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Synthesis of Green Surfactant for Remediating Petroleum Contaminated Soil

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Abstract: ***This study focuses on synthesis and pilot scale insitu application of green surfactant of vegetable oil origin in remediating petroleum contaminated soil. The objectives include production of methyl ester sulphonate (MES) surfactant from groundnut oil, characterization of the surfactant and testing of its effectiveness in remediating engine oil contaminated soil. The methods employed were bench scale production of the surfactant through transesterification, sulphonation, and interesterification reactions. The surfactant was applied on a simulated contaminated site and remediation efficiency analyzed using GC-FID and GC-MS. Results obtained indicates that triglycerides can be applied in the synthesis of an ecofriendly surfactant for petroleum spill remediation. The produced surfactant was able to remediate 61.7 percent total petroleum hydrocarbon (TPH) and 96.0 percent polycyclic aromatic hydrocarbon (PAH) in the simulated contaminated soil. MES is recommended as petroleum spill dispersant and remediating agent in restoring petroleum impacted soils. Manufacturing effort should be made toward commercializing vegetable oil based ecofriendly surfactant for petroleum spill remediation and other industrial and domestic application.***

Keywords: green surfactant, remediation, petroleum spill, methyl ester sulphonate

1. Introduction

Remediation shall consist of actions on the soil aimed at the removal, control, containment or reduction of contaminants so that the contaminated site, taking account of its current use and approved future use, no longer poses any significant risk to human health or the environment [42]. These technologies can extract, remove, transform, or mineralize petroleum pollutants in a contaminated environment, transforming them into a less damaging, harmless, and stable form [37]. In reality, because of the complex composition of petroleum pollutants, a single repair method often does not work well [41]. Soil pollution caused by high volatile TPH are generally treated by physical methods, such as soil vapor extraction (SVE) and air sparging (AS). For soils with low volatile TPH contamination, chemical, biological, or thermal treatment techniques are more commonly used [22]. Remediation of petroleum polluted soil can be broadly classified under biological, physical and chemical methods [40, 36].

Biological remediation is often used in the moderate oil-contaminated soils. Bioremediation is the use of biological agents, mainly microorganisms (e.g., yeast, fungi or bacteria) or their enzymes to destroy or reduce the concentration of hazardous wastes on a contaminated site [42]. The advantages of bioremediation methods include minimal on-site operational costs, no secondary pollution, and greater public acceptance [43, 41, 37]. Bioaugmentation involves the addition of microorganisms with pollutant-degrading Capabilities. Bioaugmentation improves the treatment of oil-contaminated water in Floating Treatment Wetlands (FTWs) by at least a factor of two, indicating that the performance of full-scale systems can be improved at only small costs [33]. Microbial remediation as a single microbial remediation faces difficulties, such as inconsistent remediation effects and substantial environmental consequences [37]. According to the type of organism, the bioremediation technology generally can be divided into three categories: microbial remediation, phytoremediation and plant-microbial technology [41]. Biopolymers are also viewed as effective and eco-friendly agents in soil modification [19].

Physical remediation processes used for petroleum hydrocarbon pollutants removal from soil are ultrasonication and floation [40]. Excavation of crude oil contaminated soil is the quickest and safe way but not a sophisticated and cheap method [5]. Physical methods aim to separate contaminant from the contaminated solid by exploiting the physical characteristic differences between the contaminant and the native soil [25].

Chemical methods such as the use of dispersants are most widely applied in oil-contaminated water bodies [42]. Chemical oxidation is an efficient method to remove dangerous wastes from the soil at the oil spilled sites. Chemical method is a quick way to treat contaminated soil [5, 24]. Several chemical compounds can be used as oxidants. They include: hydrogen peroxide, Fenton’s reagent, potassium or sodium persulfate, potassium or sodium dichromate, potassium permanganate [28]. There are a lot of studies which report remediation of petroleum polluted soil by the use of thermal decontamination, vapor extraction, surfactants or solvent flushing, chemical oxidation, steam stripping as well as biological treatment. Thermal methods showed great efficiency of 99%, in decontamination of organic polluted soils [36]. Soil washing is a simple and efficient technology that has been practiced successfully for many years for the effective removal of hydrocarbons. Soil washing usually employs different extractants such as acids, bases, chelating agents, electrolytes, oxidizing agents, and surfactants [10]. A ternary mixture of 5% 1-pentanol, 10% water, and 85% ethanol used in a three stage cross-current solvent washing process with contact time of 1 h per stage is capable of removing more than 95% of extractable PAHs [1].

High levels of polycyclic aromatic hydrocarbons (PAHs) in the soil can induce tumors, reproductive, development, and immunological problems in terrestrial invertebrates. BTEX (benzene, toluene, ethylbenzene, and xylene) can harm a person's personal neurological system, liver, kidneys, and respiratory system. Pollutants obstruct soil pores, alter the content and structure of soil organic matter, diminish the activity and variety of soil microbes and plants, and, as a result, endanger human health via the food chain. Exposure to petroleum and petroleum products, whether direct (breathing polluted air and direct contact with skin) or indirect (bathing in contaminated water and eating contaminated food), can cause significant health issues in people. Many petroleum pollutants, such as benzene and polycyclic aromatic hydrocarbons, are toxic, mutagenic, and carcinogenic. Some aromatics have a negative impact on human liver and kidney functioning, even causing cancer [37].

The word surfactant is an abbreviation of the term Surface active agents having dual characteristics of hydrophilicity and hydrophobicity [14, 21, 30]. Surfactants can be grouped based on the characteristic of the charge on an individual polarity. Anionic surfactants possess negative charge, mostly because of the presence of a sulphonate or a Sulphur group [39]. The anion in anionic surfactants is the carrier of the surfactant properties; it gets its negative charge from the presence of sulfonate, sulfate, phosphate ester, carboxylate, isethionate, soap, or taurate groups in the molecule, and the presence of this polar groups is the basis for classification. The general formulae of anionic surfactants are as follows: $C_nH_{2n+1}COO^{-}X^{+}$ (carboxylates), $C_nH_{2n+1}OSO^{-3}X^{+}$ (sulfates), $C_nH_{2n+1}SO^{-3}X^{+}$ (sulfonates), and $C_nH_{2n+1}OPO(OH)O^{-}X^{+}$ (phosphates), where n is in the range 8–16 atoms and the counterion X^{+} is usually Na^{+} [10].

Surfactant molecules exist with hydrophobic and hydrophilic moiety as a simple monomeric unit. As the concentration of the solution increases, these monomeric units tend to form aggregates at the solvent-surfactant interface forming a micelle structure. Such a phenomenon of micelle formation is termed as micellization, and the concentration at which this occurs is termed as critical micelle concentration (CMC). Petroleum contaminant is either adsorbed onto the grain of soil or trapped as a droplet in the aqueous zone. Depending on the nature of the contaminant, the removal of the petroleum oil from the soil environment by surfactant occurs by two primary mechanisms; solubilization, and mobilization [21]. Generally, mobilization occurs at a faster rate than the solubilization, as the contaminants are insoluble in nature. Also, the contaminants adsorbed on the rock grain are difficult to mobilize as they are unstable and tend to detach it from the emulsion system. In this case, the surfactants molecules dissolve the contaminant by the formation of Type-I microemulsion (two-phase system, where excess oil is surrounded by surfactant phase) [20]

MES homologues are readily biodegradable with percentage of biodegradation achieved for C12, C14 and C16 MES is 73% within 6 days, 66% within 8 days and 63% within 16 days, respectively, while linear alkylbenzene sulphonates (LAS) undergo 60% biodegradation within 8 days [4]. It is an important fact that the commercial implementation of the chemical surfactant based technology depends on the environmental properties (biodegradability and toxicity) of the surfactants [20]. Sodium lauryl sulfate (SLS), also known as sodium lauril sulfate or sodium dodecyl sulfate, is an anionic surfactant commonly used as an emulsifying cleaning agent in household cleaning products (laundry detergents, spray cleaners, and dishwasher detergent). Sodium lauryl sulphate (SLS) is a synthetic product that is broadly utilised in toothpaste [29].

Biosurfactant is made up of a hydrophobic and hydrophilic component. The polar part of biosurfactant can be an amino acid, a carbohydrate, and/or a phosphate group. Long chain fatty acid constitutes the nonpolar portion. Biosurfactants or Natural surfactants can be produced extracellular by a wide range of microorganisms including bacteria, fungi, and yeast. Bacillus salmalaya, Candida lipolytica, Pseudomonas aeruginosa, and Saccharomyces lipolytica are examples of microorganism able to produce biosurfactant. The hydrophobic portion of biosurfactant is due to the presence of long chain fatty acids groups, and it can also be a phosphate, alcohol, carboxylic acid, carbohydrate, amino acid or cyclic peptide [18]. Biosurfactants are grouped mainly based on their microbial origin or chemical contents/composition such as fatty acids, antibiotics, peptides, glycolipids, phospholipids, lipopeptides. Glycolipids consist of monosaccharides, disaccharides, trisaccharides, and tetra saccharides including glucuronic acid, galactose sulphate, galactose, mannose, glucose, and rhamnose. The glycolipids can be categorized as Trehalose lipids, Sophorolipids (produced by different strains of the yeast), and Rhamnolipids. Biosurfactants can be classified into two main categories based on the molecular weight they have, high-molecular weight polymers or bioemulsans and low-molecular-weight molecules called biosurfactants. Surfactin and rhamnolipids are low-molecular mass biosurfactants with molecular weight of 1036 and 802 Da, respectively. High molecular weight biosurfactant are generally polyanionic heteropolysaccharides containing proteins and polysaccharides. Extracellular lipopolysaccaharide biosurfactant produced by Acinetobacter calcoaceticus, Acinetobacter radioresistens KA53 are a high-molecular-weight bioemulsifier (1000 kDa and 1MDa). Hydrocarbons, oil wastes, olive oil, vegetable oils and carbohydrates are used as carbon sources for biosurfactant production [18]. TX100 surfactant can potentially and successfully be used for the remediation of soils contaminated with PAHs in the industrial sites [12].

The idea of going green has launched the use of renewable materials for surfactant synthesis resulting in green surfactants. This new class of biodegradable and biocompatible product is a response to the increasing consumer demand for products that are greener, milder and more efficient. Green surfactants are defined as biobased amphiphilic molecules obtained from nature or synthesized from renewable raw materials. Various renewable raw materials particularly triglycerides, carbohydrate sources and organic acids (produced by fermentation) serve as starting materials in surfactant synthesis, of which, triglycerides/sterols contribute to the hydrophobic part while sugars/amino acids contribute to the hydrophilic part of green surfactants [32]

Babalola *et.al*, 2021 used a slurry-phase bioreactor to remediate Ogoni land crude oil contaminated soil. P. aeruginosa and B. subtilis strain were found to be effective species of micro-organism for bioremediation.

Babalola *et.al*, 2020 evaluated the variations in factors affecting bioremediation and identified urea as effective agent in degrading crude oil soil contamination. pH of 6.5 to 8.5 was observed to be acceptable range for bioremediation.
Babalola *et.al*, 2021 applied urea as agent in remediating crude oil contaminated soil in Ogoni land and recorded 28.04% reduction.

Ojinnaka *et.al*, 2012 and Adipah, 2018 studied remediation of hydrocarbons in crude oil contaminated soils using Fenton’s reagent. The method was effective only in acidic medium.

Rehman *et.al*, 2021 looked at bioaugmentation-Enhanced Remediation of Crude Oil Polluted Water in Pilot-Scale Floating Treatment Wetlands. The degradation of contaminant was limited to few species of micro-organism that are not readily available.

Soleimani and Jaberi, 2014 compared biological and thermal remediation methods in decontamination of oil polluted soils. Biological method was noted to take a long time while thermal process was expensive.

Emmanuel *et.al*, 2019 used poultry dung (chicken manure) for Crude oil polluted soil remediation. The method depended on a limited species of microbes in the dung. Efficiency was 60%.

Ogbonna *et.al*, 2019 evaluated organic nutrient supplements and bioaugmenting microorganisms on crude oil polluted soils. The method was limited to a small range of microbes.
Jung *et.al*, 2016 characterized polyacrylamide solution for remediation of petroleum contaminated soils. The effectiveness of the biopolymer may be negatively be affected by temperature.

Njoku *et.al*, 2012 worked on phytoremediation of crude oil polluted soil: effect of cow dung augmentation on the remediation of crude oil polluted soil by glycine max. They noticed that at some point the micro-organism would leave degrading the petroleum and be degrading the cow dung.

Achugasim *et.al*, 2014 made use of Potassium permanganate as an oxidant in the remediation of soils polluted by Bonny light crude oil. The method was pH specific and also has the tendency of introducing a heavy metal like manganese into the soil.

Liu *et.al*, 2021 evaluated the effects of surfactants on the remediation of petroleum contaminated soil and surface hydrophobicity of petroleum hydrocarbon degrading flora. The observed that sodium dodecyl benzenesulphonate (SDBS), at high concentration had inhibitory effect on hydrocarbon degrading bacteria.

Daâssi and Almaghribi, 2021 studied soil microcosms for bioaugmentation with fungal isolates to remediate petroleum hydrocarbon contaminated soil. The method depends on a narrow availability of enzyme.

Ismail *et.al*, 2016 applied biosurfactants in environmental biotechnology; remediation of oil and heavy metal. Biosurfactants have not yet been produced in large scale and tested in the field.

Teka, *et.al*, 2022 and Kasman *et.al*, 2021 evaluated the effect of linear alkylbenzene sulphonate on bacterial population and hydrocarbon degradation in crude-oil polluted soil. It was observed that a high concentration of LAS in the absence of petroleum contaminant will be harmful to micro-organisms.

Adlina *et.al*, 2017 applied oil spill dispersant formulation from diethanolamine (dea) and methyl ester sulfonate (MES) for bioremediation process. The value of critical michelle concentration (CMC) for MES surfactant was found to be 0.9 % concentration. From the lab result, there was need to test the surfactant in field at pilot scale.

Benson *et.al*, 2016 studied the enhancement of crude oil polluted soil by applying single and combined cow-dung and hydrogen peroxide as remediating agents. Combining hydrogen peroxide did not have any advantage over single use of cow dung

Rosik-Dulewska *et.al*, 2015 used Hydrogen peroxide as a biodegradation stimulator in remediation processes of soils heavily contaminated with petrochemicals. After 60 days, there was 35% decomposition efficiency of aliphatic hydrocarbons (C8-C40), TPH and about 50% polycyclic aromatic hydrocarbons, PAH’s. Application of hydrogen peroxide to stimulate the process showed no relevant impact on the change of monoaromtic hydrocarbons (BTEX)

Radzuan, 2018 worked on biosurfactant production by fermentation of palm oil agricultural refinery waste. The process of culturing, isolating and purifying the micro-organism was found to be expensive.

There is an ongoing need to develop an efficient and environmentally safe process for remediation of petroleum contaminated soil, hence the motivation for this study.

2. Materials and Methods

2.1 Tools/ Equipment

A bench scale laboratory set up at the Chemial/ Petrochemical Engineering Department, Akwa Ibom State University, Mkpat Enin, Akwa Ibom State, Nigeria was used for the study. This comprised of: 4litre capacity stainless steel mixing vessel, 2800rpm hand held mixer, 1300W capacity heating system with temperature regulator, and thermometer.

2.2 Reagents/ Feedstock

Groundnut oil, Methanol (99.8%, BDH chemicals limited, Boole, England), Potassium hydroxide (KOH) (85% extra pure, Loba Cheme PVT Limited, India), Calcium oxide (CaO) (Lab grade, Lab Alley Essential Chemicals, Texas), Sodium hydrogen sulphite (NaHSO3) (Extra pure, Loba Cheme PVT Limited, India), n-hexane (99%, Loba Cheme PVT Limited, India) and methylene chloride (100%, Sydney Solvents, South Pennith). All chemical reagents used were of analytical grade. Ground nut oil was purchased at Nka Market, Eket, Akwa Ibom State, Nigeria.

2.3 Methods

Synthesis of the surfactant was carried out by modifying method used by Sahila *et.al*, 2020.

2.3.1 Transesterification

The transesterification process was be carried out by reacting groundnut oil with methanol in the ratio of 1:9 and KOH catalyst as much as 1% wt% of groundnut oil was used. KOH catalyst and methanol were first mixed to achieve homogeneity and then groundnut oil was added to the methoxide. The mixture was then heated and maintained at 60ºC with continous stiring for 10minutes. The glycerol formed was separated from the methyl ester. The glycerol was kept aside as feedstock for soap production in the crude state in order to create cost benefit for the process. The methyl ester was purified by hot water washing till the pH was neutral and then dried for the next process.

2.3.2 Sulphonation

The sulphonation process was carried out by reacting methyl ester with sodium bisulphite which has been dissolved in distilled water with a mole ratio of 1:2. The CaO catalyst used was 1.5% by weight of oil. Then the mixture was heated with constant stiring and maintained at a temperature of 100ºC for 40minutes. Methyl ester sulphonate was separated from the CaO catalyst and the remaining sodium bisulphite. An interesterification reaction was carried out in which the methyl ester sulphonate was then purified by adding methanol as much as 35% v/v and heated with constant stiring for 10minutes with temperature maintained at 55ºC. After that, evaporation was carried out to evaporate the methanol and the remaining water. The next step was neutralization process which was carried out by adding 20% NaOH to the methyl ester sulphonate until pH reaches 6 - 7. The compounds present in the synthesized surfactant were analyzed using (GC-MS).

2.4 Pilot Scale Remediation Study

This was conducted following method used by Ogbonna *et.al*, 2019. The test was done in a simulated site at the Akwa Ibom State University, Akpaden Campus, Nigeria. Randomized Complete Block Design (RCBD) of the land was partitioned into 2 blocks of 2feet by 1 foot each. One of these plots was designated as control and polluted with fresh engine oil without remediation. The other block was contaminated with fresh engine oil and the synthesized surfactant applied for remedation. 1litre of fresh engine oil was used to contaminate each block of the soil. The produced surfactant was applied to the soil and the soils sampled and tested after for 3weeks for performance of the produced surfactant. GC-FID method was used to monitor the effectiveness of the surfactant.

2.5 GC Analysis of the Soil and Surfactant

The soil was characterized using Agilent 6890 GC-FID and the surfactant was characterized using Agilent GCMS 6890-5975B. This was done by following US EPA 3550 Standard. Extraction solvents of n-hexane and methylene chloride were prepared in the ratio 3:1. 10g of aliquot of well mixed sample was measured into a solvent rinsed beaker. Wet samples were dried with anhydrous sodium sulphate until particles were loosed. The anydrous sodium sulphate was the drying agent for the sample. 20ml to 50ml of the solvent was mixed with the sample. The mixture was spiked with ortho-Terpenyl, shaked in a vortex mixture for 1 - 5 min and placed in a sonicator for 5 - 10 min at about 70°C. The extraction was done with a glass wool and anhydrous sodium sulphate. The extract was transferred to a Teflon-lined screw cap vial ready for analysis.

3. Results and Discussion

3.1 Characterization of Synthesized Methyl Ester Sulphonate Surfactant

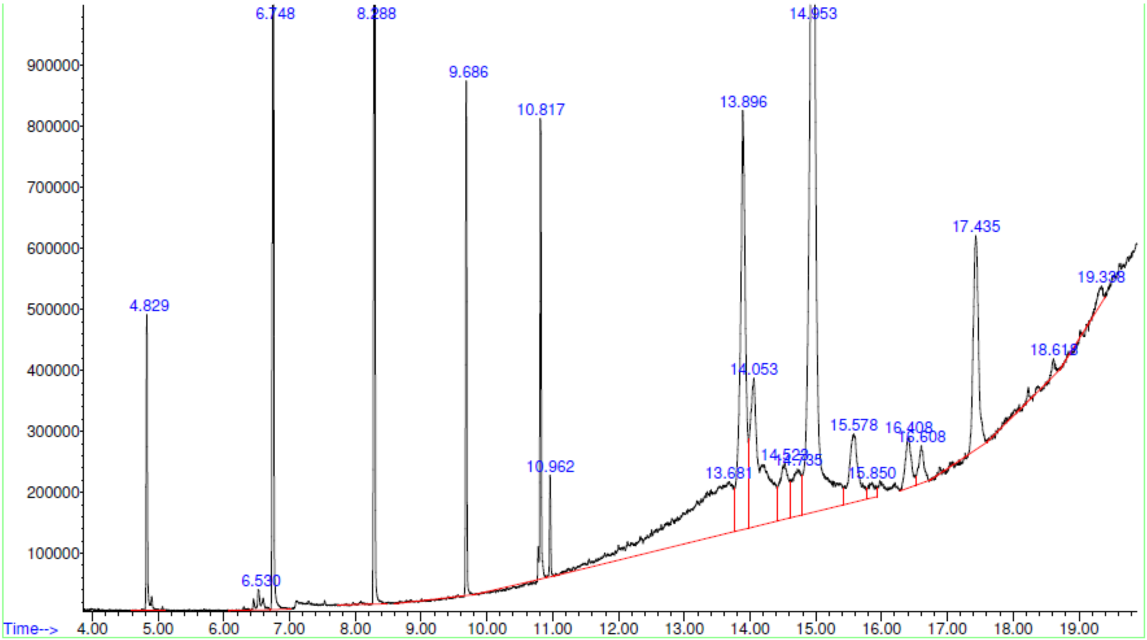

Figure 1: GC-MS Result showing MES Surfactant

Table 1: Compounds present in the Synthesized Surfactant

S/N	Compounds	Comment
1.	2-Undecanone	Molecular weight: 170.2918. Also known as methyl nonyl ketone (MNK). It is soluble in ethanol, benzene, chloroform, and acetone.
2	2-Dodecanone	Molecular weight: 184. 3184. Methyl decyl ketone. 2-Dodecanone is a very hydrophobic molecule, practically insoluble (in water), and relatively neutral.
3	2-Tridecanone	Methyl undecyl ketone. Molecular weight: 198.3449.
4	Dodecanoic acid, methyl ester	Molecular weight: 214.3443. Dodecanoic acid methyl ester. It has been used in selective synthesis of the secondary amide surfactant, N-methyl lauroylethanolamide.
5	Methyl tetradecanoate	also known as myristate methyl ester. myristic acid methyl ester. Palmitoyl-myristoyl-phosphatidylcholine is one of the major components of surfactant.
6	Tridecanoic acid, 12-methyl-, methyl ester	Molecular weight: 242.3975. 12-methyl Tridecanoic Acid methyl ester.
7	Hexadecanoic acid, methyl ester	Molecular weight: 270.4507. Methyl palmitate
8	7-Octadecenoic acid, methyl ester	Molecular Weight 296.5. Methyl 7-octadecenoate
9	9-Octadecenoic acid, methyl ester,	Molecular weight: 296.4879. Methyl-trans-oleate.
10	Methyl stearate	Molecular weight: 298.50. Methyl stearate is used as a nonionic surfactant, thereby enhancing the solubility of chemicals by dissociating aggregates and unfolding proteins.

The synthesized surfactant contained compounds which are effective and environmentally friendly. This includes alkanones, carboxylic acids and esters, as shown in fig. 1 and summarized in Table 1. GCMS results revealed that the surfactant has a blend of anionic and nonanionic blend of surface active agent. This provides the lipophilic tail which is soluble in petroleum pollutant and the lipophobic head which dissolves in water. As a result the surfactant possesses the ability emulsify and reduce surface tension between the soil and bonded contaminant. It also has the potency of breaking down the large hydrocarbon content of the pollutant into simpler ones. The surfactant is free from components that will pose threat to the environment as residual products. All the components revealed in the surfactant are non-toxic and biodegradable.

3.2 Simulated Petroleum Contaminated Soil Remediation Study

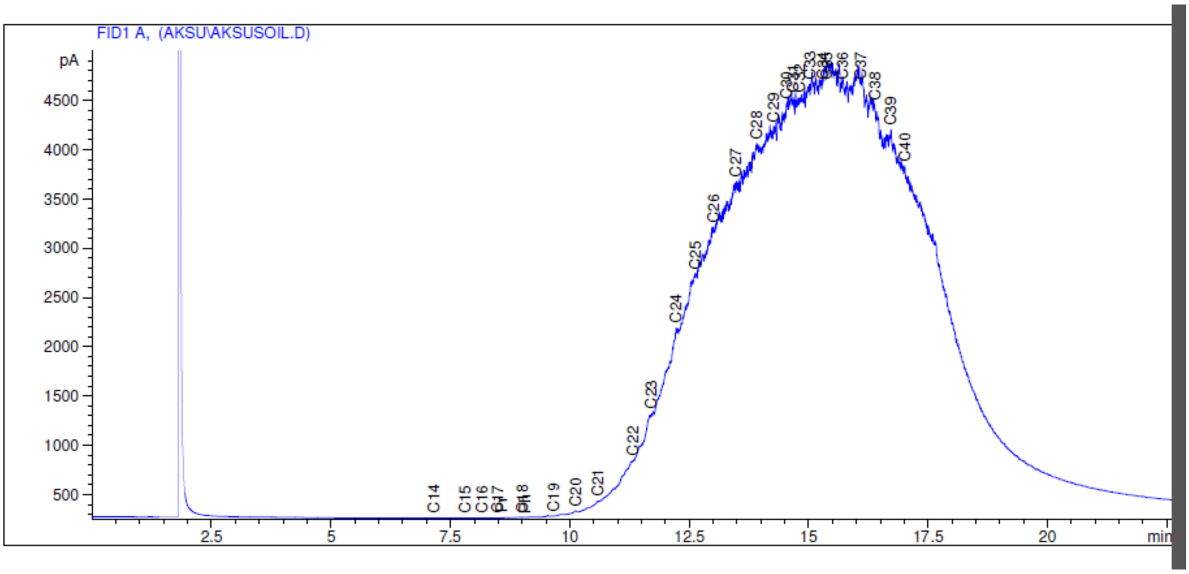

Figure 2: TPH peak in the contaminated control soil

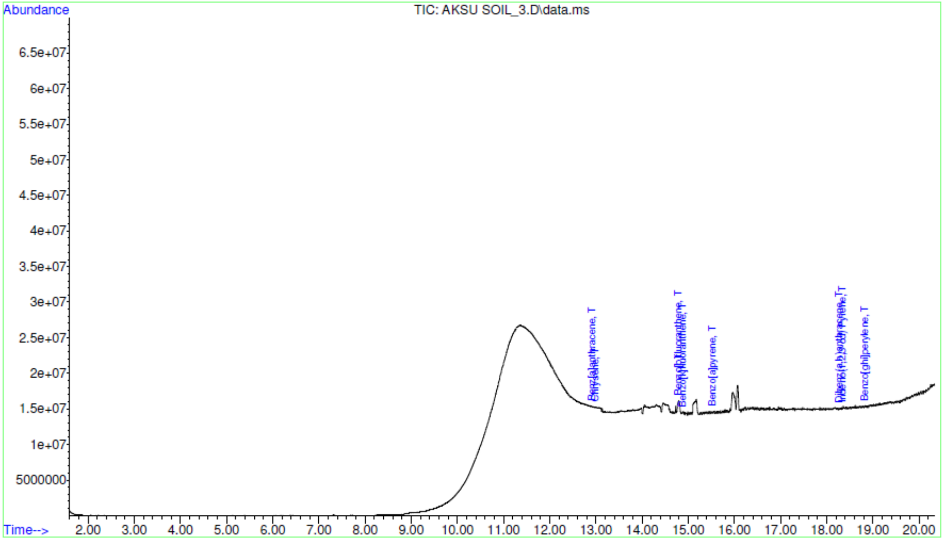

Figure 3: PAH peak in the contaminated control soil

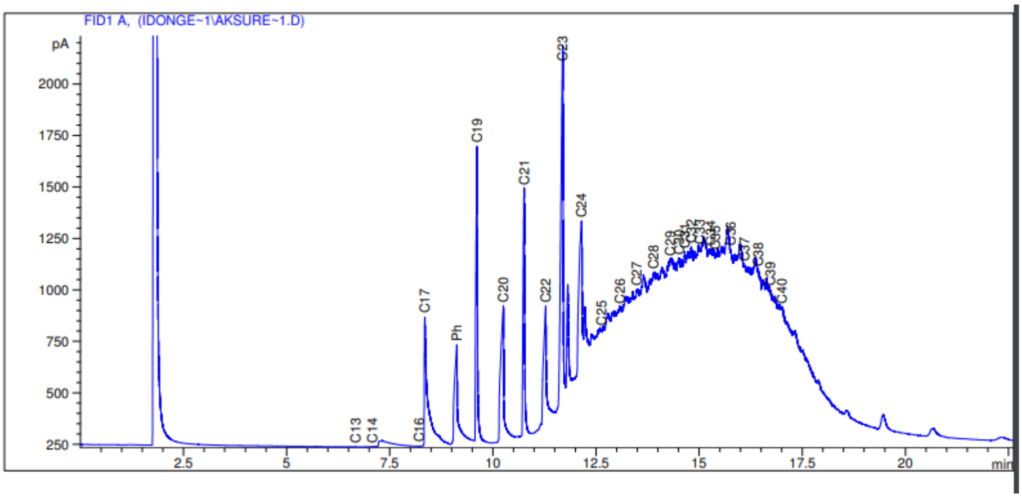

Figure 4: TPH peak in the remediated contaminated soil

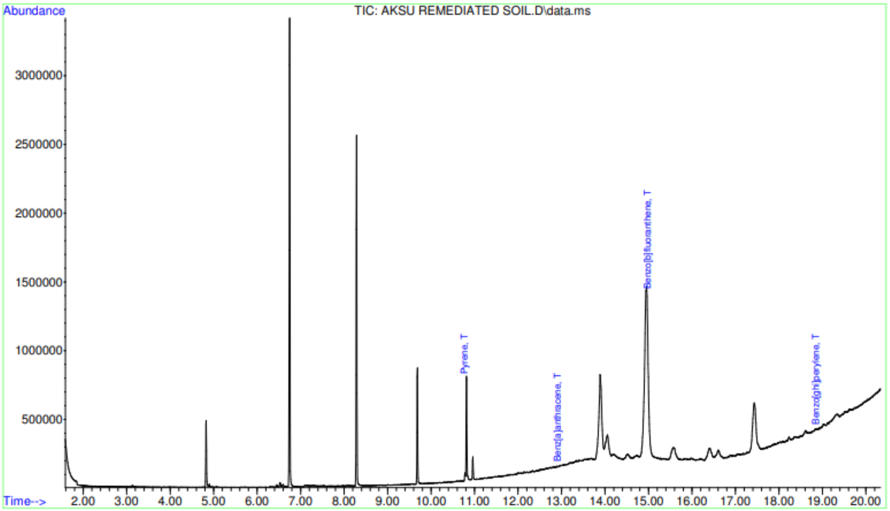

Figure 5: PAH peak in the remediated contaminated soil

The synthesized surfactant was found to be effective in remediating petroleum polluted soil in the simulated area as shown in fig. 2, fig. 3, fig. 4, fig. 5 and in table 2.

Table 2: Percentage reduction in petroleum contamination

S/N	Pollutant	Chemical Concentration in Control Soil (mg/kg)	Chemical Concentration in Remediated soil (mg/kg)	Percentage Pollutant Remediated (%)
1	Total Petroleum Hydrocarbon (C14 to C40)	28, 241.5	10,810	61.7
2	Benz[a]anthracene	8.61	0.16	98.1
3	Chrysene	8.85	0	100
4	Benzo[b]fluoranthene	25.08	0.84	96.7
5	Benzo[k]fluoranthene	24.93	0	100
6	Benzo[a]pyrene	17.65	0	100
7	Dibenz(a,h)anthracene	19.15	0	100
8	Indeno(1,2,3-cd) Pyrene	23.43	0	100
9	Benzo[ghi]perylene	7.00	4.27	39

3.3 Simulated Petroleum Contaminated Soil Remediation Study

The synthesized surfactant was found to be effective in remediating petroleum polluted soil in the simulated area as shown in table 2.

There was a total reduction of total petroleum hydrocarbon (TPH) upto 61.7% and 96.0% reduction in PAH. The TPH value of the remediated soil was still higher than the EGASPIN stipulated range for TPH in a remediated site. PAHs were effectively remediated - from 134.7ppm to 5.27ppm which was far below EGASPIN standard for PAH. The values of TPH and PAH stipulated by EGASPIN, the regulatory agency in Nigeria are 5000mg/kg and 40mg/kg respectively [17]. The moderate remedation effectiveness of the synthesized surfactant is linked to the high pollution load at the simulated site. Revealing that the surfactant can be effectively used to remediate a site with a moderate TPH value or used to reduce the petroleum content of heavy petroleum contamination before other remediation methods are employed. The high reduction of PAH value in the simulated site indicates that the surfactant can be used to tackle a broad range of PAH chemicals in polluted sites. Though PAH pollutants were effectively remediated, Benzo[ghi]perylene however showed lowest level of reduction which is linked its complexed stable structure. Revealing that Benzo[ghi]perylene is typical persistent organic pollutant (POP) and hence further reseach work is required to effectively remediate it from petroleum contaminated sites.

The synthesized surfactant from this research competes favourably with past works. Tween80, rhamnolipid and TRS-1 removed petroleum hydrocarbon upto 65% (Liu *et.al*, 2021). Non-ionic surfactant achieved 52% - 72% TPH reduction. A75% - 84% degradation of artificially added polycyclic aromatic hydrocarbon (PAHs) occurred after 106 days [6]. The removal efficiency of heavy metals and PAHs were found to be low as the volume of used motor oil increased [15].

4. Conclusions

Remediation method that is promising for entire range of petroleum sector is surfactant assisted. Surfactant has proven to be able to break that large petroleum molecule and enable it to be converted into less harmful easily degradable substances. Methyl ester sulphonate is a green surfactant, ecofriendly, less toxic, and biodegradable option which can be locally synthesized for application in the petroleum sector.

This work demonstrates that a locally produced Methyl Ester Sulphonate surfactant is capable of remediating petroleum polluted soil and can compete favourably with imported

Methyl Ester Sulphonate (MES), Linear Alkyl Benzene Sulphonate (LAS), and Sodium Dodecyl Sulphate (SDS). The raw material can be sourced locally from the renewable abundance of vegetable and animal oil, including waste oil, non-edible and non-food grade options.

MES is recommended as surfactant for petroleum spill dispersant as well as remediating medium for petroleum polluted soils. A pilot plant should be designed to gather process information towards commercial production of methyl ester sulphonate for use as petroleum remediation solution to the oil impacted Niger Delta. Various waste oil, non-food grade and nonedible vegetable and animal source triglyceride should be harnessed as feedstock for the manufacture of this green surfactant.

References

[1] **Abdelhafeeza, I. A., El-Tohamya, S. A., Abdul-Malikb, M. A., Abdel-Raheema, S. A. and El-Achugasim, O., Ojinnaka, C. M and Osuji, L. C. (2014)**. Potassium Permanganate as an Oxidant in The Remediation of Soils Polluted by Bonny Light Crude Oil. Sky *Journal of Soil Science and Environmental Management* Vol. 3(2), pp. 4 - 19

[2] **Adipah, S. (2018).** Remediation of Petroleum Hydrocarbons Contaminated Soil by Fenton's Oxidation. Journal of Environmental Science and Public Health. Volume 2, Issue 4

[3] **Adlina, S., Hambali, E. and Yan, M. (2017).** Oil Spill Dispersant Formulation from Diethanolamine (DEA) and Methyl Ester Sulfonate (MES) for Bioremediation Process. Chemical and Process Engineering Research. Vol.53.

[4] Afida, S., Razmah, G. and Zulina, A.M. (2016). Biodegradation of Various Homologues of Palm-based Methyl Ester Sulphonates (MES). Sains Malaysiana 45(6)(2016): 949–954

[5] **Ahmad, A. A., Muhammad, I., Shah, T., Kalwar, Q., Zhang, J., Liang, Z., Mei, D., Juanshan, Z., Yan, P., Zhi, D. X. and Rui-Jun, L. (2020).** Remediation Methods of Crude Oil Contaminated Soil. World Journal of Agriculture and Soil Science. Volume 4-Issue 3.

[6] **Asquith, E. A., Geary, P. M., Nolan, A. L., and Evans, C. A. (2012)**. Comparative Bioremediation of Petroleum Hydrocarbon-contaminated Soil by Biostimulation, Bioaugmentation and Surfactant Addition. *Journal of Environmental Science and Engineering.* A1: 637 - 650

[7] **Babalola, R., Efeovbokhan, V. E., Atiku, Y. O., Usoro, U. E., Ibeh, M. A., Alagbe, E. E., Omoleye, J. A., Abatan, O. G. (2021)**. Slurry-Phase Bioremediation of Ogoni Land Crude Oil Contaminated Soil. International Conference on Engineering for Sustainable World. 1107: 1 - 11

[8] **Babalola, R., Atiku, Y. M., Ukeme, I. O, Duff, I. D. (2020).** Evaluation of Variations in Factors Affecting Bioremediation. APWEN 2020 National Conference. Vol. (37): 10 - 21

[9] Babalola, R., Atiku, Y., Isaac, U., Udoetuk, E., and Aniediong, U. (2021). Assessment of Changes in Factors Affecting Bioremediation. Journal of Engineering, Science, and Technology. 5(1): 97 - 108

[10] **Befkadu, A. A. and Chen, Q. Y. (2018)**. Surfactant-enhanced soil washing for removal of petroleum hydrocarbons from contaminated soils: A review. Pedosphere. 28(3): 383–410.

[11] **Benson, D. M., Ochekwu, E. B., and Tanee, F. G. (2016).** Enhancement of Crude Oil Polluted Soil by Applying Single and Combined Cow-Dung and Hydrogen Peroxide as Remediating Agents. J. Appl. Sci. Environ. Manage. Vol. 20 (4) 1137-1145

[12] **Chong Z. Y., Liao, X. Y., Yan, X. L., Sun, L., Zhao, D. and Liang, T. (2013)**. Enhanced Desorption of PAHs from Manufactured Gas Plant Soils Using Different Types of Surfactants. Pedosphere 24(2): 209–219

[13] **Daâssi, D. and Almaghribi, F. Q. (2021)**. Soil Microcosms for Bioaugmentation With Fungal Isolates to Remediate Petroleum Hydrocarboncontaminated Soil. Research Square.

[14] **Dave, N. and Joshi, T. (2017)**. A Concise Review on Surfactants and Its Significance. I*nternational Journal of Applied Chemistry*. ISSN 0973-1792 Volume 13, Number 3 pp. 663-672. Research India Publications

[15] **Dike B. U., Okoro, B. C., Nwakwasi, N. N. and Agbo, K. C. (2013)**. Remediation of Used Motor Engine Oil Contaminated Soil: A Soil Washing Treatment Approach. *Civil & Environmental Engineering.* 3 (1): 1-3

[16] **Emmanuel, O. O., Tope, O. D, Kayode, O. and Olayinka, S. (2019)**. Crude oil polluted soil remediation using poultry dung (chicken manure). *African Journal of Environmental Science and Technology.* Vol. 13(10), pp. 402-409

[17] **Gbarakoro, T. and Bello, A. (2022).** Assessment of the Concentration of Petroleum Hydrocarbon in Oily Wastes Residual Ash at Bodo-Ogoni Remediation Site, Nigeria. *Journal of Geoscience and Environment Protection.* 10: 1 - 15

[18] **Ismail, S., Usman, M. M., Dadrasnia, A., Lim, K. T. and Mahmud, A. F., (2016).** Application of biosurfactants in environmental biotechnology; remediation of oil and heavy metal. AIMS *Bioengineering*, 3(3): 289-304.

[19] **Jung, J., Jang, J. and Ahn, J.(2016).** Characterization of a Polyacrylamide Solution Used for Remediation of Petroleum Contaminated Soils. *Materials*, 9, 16

[20] Karthick, A., Roy, B., Chattopadhyay, P. (2019). A review on the application of chemical surfactant and surfactant foam for remediation of petroleum oil contaminated soil. *Journal of Environmental Management 243* (2019) 187–205

[21] **Khodadadi, A., Ganjidoust, H. and Razavi, S. N. (2012)**. Treatment of crude-oil contaminated soil using biosurfactants. *Journal of Petroleum and Gas Engineering* Vol. 3(6), pp. 92-98,

[22] **Lin, M. S., Huang, C. Y., Lin, Y. C., Lin, S. L., Hsiao, Y. H., Tu, P. C., Cheng, P. C., and Cheng, S. F. (2022).** Green Remediation Technology for Total Petroleum HydrocarbonContaminated Soil. *Agronomy*, 12, 2759.

[23] **Liu, J., Xu, L., Zhu, F., Jia, S. (2021).** Effects of Surfactants on The Remediation of Petroleum

Contaminated Soil and Surface Hydrophobicity of Petroleum Hydrocarbon Degrading Flora. *Environmental Engineering Resources.* Volume 26(5)

[24] **Mambwe, M., Kalebaila, K. K., Johnson, T. (2021)**. Remediation technologies for oil contaminated soil. *Global Journal of Environmental Science and Management (GJESM).* 7(3): 419-438, Summer 2021

[25] **Marchand, C. (2017)**. Phytoremediation of Soil Contaminated with Petroleum Hydrocarbons and Trace Elements. Doctoral dissertation, Department of Biology and Environmental Science, Linnaeus University, Kalmar. Växjö: Linnaeus University Press

[26] **Njoku, K. L., Akinola, M. O. and Oboh, B. O. (2012)**. Phytoremediation Of Crude Oil Polluted Soil: Effect Of Cow Dung Augmentation On The Remediation of Crude Oil Polluted Soil By Glycine Max. *Journal of Applied Sciences Research*, 8(1): 277-282

[27] **Ogbonna, D. N., Ekweozor, I. K. E., Nrior, R. R. and Ezinwo, F. E. (2019).** Evaluation of Organic Nutrient Supplements and Bioaugmenting Microorganisms on Crude Oil Polluted Soils. *Current Journal of Applied Science and Technology.* 38(6): 1-19

[28] **Ojinnaka, C., Osuji, L. and Achugasim, O. (2012).** Remediation of hydrocarbons in crude oil-contaminated soils using Fenton's reagent. *Environmental Monitoring and Assessment* 184:6527–6540

[29] Pereira, A. C., Walmsley, A. D. (2019) Games in dental education: playing to learn or learning to play? Br Dent J 2019; 227: 459–460.

[30] **Qadariyah, L., Sahila, S., Sirait, C., Purba, C. P. E., Bhuana, D. S., and Mahfud, M. (2022).** Surfactant Production of Methyl Ester Sulfonate from Virgin Coconut Oil using Aluminum Oxide with Microwave Assistance. *International Journal of Technology* 13(2) 378-388

[31] Radzuan, M. N. (2018). Biosurfactant Production by Fermentation of Palm Oil Agricultural Refinery Waste Student thesis: PhD. University of Manchester, UK

[32] **Rebello, S., Asok, A. K., Mundayoor, S. and Jisha, M. S. (2014)**. Surfactants: Toxicity, Remediation and Green Surfactants. *Environmental Chemistry Letters* (2014) 12:275–287

[33] **Rehman, K., Arslan, M., Müller, J. A., Saeed, M., Imran, A., Amin, I., Mustafa, T., Iqbal, S. and Afzal, M. (2021).** Bioaugmentation-Enhanced Remediation of Crude Oil Polluted Water in Pilot-Scale Floating Treatment Wetlands. *Water*. 13, 2882. https://doi.org/10.3390/w13202882.

[34] **Rosik-Dulewska, C., Krzyśko-Łupicka, T., Ciesielczuk, T., Kręcidło, Ł. (2015)**. Hydrogen peroxide as a biodegradation stimulator in remediation processes of soils heavily contaminated with petrochemicals. *Polish Journal of Chemical Technology*, 17, 2, 17 — 22

[35] **Sahila, S., Qadariyah, L., Mahfud, M. (2021).** The Study on Factors Affecting the Synthesis of Methyl Ester Sulfonate from Palm Oil using CaO Catalyst with Microwave-Assisted. *Journal of Physics: Conference Series.* 1845 (2021) 012004

[36] **Soleimani, M. and Jaberi, N. (2014).** Comparison of Biological and Thermal Remediation Methods in Decontamination of Oil Polluted Soils. *Journal of Bioremediation & Biodegradation.* 5:3

[37] **Sui, X., Wang, X., Li, Y. and Ji, H. (2021)**. Remediation of Petroleum-Contaminated Soils with Microbial and Microbial Combined Methods: Advances, Mechanisms, and Challenges. *Sustainability* 13, 9267. https://doi.org/10.3390/su13169267

[38] **Teka, G. E., Barika, P. N., Peekate, L. P. (2022).** Effect of Linear Alkylbenzene Sulphonate on Bacterial Population and Hydrocarbon Degradation in Crude-oil Polluted soil. *Journal of Advances in Microbiology.* 22(1): 24 - 31

[39] **Usman, M. M., Dadrasnia, A., Lim, K. T., Fahim, Mahmud, A., Ismail, S. (2016).** Application of biosurfactants in environmental biotechnology; remediation of oil and heavy metal. *AIMS Bioengineering*, 3(3): 289-304.

[40] **Varjani, S. J. (2017).** Remediation Processes for Petroleum Oil Polluted Soil. *Indian Journal of Biotechnology.* 16: 157 - 163

[41] **Wang, S., Xu, Y., Lin, Z., Zhang, J., Norbu, N., Liu, W. (2017).** The Harm of Petroleum-Polluted Soil and its Remediation Research. Green Energy and Sustainable Development I. *AIP Conference Proceedings* 1864, 020222 (2017); https://doi.org/10.1063/1.4993039

[42] **Yan, L. (2012).** The use of plants, including trees, to remediate oil contaminated soils: a review and empirical study. Thesis submitted for a M.Sc. degree in Forest Ecology and Management. University of Helsinki

[43] **Yu, Y. , Zhang, Y., Zhao, N., Guo, J., Xu, W., Ma, M. and Li, X. (2020).** Remediation of Crude Oil-Polluted Soil by the Bacterial Rhizosphere Community of Suaeda Salsa Revealed by 16S rRNA Genes. *International Journal of Environmental Research and Public Health.* 17, 1471; doi:10.3390/ijerph17051471 www.mdpi.com/journal/ijerph