/Physicochemical Analysis

Soil physicochemical characteristics such as soil texture, pH, total organic carbon, total organic matter, total nitrogen, total phosphorus, soil conductivity, and heavy metals (V, Pb Ni, Cd, and Cr) were determined before contamination, after contamination and after the remediation process. Soil pH was determined electrometrically following the procedure outlined by Mylavarapus and Kennelley (2002). Particle size analysis was done using bouyoucos hydrometer method (Bouyoucos, 1951). Total organic carbon and matter were determined by the wet dichromate acid oxidation method of Nelson and Sommers (1982). Total Nitrogen was determined using the method of Radojevic and Bashkin (1999). Total Phosphorus was determined by the Bray and Kurtz method (1943). Electrical conductivity was carried out as described by Chopra and Kanzer (1988). Heavy metals were determined by digesting the samples with concentrated mixtures of hydrofluoric, nitric and perchloric acid (AOAC, 1970), so as to convert all the metals present in the sample into such a form that they can be analyzed by the atomic absorption spectrophotometer.

Optimization Study

Optimization study was carried out to determine the optimum condition for concentration of the treatment solution. Sodium dodecyl sulphate, an anionic synthetic surfactant was employed for the remediation of the crude oil contaminated soil. The desired concentration of the anionic surfactant needed for optimum performance was determined from the optimization study conducted by preparing different concentrations within a

concentration range of between 1% - 6% corresponding to between 10,000 ppm to 60,000 ppm. Surfactants are reported to be generally used in water or other solvents at a concentration of 0.004 to 5 weight % (US Patent, 2003 and Urum et al., 2004), which gave the basis for the concentration ranges used in this optimization study. The different concentrations were then separately applied on 1kg of crude oil contaminated soils each and allowed to stand for a period of three hours. The remediation efficiencies for the different concentrations of treatment solutions were determined by measuring their respective rate of contaminant (total petroleum hydrocarbon) removal using a spectrophotometer from which its optimum concentration was obtained. The technique was carried out at ambient temperature (22-32°C) since this is the temperature range that is observed and peculiar to the natural environment in which the study was carried out. These conditions were subsequently been applied to the kinetics study.

Remediation of Crude Oil Contaminated Soil by Surfactant Treatment

1kg of crude oil contaminated soil was subjected to chemical remediation by treating the sample with a surfactant, SDS. Surfactant concentration of 4%wt/v (40,000 ppm) obtained from optimization study for the treatment of crude contaminated soil was prepared by dissolving 40g of sodium dodecyl sulphate in 1dm³ of distilled water and shaken thoroughly until the surfactant completely dissolved. The contaminated soil was mixed with the surfactant solution at a soil to surfactant ratio of 1:5 corresponding to 1kg of contaminated soil per 5 dm³ of surfactant solution. The treated sample was kept for analysis.

Prior to total petroleum hydrocarbon analysis, aliquot portion of the soil and solution layer of surfactant were collected in a 1:5 ratio at intervals, that is 20g of soil and 100ml of surfactant solution from the reaction vessel. Aliquot portions containing the mixture of soil and surfactant solution were removed from the bulk mixture and subjected to mechanical shaking at hourly intervals using a mechanical shaker for one, two, three, four, five, six and seven hours respectively at 400 strokes/min shaking speed in order to determine the contaminant removal rate and its kinetics. The supernatant containing the

surfactant and contaminant was then decanted after shaking, leaving the treated soil which was analyzed for its total petroleum hydrocarbon content.

Determination of Total Petroleum Hydrocarbon (TPH)

Optimum wavelengths for the spectrophotometric determination of total petroleum hydrocarbon (TPH) was obtained by preparing 1000ppm standard concentration of the contaminant using hexane and taking its absorbance readings at different wavelengths within the wavelength range of 200-700nm. Total petroleum hydrocarbon for the remediation study was then determined using the optimum wavelength obtained. 1g of the soil sample was dissolved in 10ml of hexane and shaken for ten minutes using a mechanical shaker. The solution was filtered using a Whatman filter paper and the filtrate diluted by taking 1ml of the extract into 50ml of hexane. The absorbance of this solution was read at 460nm with a PG T60 U.V Visible spectrophotometer (2007 model) using n-hexane as blank. Total petroleum hydrocarbon was determined at hourly intervals for seven hours.

Quality Control

Appropriate quality control measures and recovery studies were carried out. All reagents used in this study were of pure analytical grade and were checked for possible trace metal contamination. All glasswares for metal analysis were previously soaked in 14% nitric acid (v/v) for 24 hours to remove all entrained metals, washed with detergents, and rinsed with deionized water.

Procedural blank and working standard solutions for nickel, chromium, lead, cadmium, and vanadium were prepared by diluting concentrated stock solution with distilled water, while working standards for total petroleum hydrocarbon (TPH) were also prepared from the standard stock of the hydrocarbon contaminant. A known standard was run after every five samples to check the reliability of the analytical instrument. Optimization of wavelengths for the determination of total petroleum hydrocarbon (TPH) in crude oil contaminated soil was performed to obtain the optimum or best wavelength with the most stable spectrophotometric reading. The reliability of the entire procedure was carried out by spiking

already analyzed samples with known metal and total petroleum hydrocarbon standard and re-analyzed.

The percentage recovery achieved for each metal were 92.7%, 90.5%, 91.8%, 96.3%, and 93.7% for nickel, chromium, lead, cadmium, and vanadium, respectively, while percentage recovery achieved for total petroleum hydrocarbon in contaminant was 96.3%. Triplicate analyses were performed on all the samples to yield a mean which was used to determine trueness and also standard deviation of the mean to measure precision (Stanton 1966; Valcarcel, 2000).

Statistical Treatments

Samples were prepared in replicate of three to provide data for statistical treatment. Standard deviation, relative standard deviation and coefficient of variation (CV) calculations were used to checkmate indeterminate (random) error. Sets of replicate results obtained from the study were found to have measurement uncertainty and precision of less than 5% in terms of their coefficient of variations in all cases. Therefore the results are said to be of very high precision. Blank runs were also conducted to reduce the

occurrences of determinate errors. Analysis of variance and regression statistics were used in analyzing the results.

RESULTS AND DISCUSSION

Soil Physicochemical Properties

The results of soil physicochemical properties are presented in the Table 1.

A reduction in pH, conductivity and phosphorus content were observed from 6.1 to 4.5, 191.7 μ S/cm to 174.0 μ S/cm and 6.1mg/kg to 4.3mg/kg respectively on contamination of the soil with 10% crude oil as seen in Table 1. The findings of Akpoveta et al. (2011) supports this observation. The authors explained that the reduction in pH of the contaminated soil was due to the weak acidic property of the crude oil; reduced conductivity due to the non polar nature of the crude oil bringing about reduced ionic movement in the soil and reduced phosphorus level due to possible oxidation of free phosphorus in the soil to phosphates because hydrocarbons act as electron acceptors or oxidizing agents due to the presence of oxygen in them thereby producing a reducing environment..

Table 1: Results of Soil Physicochemical Properties and Heavy Metals Before Contamination, After Contamination, and After the Remediation Process.

Parameters	Soil	Soil+ Crude	Remediated Soil
pH	6.1 \pm 0.10	4.5 \pm 0.21	6.71 \pm 0.01
Conductivity(μ S/cm)	191.7 \pm 0.1	174.0 \pm 1.8	199.7 \pm 0.1
Nitrogen (mg/kg)	0.15 \pm 0.01	0.22 \pm 0.02	1.75 \pm 0.01
Phosphorus (mg/kg)	6.1 \pm 0.25	4.3 \pm 0.21	1.25 \pm 0.02
% Organic Carbon	2.34 \pm 0.01	5.93 \pm 0.03	1.98 \pm 0.03
% Organic Matter	4.03 \pm 0.03	10.22 \pm 0.05	3.41 \pm 0.05
Total petroleum hydrocarbon (mg/kg)	8.64 \pm 0.02	1587.5	185.44 \pm 0.876
Lead(mg/kg)	<0.001	<0.001	<0.001
Cadmium(mg/kg)	0.025 \pm 0.004	0.015 \pm 0.004	0.025 \pm 0.002
Nickel(mg/kg)	0.419 \pm 0.001	0.284 \pm 0.004	0.182 \pm 0.002
Vanadium(mg/kg)	0.792 \pm 0.008	0.537 \pm 0.002	0.294 \pm 0.002
Chromium(mg/kg)	<0.001	<0.001	0.015 \pm 0.002
% Sand	83.31 \pm 0.01	83.11 \pm 0.01	83.10 \pm 0.03
% Silt	1.22 \pm 0.02	1.43 \pm 0.02	1.45 \pm 0.02
% Clay	15.4 \pm 0.01	15.46 \pm 0.02	15.45 \pm 0.01

Statistical evidence shows that at 95% confidence limit there was significant effect of crude oil contamination on soil properties as observed in the reduction in pH, total phosphorus and electrical conductivity. The increase in pH from 4.5 to 6.7 after surfactant treatment process is due to the removal of the hydrocarbons which initially caused a reduction in pH. Sodium doceyl sulphate is an anionic surfactant with a pH of between 7.0-9.5, hence will not significantly alter the pH of the soil. Since the surfactant is slightly alkaline an increase in the pH of the soil could possibly result from the treatment process which can also be a contributing factor that accounts for the drift in pH to neutrality.

The high value of 199.7 μ S/cm observed for electrical conductivity after the remediation process as seen in Table 1 must be due to the removal of the hydrocarbons which initially provided a non polar environment for the soil ions, while the observed reduction in total phosphorus to 1.25mg/kg after the treatment process could be due to possible reaction/complexation of the element with polar sites of the surfactant since phosphorus is known to be highly reactive. Surfactant technique was found to improve the pH and conductivity property of the soil after treatment. An increase in total nitrogen, total organic carbon and matter were observed from 0.15 to 0.22mg/kg, 2.34 to 5.93% and 4.03 to 10.22%, respectively, on contamination of the soil with crude oil as seen in Table1.

Previous explanation by Akpoveta et al. (2011) that such increase could be due to nitrogenous and carbonaceous input from the crude oil since it is highly carbonaceous and contains varying proportions of nitrogenous substances in it justifies this observation. Subsequent increase in total nitrogen content from 0.22mg/kg in the contaminated soil to 1.75mg/kg in the treated soil after the treatment process could be due to the fact that nitrification process increased in the absence of biodegradation activities by the hydrocarbon utilizing microbes, because according to Odu et al. (1985), oil degrading or hydrocarbon-utilizing microbes such as *Azobacter sp.* normally become more abundant while nitrifying bacteria such as *Nitrosomonas sp.* become reduced in number. The observed reduction in organic carbon and matter from 5.93% in contaminated soil to 1.98% in treated soil and 10.22% in contaminated soil to 3.41% in

treated soil, respectively, after the treatment process as seen in table1 is due to the removal of the hydrocarbon. The values obtained after the treatment process were however found to be in the same range with those of the control soil, hence could be inferred that there was no significant influence on total organic carbon and matter content of the treated soil by this method.

Particle size analysis showed that the sand (83.10-83.31%), silt (1.22-1.44%) and clay (15.46-15.47%) fractions were all in the same range for the control, contaminated and surfactant treated soil, indicating no effect on soil texture. A classification of the soil based on the USDA textural class (2002) showed that the soil is loamy sand (coarse textured soil) and its classification according to the soil taxonomy classes showed that it is typic paleudite.

Lead and chromium had concentration of <0.001mg/kg in the control, contaminated and remediated soil, except for chromium which showed a slightly different concentration of 0.015mg/kg in the remediated soil, indicating very low availability of the metals. The concentrations of cadmium, nickel and vanadium in the control soil were found to be 0.025mg/kg 0.419mg/kg and 0.792mg/kg, respectively, but gave lower concentrations of 0.015mg/kg, 0.284mg/kg, and 0.537mg/kg in the crude oil simulated soil as seen in Table 1, suggesting no hydrocarbon influence on the metals. Similar observation was seen in the report of Akpoveta et al. (2011), and it was explained that less availability of the metals in the contaminated soil accounted for the observed decreased concentration.

The same concentration of 0.025mg/kg was recorded for cadmium after the treatment process, while nickel and vanadium had reduced concentrations of 0.182mg/kg and 0.294mg/kg respectively as against their values in the control soil after the treatment process, which could be possibly due to complexation of the metals with surfactant molecules thereby presenting them in less available concentrations.

Heavy metals present in the contaminated soil are capable of reacting with the surfactant molecules to form complexes thereby reducing the heavy metal content of the soil as these complexes goes with the waste surfactant-hydrocarbon product. This metal removal mechanism could however reduce surfactant oil

removal rate as complex formation of the metal with surfactant could reduce the concentration of surfactant making it less available for hydrocarbon solubilization. The values of the metals reported were all found to be lower than the natural range in normal soils (EGASPIN, 2002. and Eddy et al. 2006). Statistical analysis shows that there was no significant effect of crude oil pollution on heavy metals and soil texture at 95% confidence.

Optimization Study

The result of optimization of wavelengths studies for the determination of total petroleum hydrocarbon (TPH) in crude oil contaminated soil and optimization studies for determining optimum concentration of SDS for the surfactant treatment of crude oil contaminated soil are presented below.

Table 2: Data for Wavelength Optimization.

Wavelengths (nm)	200	250	300	350	400	450	500	550	600	650	700
Absorbances For crude	2.674	3.052	2.961	1.13	0.318	0.143	0.094	0.077	0.067	0.062	0.058

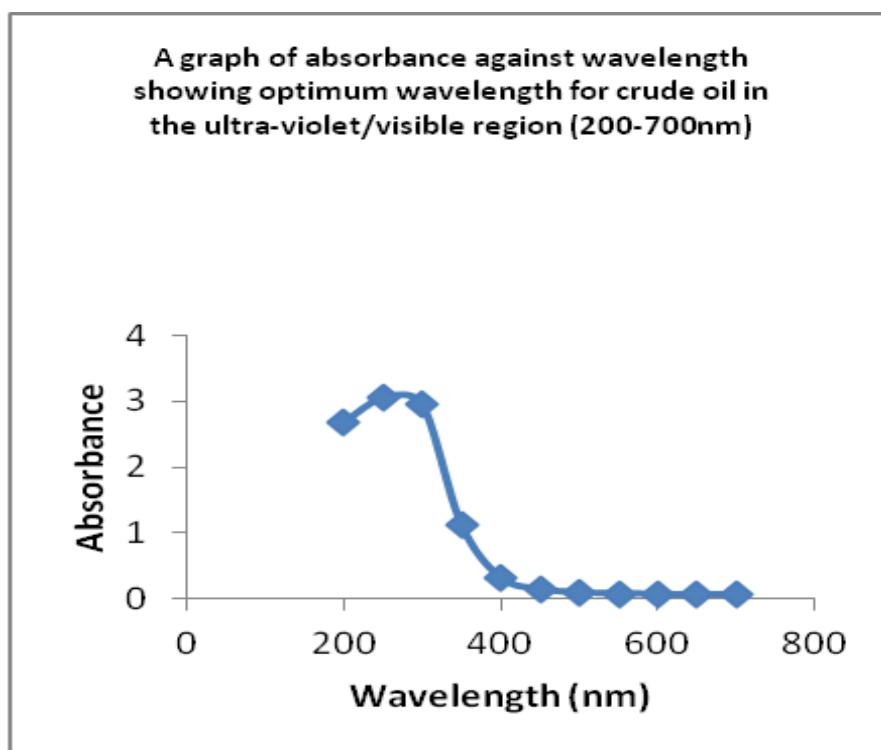


Figure 1: A Graph of Absorbance against Wavelength showing Optimum Wavelength for Crude Oil in the Ultra-Violet/Visible Region (200-700nm).

Table 3: Optimization Studies for the Chemical Remediation of Crude Oil Simulated Soil using Surfactant Treatment Technique.

Surfactant Conc.(ppm)	% decrease	Mean of TPH remediated	Standard Deviation of Mean TPH	R.S.D $\times 10^{-3}$	C.V 10^{-2}
10000	43.69	693.65	693.65 \pm 3.282	4.732	47.32
30000	59.27	941.01	941.01 \pm 4.448	4.727	47.27
40000	76.42	1213.30	1213.30 \pm 5.734	4.726	47.26
50000	60.17	955.30	955.30 \pm 4.513	4.724	47.24
60000	53.47	848.93	848.93 \pm 4.013	4.727	47.27

R.S.D- Relative standard deviation

C.V- Coefficient of variation

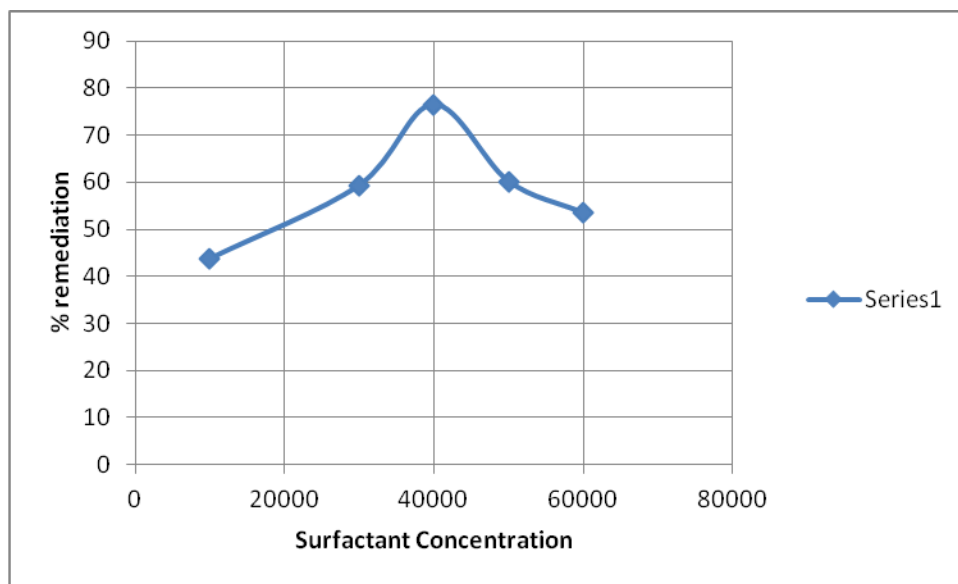


Figure 2: Plot of % Decrease (Remediation) of TPH in the Soil against Concentrations of Surfactant (SDS) for the Optimization Study of Crude Oil Contaminated Soil using Surfactant Treatment Remediation Technique.

Stable spectrophotometric reading was practically observed at 460nm as seen in Figure 1, which was taken as the optimum wavelength for total petroleum hydrocarbon determination.

Optimization study conducted within a concentration range of 10,000 ppm to 60,000 ppm as seen in Table 3 recorded highest contaminant removal rate of 76.42% at 40,000 ppm for the crude oil contaminated soil with the plot of percentage remediation against concentration giving its highest peak at this optimum concentration as seen in Figure 2.

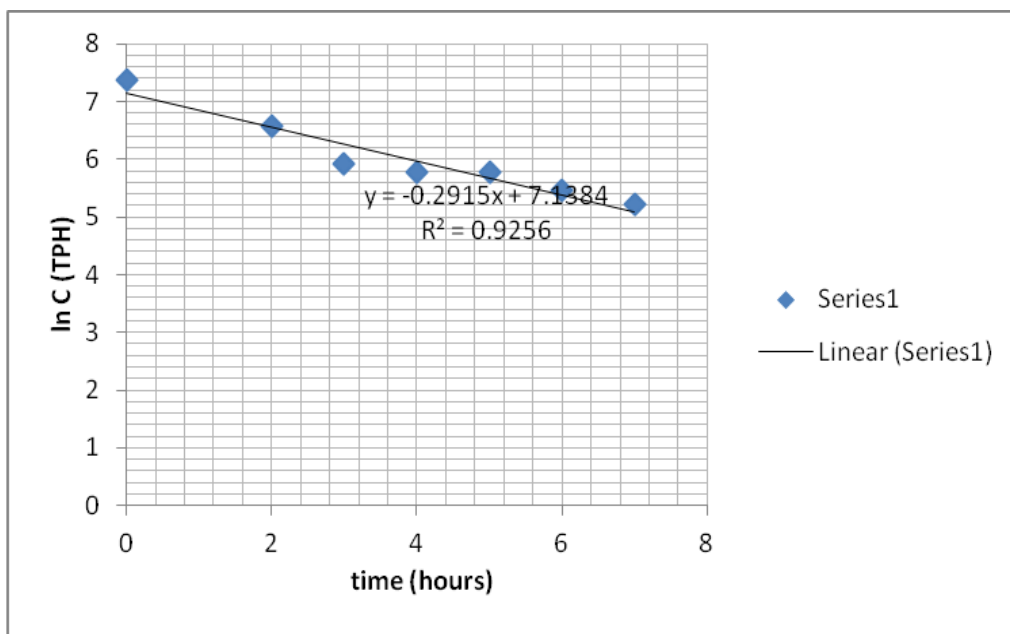
This optimum concentration was used in preparing the treatment solution of the surfactant for treating the contaminated soil.

Surfactant Treatment of Crude Oil Contaminated Soil and its Kinetics

The results obtained for the chemical remediation of crude oil contaminated soil using sodium dodecyl sulphate and its kinetics are presented below.

Table 4: Rate of Change of Total Petroleum Hydrocarbon with Time for the Chemical Remediation of Crude Oil Simulated Soil using Surfactant (Sodium Dodecyl Sulphate) Treatment Technique.

Time (hours)	Mean of TPH	In of Mean TPH	Std Deviation of Mean TPH	R.S.D× 10 ⁻³	C.Vx10 ⁻²	% decrease
0	1587.67	7.37	1587.67±7.506	4.728	47.28	0
2	713.81	6.571	713.81±3.372	4.714	47.14	55.04
3	374.37	5.925	374.37±1.771	4.731	47.31	76.42
4	321.66	5.773	321.66±1.521	4.729	47.29	79.74
5	321.50	5.773	321.50±1.521	4.731	47.31	79.75
6	236.24	5.465	236.24±1.121	4.745	47.45	85.12
7	185.44	5.223	185.44±0.876	4.724	47.24	88.32



Rate constant k equals 0.291 since $-k = -0.291$.

Figure 3: Plot of $\ln C(\text{TPH})$ against Time for the Chemical Remediation of Crude Oil Simulated Soil using Surfactant Treatment Technique.

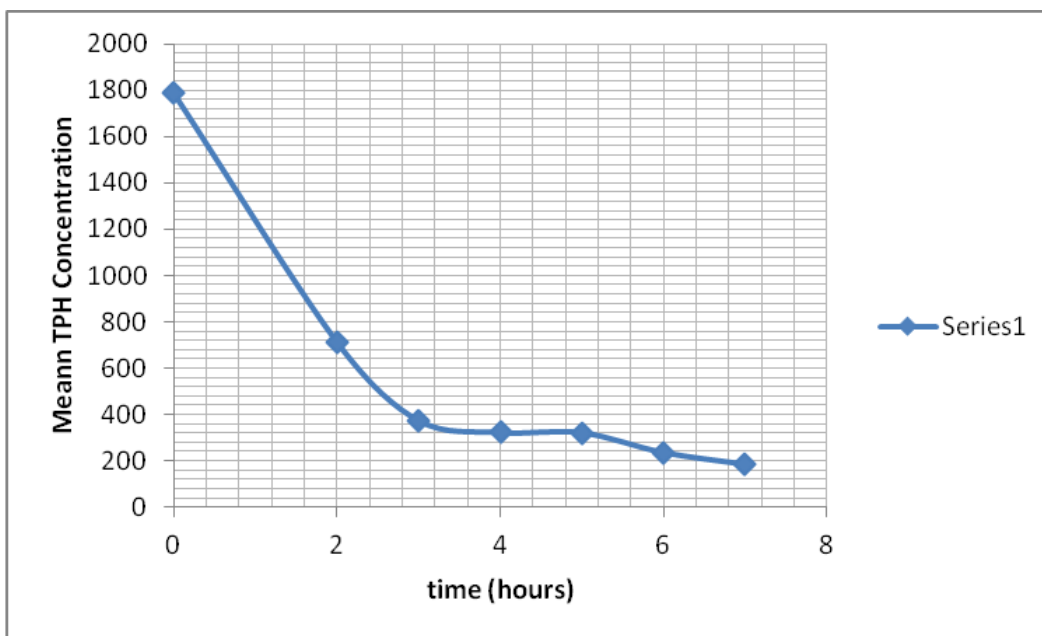


Figure 4: Plot of Mean TPH Concentration against Time for the Chemical Remediation of Crude Oil Simulated Soil using Surfactant Treatment Technique.

The treatment process conducted within a time interval of seven hours yielded an impressive 88.32% at the end of the treatment, corresponding to a total petroleum hydrocarbon content (TPH) of 185.44mg/kg from an initial TPH content of 1587.67ppm as seen in Table 4.

Apart from the high efficiency observed in TPH removal, the technique also finds relevance in reducing heavy metal concentration through complexation of the metals with the surfactant molecules as evident in the reduced concentration of nickel and vanadium observed after the remediation process.

Statistical analysis with the aid of ANOVA single factor on the degree or rate of remediation of the crude oil contaminated soil using this technique showed that the TPH removal rate or treatment efficiency was found to be significant as there was significant difference at $p < 0.05$ or 95% confidence limit.

The mechanism behind surfactant-enhanced removal of oil from soil has been proposed to occur in two steps; solubilization and mobilization (Deshpande et al., 1999., Mulligan et al., 2001, and Matthews, 2004). Surfactants removes

hydrocarbon by solubilisation and mobilization of the contaminant which is usually achieved by reducing the surface and interfacial tension between air/water, oil/water and soil/water systems.

The kinetics of the process was analyzed by plotting concentrations of TPH left in the soil at hourly spaced interval against time and natural logarithm of TPH concentration against time as presented in Figures 3 and 4. A linear graph was obtained for the plot of natural logarithm of TPH concentrations (\ln TPH) against time, while an exponential curve was obtained for the concentration-time graph indicating that the degradation process followed first order kinetics. The solubilization and removal of the contaminant was dependent only on the concentration of the hydrocarbon. The rate law is giving by $r = K[\text{TPH}]$. The rate constant was found to be 0.291 hour^{-1} for the crude oil treated soil with a calculated half life of 2 hours 24 minutes.

Degradation isotherm at ambient temperature for the surfactant treatment process was determined by plotting the concentrations of total petroleum hydrocarbon solubilized and removed by the surfactant against the residual concentration left

in the soil at each time as presented in Table 5 and illustrated in Figure 5 below. Concentration of total petroleum hydrocarbon (TPH) removed by the surfactant was obtained by subtracting the amount of residual TPH left after remediation at each time interval from the initial concentration.

The plots of C_s versus C_d for the crude oil treated soil using this technique gave a straight line graph with the values of C_s and C_d linearly related. The line plotted through the points is known as the linear degradation isotherm and it is giving as $K_d = C_s/C_d$. The value of K_d was calculated using a

linear regression analysis as shown in the linear regression equation. The negative value of unity for k_d indicates the opposite trend between C_s and C_d , which explains that as the residual concentration of the contaminant in the soil (C_s) is decreasing with time, the concentration removed by the effect of the surfactant (C_d) is increasing. The correlation coefficients (R^2) values of unity for the chemical degradation isotherms indicates a very positive correlation between the amount of contaminant removed and the parent contaminant left in the soil during the remediation process at each time.

Table 5: Concentration of Residual Total Petroleum Hydrocarbon (TPH) in Soil (C_s) and TPH Degraded (C_d) at Different Times for the Chemical Remediation of Crude Oil Contaminated using Surfactant Treatment Technique.

Time (hrs)	0	1	2	3	4	5	6
C_s	1587.67	713.81	374.37	321.66	321.50	236.24	185.44
C_d	0	873.86	1213.30	1266.01	1266.17	1351.43	1402.23

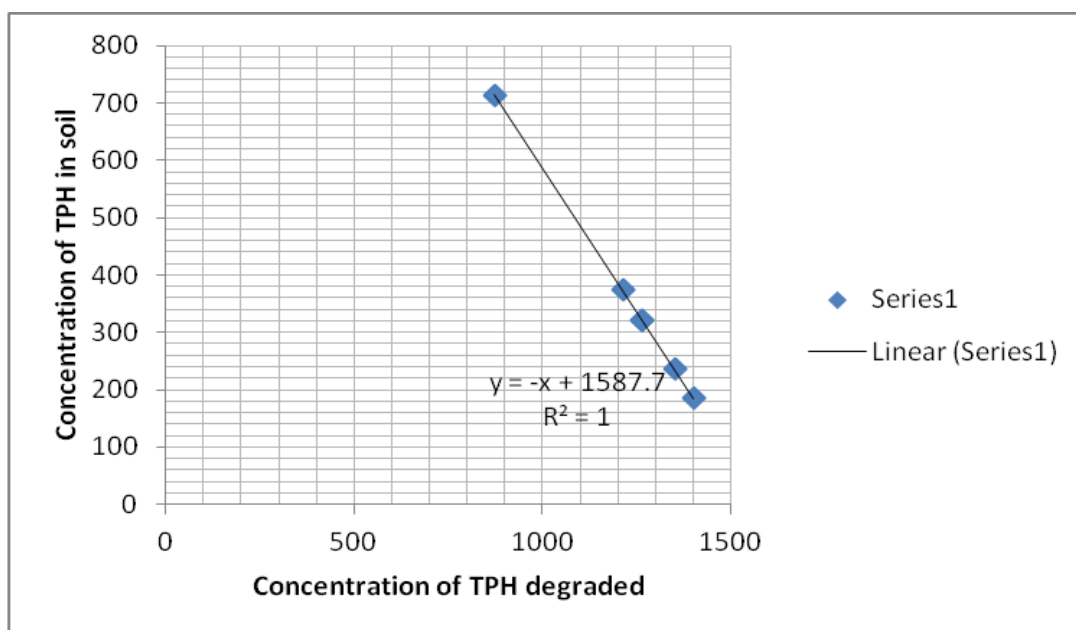


Figure 5: Linear Degradation Isotherm for the Chemical Degradation of Crude Oil Contaminated Soil using Surfactant Treatment Technique.

CONCLUSION

The negative impact of crude oil contamination was evident on soil properties such as pH, total phosphorus and electrical conductivity which were significantly reduced. However, these deteriorated soil properties were improved on treating the soil using this technique.

The established optimum condition for the treatment process was found to yield very excellent result on application. The biodegradability of the surfactant makes this method an environmentally friendly technique. Due to the fact that the surfactant was used at low concentration, a minor amount of surfactant adsorption to soil particles will be deemed acceptable because of its biodegradability. However, this technique suffers some shortcomings because of its infrastructural requirement and post treatment of waste necessary to reduce environmental impact. But on the overall, the method was found to be very promising because it is capable of reducing both hydrocarbon and heavy metals concentration as well as improving the deteriorated properties of the soil which are essential for soil quality and productivity.

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