

A review on green remediation techniques for hydrocarbons and heavy metals contaminated soil

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ABSTRACT

Organic pollutants cause many environmental problems to our environment because of their toxicity, non-degradation and ability to long-range transport. The most common organic pollutants are known as persistent organic pollutants (POPs) and are known as hydrocarbons. Effective techniques for the removal of hydrocarbons and heavy metals from soil have drawn great attention. Remediation techniques represent one of the most important of these techniques because of their gentle impact on the environment. The study highlights numerous methods for Physical and chemical remediation techniques with explanation of the ability of some plants and agricultural wastes for remediation.

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1. Introduction

Oil is the largest source of contamination of soil and water in the world despite its modernity and oil pollution occurs when oil leaking materials to soil or water.^{1,2} This pollution affects soil structure itself and microorganism such as bacteria and fungi, as well as, on the roots of plants.³ Remediation of oil contaminated soil is considered one of the main challenges which facing scientists. High costs, complexity, destruction of soil texture and characteristics and secondary pollution of underground water of chemical and physical remediation are obstacle to their use.⁴ On the other hand, bioremediation is a promising technology which uses plants and microorganism for remediation organic and inorganic pollutants which is a low cost, simple, highly efficient, and safe.⁵

2. Impact of oil contaminants on soil and the environment

Soil pollution from petroleum may be caused by oil exploitation, oil transportation, oily wastewater discharge and irrigation, as well as incomplete combustion of petroleum products, etc.⁶ This practice adversely affects plants, microbes and aquatic lives because of the large amount of hydrocarbons and highly toxic polycyclic aromatic hydrocarbons contained in these oils.^{7,8} Oil contaminated soil is unsuitable for agricultural, residential or recreational uses that has become a major

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environmental issue in many industrialized countries. Furthermore, soil pollution may cause enormous economic loss, ecological disaster and destroy agricultural production.⁹

Pollution of the soil with petroleum derivatives is often observed in municipal soils, around industrial plants and in areas where petroleum and natural gas are obtained.^{10,11} Changes in soil properties due to contamination with petroleum derived substances can lead to water and oxygen deficit as well as shortage to available forms of nitrogen and phosphorous.¹²

Prolonged exposure to high oil concentration may cause the development of liver or kidney disease, possible damage to the bone marrow, and an increased risk of cancer.¹³⁻¹⁵

2.1 Hydrocarbons.

Accidental contamination of soil with petroleum hydrocarbons results from oil production and shipping. About 8.8 million metric tons of oil are spilled on land each year.¹⁶ Hydrocarbon components have been known to belong to the family of carcinogens and neurotoxic organic pollutants.¹⁷ Hydrocarbon contaminates the air, soil, freshwater (surface water and groundwater) especially by polycyclic aromatic hydrocarbons (PAHs) which have drawn public concerns because many PAHs are toxic, mutagenic, and carcinogenic.¹⁸⁻²⁰ The PAHs toxicity is reported to increase as molecular weight increases and with increase in alkyl substitution in the aromatic ring.²¹ The hydrocarbons spread horizontally on the groundwater surface thereby causing extensive ground water contamination.²² (The toxicity of petroleum hydrocarbons is strongly correlated with the lower boiling-point fractions and especially with those within the C10–C19 range. Some of metabolic compounds such as aromatic ketones, aldehydes, carboxylic acids, fatty acids, esters, also contributed to the biota toxicity of petroleum pollutants. The toxicity of organic contaminated soil can be evaluated using Microtox, earthworm, and seed germination assays.⁶

Total petroleum hydrocarbon (TPH) is a complex mixture composed of a variety of materials, mainly saturated hydrocarbons, aromatic compounds, asphaltenes and resins.⁶ In the severely polluted soil, high concentrations of total petroleum hydrocarbons (TPH) inhibited seed germination and create nutrient-deficient conditions, where the plants cannot survive. Therefore, certain soil environmental conditions (e.g., oxygen permeability, water availability, nutrient sufficiency) need to be improved for effective rhizodegradation.¹ Crude oil, used engine oil (spent oil) and diesel are considered the main sources of hydrocarbon contaminants.

2.1.1 Crude oil.

The amount of natural crude oil seepage was estimated to be 600,000 metric tons per year with a range of uncertainty of 200,000 metric tons per year.²³ Crude oil when spilled on the land, affects the physicochemical properties of the soil such as temperature, structure, nutrient status and pH. Crude oil hampers proper soil aeration as oil film on the soil surface acts as physical barrier between air and soil thereby causing a breakdown of soil texture followed by soil dispersion. Crude oil destroys soil microorganisms causing reductions in biomass. The damaging effects are due to suffocation and toxicity of the crude oil.²⁴ Crude oil changes the soil's redox potential ratio and increases the soil's pH. Thus, as crude oil pollution levels increase, soil pH also increases. The presence of PAHs like acenaphthene, pyrene and anthracene compounds in the crude oil suspected to increase the risk of various types of cancer.²⁵

2.1.2 Diesel.

Among petroleum products, diesel has become one of the most common organic pollutants of large soil surfaces, and eventually is considered a major environmental problem due to its a complex mixture of alkanes and aromatic compounds that are frequently reported as soil contaminants leaking from storage tanks and pipelines or released in accidental spills.^{26,27}

2.1.3 Spent engine oil.

As the usage of various kinds of automobiles and machinery vehicles in recent times increased, the use of engine oil increased and became one of the major environmental problems.²⁸ Numerous chemicals are formed when the oil is exposed to high temperatures and pressures inside the engine. The chemicals found in used engine oil vary according to the brands and types of engine used, the mechanical condition of the engine that it comes from, the various sources (automobile, airplanes, trains, ships, tractors or lawn mowers) of the used oil and the number of kilometers driven between oil changes.²⁹ Spillages of used engine oils such as jet fuels contaminate natural environment with hydrocarbons.³⁰ Used motor oil is managed as an auxiliary fuel, re-refined, incorporated into asphalt, and disposed in landfills.⁴ Used lubricating oil contains several toxic components, due to physical and chemical reactions occurring during its use, such as chlorinated and aromatic hydrocarbons e.g. benzene, toluene, xylene and Polychlorinated biphenyls. Additionally, it contains impurities such as heavy metals e.g., zinc, barium, chromium, copper, arsenic, calcium, aluminum, nickel and vanadium that could contribute to chronic hazards including mutagenicity and carcinogenicity.³¹⁻³³

Millions of gallons are disposed in trash, on land or into sewers, with the potential for contaminating soil, groundwater and surface water.³⁴ In the United States, approximately 800 million gallons of used motor oil are recycled annually.³⁵ Also,

in Nigeria and some developing countries, about 20 million gallons of waste engine oil are generated annually from mechanic workshops and discharged carelessly into the environment.^{36,37} According to EPA,³⁸ only 1 liter of used engine oil is enough to contaminate one million gallons of freshwater.

2.2 Heavy metals.

Among the heavy metals found in unused lubricating oils: vanadium, lead, aluminum, nickel and iron in unused lubricating oils, with high values in used ones.³¹ Some heavy metals are dangerous to health or to the environment (e.g. mercury, cadmium, lead, chromium), some may cause corrosion (e.g. zinc, lead), some are harmful in other ways (e.g. arsenic may pollute catalysts). Some of these elements are actually necessary for humans in minute amounts (cobalt, copper, chromium, manganese, nickel) while others are carcinogenic or toxic, affecting, among others, the central nervous system (manganese, mercury, lead, arsenic), the kidneys or liver (mercury, lead, cadmium, copper) or skin, bones, or teeth (nickel, cadmium, copper, chromium).²

Heavy metals may adversely affect certain tissues, reproduction and development.³⁹ This may also cause anemia, nervous system disorders and depressed immune systems, resulting in mortality and effects on population levels.

Chromium which is a heavy metal component of spent engine oil has been designated as a priority pollutant and found to be toxic, carcinogenic, and teratogenic when present at high concentration. Hexavalent chromium has a high tendency to bind with oxygen, and unless it is rapidly reduced, it can oxidatively damage the DNA via the production of free radicals. It has been reported that hexavalent chromium causes lung cancer, chromate ulcer, perforation of nasal septum, and kidney damage in humans, and it is also toxic to other organisms as well.⁵ Copper is widely used in engine parts due to its high ductility and thermal conductivity. Copper is an essential nutrient for plants and is a required constituent in many enzyme systems.⁴⁰ However, it can also be phytotoxic at high concentrations.

Small quantities of Ni (0.01 to 5 $\mu\text{g/g}$ dry wt) are essential for some plant species. On the other hand, Ni is not as important for plant metabolism as Zn and Cu. However, same as with other heavy metals, high Ni concentrations may turn toxic to plants.⁴¹ Nickel exposure causes formation of free radicals in various tissues in both human and animals which become neurotoxic, genotoxic, reproductive toxic, pulmonary toxic, nephrotoxic, hepatotoxic and carcinogenic agent.⁴²

3. Methods for recycling and utilization of used engine oil

Lubricating oil is used in automobile engines to lubricate moving parts of the engine, reducing friction, protecting against wear, and removing contaminants from the engine, act as a cleaning agent, and act as an anticorrosive and cooling agent. It picks up several impurities and additional components from engine wear. These components include metal particles (iron, steel, copper, lead, zinc, etc.) and other compounds of barium, sulfur, water, dirt, burnt carbon, and ash, most of them are highly toxic in nature; therefore these contaminants must be separated in order to reuse the engine oil.⁴³ Recycling of such contaminated materials will be beneficial in reducing engine oil costs. In addition, it will have a significant positive impact on the environment and it is considered a valuable resource and a vital source of energy.^{44,45} Recycling used lubricants is not an altogether new idea, there are many recycling processes in use nowadays include; solvent extraction, solvent extraction followed by adsorption, desludging and adsorption processes.⁴⁵ Several authors investigated ability of solvent extraction such as butanol, propane and butanone either as single solvent or composite solvent and distillation for recycling and improving the characteristics of used engine oil.^{43,46,47} Various methods for recycling purposes such as distillation/clay, acid/clay, acid, and activated charcoal/clay treatment methods.⁴⁸ The results showed that the distillation/clay and activated charcoal/clay methods were the best in terms of recovery of the oil after treatment and recovered about 80% of used lubricating oil. Recently, a technology has been invented to recycle a waste automotive engine oil using microwave-heated pyrolysis.⁴⁹ Examination of the composition of the oils showed the formation of light aliphatic and aromatic hydrocarbons that could also be used as a chemical feedstock. The oil product showed significantly high recovery (90%) of the energy present in the waste oil.

4. Remediation techniques for hydrocarbons contaminated soil

Remediation techniques include isolation and containment, mechanical separation, pyro-metallurgical separation, permeable treatment wall, soil flushing, molecular and phase separation, chemical destruction, soil washing, vapor extraction, electro kinetics and biodegradation. All these techniques can be successfully applied if the physicochemical properties of pollutants and soil particles are well understood before selecting any method.³³

4.1 Physical and chemical remediation techniques.

There are many chemical and physical techniques for remediation of contaminated soils,⁴ like soil washing, vapor extraction, etc. All these remediation ways are expensive, and have adverse effects on underground water.

4.1.1 Soil washing with water and organic solvents.

In solvent extraction technology, hydrocarbons are removed from soil using an individual solvent or mixtures of solvents. The two steps involved in the extraction of a compound from a solid matrix are desorption from the binding site in (or on) the solid matrix followed by elution from the solid into the extraction fluid.⁵⁰

In laboratory-scale, water and various organic solvent have been tested to remove 19 PAHs from highly contaminated soil.⁵¹ Using ethanol, 2-propanol, acetone and 1-pentanol with a soil:solvent extraction ratio of 1 g: 100 ml and extraction time of 24 h resulted in similar removal efficiencies of PAHs. Ternary mixtures of water, 1-pentanol, and either ethanol or 2-propanol were also tested with a volume fraction of 1-pentanol ranging from 5% to 25% and a volume fraction of water ranging from 5% to 30%. The results indicated that ethanol was a better extraction solvent for PAHs removal from soil than 2-propanol. It was also shown that 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 was capable of removing more than 95% of extractable PAHs.

The extraction efficiency from contaminated soil is also dependent on soil: solvent ratio. For instance, the capacity of 40% acetone–50% ethyl acetate–10% water to remove naphthalene from soil at different soil:solvent ratios of 1:1, 1:2, 1:3, 1:4 and 1:8 (w/v) using magnetic agitation. A ratio of 1:8 was recorded the highest removal efficiency in the order of 95%.⁵²

Regarding the efficiency of organic solvents, there are many organic solvents such as cyclohexane and ethanol mixture (3:1), dichloromethane, ethanol, methanol, methyl ethyl ketone, N,N-dimethylacetamide, N,N-dimethylformamide, N-butyl acetate, N-propyl acetate and toluene on extraction of fluoranthene from contaminated soil. It was observed that the 3:1 mixture of cyclohexane and ethanol has high extraction efficiency of more than 93%.⁵³

4.1.2 Surfactants-supported soil washing.

Surfactants are used as additives to counter the low aqueous solubility of PAHs and enhance the efficiency of soil washing/flushing using water. These amphiphilic molecules comprise of two major components, the hydrophobic or water insoluble tail group and the hydrophilic or water soluble head group. Surfactants can be classified as either cationic, anionic or non-ionic surfactants depending on the head group type. They enhance the solubility of PAHs in water by partitioning them into the hydrophobic cores of surfactant micelles. The presence of surfactant micelles also decreases surface and interfacial tensions.⁵⁰

A study was directed to investigate the washing performance of four different non-ionic surfactants, on phenanthrene-saturated soil.⁵⁴ It was noted that Brij 30 had the highest washing efficiency with 84.1% phenanthrene removal at a surfactant concentration of 2 g/l. This was due to the high solubilising ability of Brij 30 for phenanthrene and its low adsorption onto soil. Subsequent selective adsorption tests indicated that phenanthrene removal by activated carbon from Brij 30 solution was only 33.9% compared to the significantly higher removal efficiencies of 54.1–56.4% with other surfactant solutions. The overall performance combining both washing and surfactant recovery steps was best with Tween 80 and Brij 35.

Other non-ionic surfactants such as T-Maz 80, T-Maz 20, CA 620 and Terrasurf 80 as well as anionic surfactants such as Dowfax 8390, sodium dodecyl benzene sulfonate, sodium dodecyl sulphate and Steol 330 have also been shown to be effective for phenanthrene removal.⁵⁵

As a result of the recent concern about the use of surfactants and although micelles aid in the transport of dissolved PAHs, they can also be absorbed by the soil matrix and result in the partitioning of PAHs into immobile surfactants which enhances absorption of PAHs onto soils.⁵⁶ Due to this phenomenon, the authors utilized a model to evaluate the performance of surfactant in enhancing desorption for PAHs relative to water. It was found that the efficiency of surfactants in aiding PAH desorption was strongly dependent on soil composition, surfactant structure and PAH properties.

4.1.3 In situ soil vapor extraction.

Volatile and some semi-volatile organic compounds (VOCs and Semi-VOCs) can be removed from unsaturated soils by a process known as soil vapor extraction (SVE). SVE as an in situ clean-up process allows contaminated soil to be remediated without disturbance or excavation.⁵⁷ Soil vapor extraction (SVE) is an in situ unsaturated (vadose) zone soil remediation technology in which a vacuum is applied to the soil to induce the controlled flow of air and remove volatile and some semi-volatile contaminants from the soil. The gas leaving the soil may be treated to recover or destroy the contaminants. The drawback in the use of SVE for remediation of contaminated sites is that SVE cannot remove heavy oils, metals, PCBs, or dioxins from contaminated soil; it is only effective for remediation of soil contaminated with VOCs and Semi-VOCs. Because the process involves the continuous flow of air through the soil, however, it often promotes the in situ biodegradation of low volatility organic compounds that may be present.

4.1.4 *In situ steam injection vapor extraction.*

Cold soil vapor extraction is a common technique for remediating volatile organic compounds from the unsaturated subsurface. Limitations in efficiency can be overcome by using thermal enhancement, e.g., steam as a fluid heat transport medium to speed up the process.⁵⁸ *In situ steam extraction* is a new technology and has had limited use across the globe. Steam extraction can be used in two different systems; mobile and stationary. The mobile system has a unit that volatilizes contaminants in small areas in a sequential manner by injecting steam and hot air through rotating cutter blades that pass through the contaminated medium. The stationary system uses steam injection as a means to volatilize and displace contaminants from the undisturbed subsurface soil. In both systems, steam (at 200^o C) and compressed air (at 135^o C) are forced through the soil medium and the mixture of air; vapor and chemicals are collected by extraction wells.⁵⁷

4.1.5 *Air sparging.*

Air sparging is an *in situ* technology in which air is injected through a contaminated aquifer. Injected air traverses horizontally and vertically in channels through the soil column, creating an underground stripper that removes contaminants by volatilization.³⁵ Air sparging can also be explained as a method of site remediation that introduces air (or other gases) into the saturated zone contaminated with VOCs. In addition to volatilization of VOCs, air sparging promotes the growth of aerobic bacteria in saturated zones and may oxidize reduced chemical species.⁵⁷ Air sparging has been shown to be effective in removing several types of contaminants such as the lighter petroleum compounds (C3–C10) and chlorinated solvents.^{59,60}

4.1.6 *Excavation.*

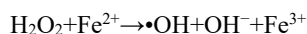
Excavation (removal) is a fundamental remediation method involving the removal of contaminated soil/media, which can be shipped off-site for treatment and/or disposal, or treated on-site when contaminants are amenable to reliable remediation techniques. Excavation is generally utilized for localized contamination and point source and is also used for the removal of underground structures that are out of compliance or have been identified as a potential or actual point source of contamination. The limiting factor for the use of excavation is often represented by the high unit cost for transportation and final off-site disposal.² EPA,⁶¹ has identified some of the limiting factors that may limit the applicability and effectiveness of the process to include:

- i. Generation of fugitive emissions may be a problem during operations.
- ii. The distance from the contaminated site to the nearest disposal facility will affect cost.
- iii. Depth and composition of the media requiring excavation must be considered.
- iv. Transportation of the soil through populated areas may affect community acceptability.

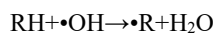
In this respect, the on-site removal and treatment can often yield significant savings and, in addition, the treated soil may have beneficial secondary use (e.g. as construction fill or road base material) at the same site.

4.1.7 *Fenton's reagent as oxidant.*

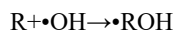
The Fenton's reagent (Fe(II)–H₂O₂), developed in the 1980s by Henry John Horstman Fenton, can be used to treat hydrocarbons contaminated soil. Typically, the major steps involved in Fenton's reaction are as follows. Hydrogen peroxide (H₂O₂) decomposition into hydroxyl radicals (•OH) in the presence of ferrous iron (Fe²⁺):⁶²



The unstable hydroxyl radicals formed are used to degrade organic compounds (RH or R) either by hydrogen abstraction:



Or by hydroxyl addition:



Fenton's reagent was used to study possible desorption or degradation of fluoranthene, benzo(b)fluoranthene and benzo(a)pyrene in soil.⁶² Soil samples were mixed with water to form a solid matrix suspension prior to addition of Fe(II) solution and successive additions of hydrogen peroxide solution to instigate the Fenton oxidation. The authors observed that almost complete degradation of benzo(a)pyrene was achieved with significant degradation of fluoranthene, while benzo(b)fluoranthene remained undegraded with excess concentration of hydrogen peroxide. It was also noted that several by-products, some with possible high toxicity, were formed during the course of the treatment.

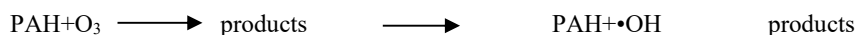
In another study,⁶³ the Fenton's reagent oxidation process was utilized to treat creosote-contaminated soil from a wood-treating site. The results showed that a total of 12 PAHs increased in the range of 13–56% in the soil samples due to the weakening of the adsorptive bonds of the PAH-complex formed with soil surfaces. This suggests that Fenton's reagent may be used as a primary remediation treatment which can provide further enhancement for a more efficient secondary remediation treatment.

Modified Fenton's reagent can be used as a stronger oxidizing agent to treat more recalcitrant hydrocarbons. Here, apart from hydroxyl radicals, other highly reactive radicals, are formed through the addition of chemicals such as chelating agents and/or high peroxide concentrations.⁶⁴ Experimental work using modified Fenton's reagent (catechol as chelating agent) to treat heavily contaminated sediments indicated that total hydrocarbons degradation was above 95%.⁶⁵

In the examination of role of soil characteristics in Fenton's reagent treatment, It was found that the susceptibility of PAHs to chemical oxidation was a function of total organic content (TOC) above a threshold value of approximately 5%.⁶⁶ For low TOC soils, oxidation strongly depended on soil porosity. Additionally, higher molecular weight PAHs tend to have stronger affinities for humic acid soil, leaving them less susceptible to the Fenton's reagent oxidation. The findings are in agreement with another work whereby it was shown that the efficiency of chemical oxidation of PAHs in soils is dependent on soil characteristics and PAH properties.⁶⁷ Lower molecular weight of PAHs with relatively high water solubilities were generally found to be more susceptible to Fenton's treatment than their heavier, highly hydrophobic counterparts.⁵⁰ For two and three rings of PAHs, organic matter, oxide content and specific surface area of soil all negatively affected the degradation process. On the other hand, degradation efficiency of 5 and 6 rings of PAHs were adversely affected by the age of contamination and pH but positively correlated to degraded organic matter. This indicated that these PAHs are released and degraded when soil organic matter undergoes oxidation.

4.1.8 Ozone as oxidant.

Ozone (O₃) can initiate indirect oxidation reactions by decomposing into hydroxyl radicals. In ozone oxidation of PAHs, PAHs undergo degradation through the direct reaction or through the radical reaction as shown by the following expressions, respectively:



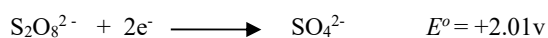
Some studies have shown that ozone generated from the air by electric discharge was used to remove several types of phenanthrene-spiked farm soils.⁶⁸ The treatment of soils was carried out in an ozone chamber at a constant room temperature of 13°C. Analyses of the treated soils showed more than 50% reduction in phenanthrene concentrations in all soils after ozone treatment for 6 h at 20 ppm concentration. It was also demonstrated that 85% phenanthrene removal could be achieved in sandy soils compared to clay soils due to its larger pore spaces, thus providing better transport of gaseous ozone through the soil matrices. Increasing moisture content was found to have an adverse effect on ozone treatment since PAHs in soil become less accessible to ozone when water occupies pore spaces.

In an experiment with ozone as a catalyst, it was found 95% removal of phenanthrene, 91% removal of pyrene, while chrysene was reduced to only 50% due to its more hydrophobic nature.⁶⁹ Similar to Fenton's reagent, several unidentified by-products were simultaneously discovered which were stated to be more polar than the parent compounds, thus having better biodegradability and aqueous solubility.

In the comparison of Fenton's reagent and ozone oxidation in treating aged PAH-contaminated soils,⁷⁰ It was reported that Fenton's reagent could more effectively degrade PAHs (degradation efficiency of 40–86%) as compared to ozone (degradation efficiency of 10–70%). Degradation of lower molecular weight of PAHs was more efficient using ozone as the oxidizing agent, while a more even degradation pattern for all ranges of PAHs resulted from the use of Fenton's reagent.

4.1.9 Persulfate as oxidant.

Persulfates as very strong oxidants have found a wide range of applications. Prominent among these is its use in the oxidation of organic contaminants especially hydrocarbons in the environment. The dissociation of persulfate salts gives the persulfate ion (S₂O₈²⁻) which is a very strong oxidant that is capable of oxidizing most organic substances especially hydrocarbons to carbon dioxide, water and other oxygenated products. The standard reduction potential for the half reaction is 2.01 volts. This is very close to that of ozone (2.2 v) and more than that of hydrogen peroxide (1.4 v) and permanganate (1.7 v):⁷¹



The sulphate radical is produced through the activation of the persulfate using heat, electromagnetic radiation or catalysts e.g. Iron (II) salts or copper (I) salts etc.



The free radical mechanism is the preferred method given the high redox potential of $\text{SO}_4^{\cdot-}$ which is 2.6 v as against 2.01 v of the persulfate ion. The high redox potential makes it possible for it to be used in the destruction of a wide range of contaminants prominent among which is the petroleum hydrocarbons.

Persulfite is used as a good removal agent for benzene, toluene, ethylbenzene, and xylene (BTEX), it was found not to be so effective in the removal of the PAHs.⁷¹ Percentage hydrocarbon removal for BTEX was about 97%, 95% and 95% at acidic, neutral and basic pH ranges respectively but less than 27%, 3% and 41% for the PAHs at the acidic, neutral and basic pH ranges respectively. The four and five ringed PAHs were degraded more than the three and two ringed ones at the indicated pH ranges.

Feasibility study of petroleum-hydrocarbon contaminated soil remediation using persulfate oxidation.⁷² It was observed that persulfate oxidation can treat diesel and fuel oil contaminated soil. Higher persulfate and ferrous ion concentrations resulted in higher diesel degradation rates within the applied $\text{S}_2\text{O}_8^{2-}/\text{Fe}^{2+}$ molar ratios. Diesel oxidation efficiencies and rates by the three oxidants followed the sequence of hydrogen peroxide > permanganate > persulfate in the limited timeframes.

In the other side, all experimental results indicated the higher efficiency of magnetite-activated persulfate oxidation (AP) for PAH removal. Experiments performed with soluble Fe (II) or without iron activation resulted in only 15–20% of PAH removal in spiked sand while 5–10% in real soil. Such similar degradation with or without soluble Fe (II) exhibits the inability of soluble Fe (II) to activate persulfate oxidation. However, magnetite was highly reactive to activate persulfate oxidation as almost 5 times higher PAH removal efficiency was observed in the AP oxidation system.⁷³

4.2 Bioremediation or biological remediation.

Bioremediation is one of the most viable options for remediation soil contaminated by organic and inorganic compounds considered harmful to environmental health. Biological remediation, a process defined as the use of microorganisms or plants to detoxify or remove organic and inorganic xenobiotic compounds from the environment, is a remediation option that offers green technology solution to the problem of environmental degradation.² Bioremediation strategies such as enhanced natural attenuation (ENA), bioaugmentation, land farming, and composting have been successfully applied for the remediation of petroleum contaminated soil.⁷⁴

Advantages of bioremediation compared to other treatment methods include:^{75,76}

- i. It is reduced cost compared to conventional techniques.
- ii. It is a permanent solution, which may lead to complete mineralization of the pollutant.
- iii. It is a non-invasive technique, leaving the ecosystem intact
- iv. Destruction-in situ- rather than transfer of the contaminants to another medium.
- v. Minimal exposure of workers to the contaminants.
- vi. Longtime protection of public health.
- vii. Possible reduction in the duration of the remediation process

4.2.1 Land farming.

In land farming, contaminated soil is periodically tilled to improve aeration and to promote soil homogeneity for biological degradation. Soil conditions are controlled by monitoring the moisture and nutrient content, frequency of aeration and soil pH to optimize the rate of contaminant degradation. Sometime, contaminated soil are spread over with waste material or mixed with soil amendments such as bulking agents and nutrients to incorporate better degradation and oxidation process by existing microbial population.⁵⁰

Combined fertilization study with 10 mg of urea and 4.3 mg of superphosphate per cm^2 area, liming with 55 mg of powdered agricultural limestone per cm^2 area and weekly tilling to a 15 cm depth with a hand shovel.⁷⁷ With these optimum conditions, the rate of total hydrocarbons degradation increased considerably, with almost complete elimination of PAHs in 12 weeks compared to untreated soil which revealed 12.5–32.5% of higher molecular weight PAHs still present after a similar duration.

Finding that without land farming, a much greater content of PAHs remains in the soil.⁷⁸ Land farming was most effective at removing volatile chemicals like naphthalene, acenaphthene, acenaphthylene, fluorene, phenanthrene and anthracene.

Also, it was found that the effectiveness for these chemicals could be due to the light exposure as these compounds are not volatile, but they are subject to photooxidation. Additionally, land farming had little effect on the larger PAHs.

4.2.2 Composting.

Composting, a process typically used to degrade solid waste materials, has also recently been studied as a remediation technology for oil contaminated soils. Maize straw and pine wood chips were added as bulking agents and most of the total petroleum hydrocarbons (mainly saturated fractions) were easily degraded at the beginning, while the degradation rates declined with time, especially after 120 days. After 150 days of composting, there was a significant decline of the soil pH in all treatment biopiles, measuring between 7.68 and 8.23, compared to the control biopile at pH of 8.74. This decrease was mainly due to the accumulation of acidic metabolites such as aliphatic acids produced during alkane degradation.¹

Mushroom compost consisting of wheat straw, chicken manure and gypsum was added to manufactured gas plants (MGP) soil in a thermally insulated composting chamber.^{79,80} Optimal temperature gradient and concentrations of oxygen and carbon dioxide were controlled by aeration. Degradation efficiencies of individual PAHs after 54 days of composting in the chamber fell in the range of 20–60%, with further removal of PAHs (37–80%) found after an additional 100 days of compost maturation in an open-air field.⁷⁹ Composting was also found to degrade 3 and 4 rings PAHs more effectively than 5 and 6 rings PAHs.⁸⁰

Organic wastes like banana skin, spent mushroom compost and brewery spent grain in earlier studies were found to enhance the biodegradation of used lubricating oil up to 90% loss of oil within the period of 3 months.^{28,81} Also the results of studies revealed the potential of melon peel shell to stimulate 75% crude oil degradation in soil contaminated with crude oil within the period of 28 days.⁸²

Soil particle size is an important factor concerning on the management of the petroleum contaminated site. It is suggested that proper regulation on the particle size can change the state of petroleum hydrocarbons in the soil and improve the degradation of petroleum pollutants. The particle size of the soil can be changed by the addition of industrial wastes such as fly ash, slag and agricultural waste such as rice straw to the contaminated soil.⁶

4.2.3 Earthworms.

Remediation of contaminated soil with earthworms known as vermiremediation and considered to be one of the most promising bioremediation techniques of oil contaminated soil due to low-costs and high-efficiency.⁸³ Several recent studies showed the ability of earthworms to stimulate the biodegradation of oil contaminated soil.^{84,85} Enhanced biodegradation of soil contaminated with hydrocarbons by earthworms could be explained by three major mechanisms: (i) improved and maintained oxidation processes and aerobic conditions due to the continuous mixing the soil which caused by burrowing activities. (ii) increased nutrients availability and enhanced microbial activity. (iii) increased bioavailability of hydrocarbons in contaminated soil to microbial activity due to bioturbation.^{86,87}

4.2.4 Microorganism.

TPH degradation may happen naturally by native microorganisms with a degradation rate of 77% after 30 months. The decrease of TPH content is mainly caused by bacterial growth, and the change of fungi number may affect the TPH degradation at only certain periods of time. Degradation of TPH can be occurred by bacterial species such as *Bacillus subtilis*, *Corynebacterium*, *Pseudomonas aeruginosa*, *Acinetobacter radioresistens*, *Rhodococcus erythropolis*.⁸⁸⁻⁹¹ Fungi were also effective in degradation of TPH in soil.⁹² Nutrient addition has enhanced the biodegradation of petroleum hydrocarbons in contaminated soils due to stimulation of native microorganisms.⁹³ High molecular weight PAHs are more resistant to microbial attack than low molecular weight PAHs.⁹⁴

Microorganisms play a significant and vital role in bioremediation of heavy metal contaminated soil and wastewater. Mechanisms by which microorganisms act on heavy metals includes biosorption (metal sorption to cell surface by physiochemical mechanisms), bioleaching (heavy metal mobilization through the excretion of organic acids or methylation reactions), biomineralization (heavy metal immobilization through the formation of insoluble sulfides or polymeric complexes) intracellular accumulation, and enzyme-catalyzed transformation (redox reactions).⁹⁵

4.2.4.1 Biostimulation.

Biostimulation of indigenous microbes is a bioremediation strategy mostly used for remediation of contaminated soil. This involves addition of nutrients, either organic or inorganic, to enhance the activities of indigenous microbes.² Nutrient enrichment, also called fertilization, is a bioremediation approach in which fertilizer similar to phosphorus and nitrogen that are applied to plant in farms are added to contaminated environment to stimulate the growth of indigenous microorganisms that can degrade pollutants.⁹⁶ In some instances, manure, wood chips and straw may provide microbes with the sources of carbon as a fertilizer. It was reported that in biopiles with C:N ratio of 20/1, the numbers of microorganisms were relatively low, probably because of the insufficient amount of nitrogen supply. (Wang *et al.*, 2012). Liebeg and

Cutright (1999) showed that the greatest stimulation was recorded with a solution consisting of 75% sulphur, 3% nitrogen and 11% phosphorus. However, excessive nutrient concentrations can inhibit the biodegradation activity,⁹⁸ and several authors have reported the negative effect of high NPK levels on the biodegradation of hydrocarbons^{99,100} and more especially on the aromatics.¹⁰¹ Increasing the amount of nitrogen and phosphorus in soil under aerobic conditions increased the degradation of PAHs by the soil fungus *Cunninghamella echinulata* var. *elegans*.¹⁰²

4.2.4.2 Bioaugmentation.

This is an approach that involves introduction of microorganisms that possess biodegradation potential into the contaminated environment to assist the indigenous microbes with biodegradative processes. Bioaugmentation is a promising and low-cost bioremediation strategy in which an effective bacterial isolates or microbial consortium capable of degrading xenobiotics is administered to contaminated sites.¹⁰³

Study of the efficiency of pollutant removal by selected microorganisms and reported: five mixed cultures and 3 single bacterial strains, *Pseudomonas* sp., *Arthrobacter* sp., and *Mycobacterium* sp. were isolated from hydrocarbon-contaminated soils by enrichment on either crude oil or individual hydrocarbons, as the sole carbon sources.¹⁰⁴ The strains were selected based on their ability to grow in medium containing crude oil, used engine oil or both. Their ability to degrade hydrocarbon contaminants in the environment was investigated using soil samples contaminated with used engine oil. The mixed starter culture #1 degraded 66 % of aliphatic compounds in the engine oil after 60 days of incubation. The mixed starter culture #5 removed 47 % of aromatic compounds during 60 days of incubation.

Sometimes, the administration of petroleum degrading microorganisms leads to a failure of bioaugmentation.¹⁰⁵ Bioaugmentation is not always an effective solution for remediation of contaminated soil because in some cases laboratory strains of microorganisms rarely grow and biodegrade xenobiotics compared to the indigenous microbes.⁹⁶

5. Ability of plants and agricultural wastes for remediation of oil contaminated soil

5.1 Plants (Phytoremediation).

Due to the fact that engineering-based remediation technologies are expensive and disruptive, there is a growing interest in developing new remediation technologies that are environmental friendly and less expensive.¹⁰⁶ Since 1991, plants have been widely studied to better understand their many endogenous genetic, biochemical and physiological capabilities to mineralize a wide variety of complex organic pollutants into non-toxic constituents such as carbon dioxide, nitrate, chlorine and ammonia.¹⁰⁷

Phytoremediation is based upon the basic physiological mechanisms taking place in higher plants and associated microorganisms, such as transpiration, photosynthesis, metabolism, and mineral nutrition. Plants dig their roots in soils, sediments and water, and roots can take up organic compounds and inorganic substances; roots can stabilize and bind substances on their external surfaces, and when they interact with microorganisms in the rhizosphere. Uptaken substances may be transported, stored, converted, and accumulated in the different cells and tissues of the plant. Finally, aerial parts of the plant may exchange gases with the atmosphere allowing uptake or release of molecules.¹⁰⁸

Phytoremediation is a promising alternative approach to soil remediation due to its cost effectiveness, convenience and environmental acceptability.¹⁰⁹ Phytoremediation is an emerging technology which uses various plants to extract, contain, degrade, and/or immobilize contaminants.¹ Plant could extract and uptake heavy metals, solvent, aromatic hydrocarbons and other organic contaminant from soil, sludge, water, underground water in their tissues, and degraded pollutant by biotic and abiotic process.¹¹⁰ The selection of phytoremediation for specific sites is empirical and based on preliminary results from pot experiments.¹¹¹⁻¹¹³ Employing native plant species that are tolerant to high concentrations of TPH in soil and capable of producing high biomass which accumulating large amount of contaminants in the biomass from the soil can be a key factor in the success of phytoremediation.^{24,114}

The most important mechanism of phytoremediation is based on the stimulation of soil microorganisms in their growth and activity by root exudates, which vary with plant age and nutritional status. Also, it can be assumed that higher root biomass means a larger rhizosphere for microbial population and it is correlated with a higher degradation of hydrocarbons in soil.¹¹⁵ Mechanisms involved in Phytoremediation process are:¹¹⁶

- i. Phytoextraction is the absorption of pollutants by plant roots such as heavy metals and it's a mechanism to accumulate contaminants in plant tissues.
- ii. Rhizodegradation is a breakdown of pollutants within the rhizosphere such as organic pollutants by root exudates and microbial activity.
- iii. Phytostabilization uses plants that are tolerant of a contaminant in soil to reduce the contaminant mobility and prevent further environmental contamination leaching into groundwater or by airborne spread.
- iv. Phytovolatilisation is the absorption of contaminants and releasing them from leaves into the atmosphere.
- v. Evapotranspiration, to control hydraulic flow in the contaminated environment.

The advantages of phytoremediation compared with other approaches are :^{117,118}

- i) Relatively low cost (costs 10-20% of mechanical treatments) and easily implemented and maintained.
- ii) Eco-friendly and fewer air and water emission and reduces landfill wastes.
- iii) High levels of microbial biomass in the soil can be achieved.
- iv) Several mechanisms for removal and faster than natural attenuation.
- v) Preservation of the natural structure and texture of soil.

Most studies on the phytoremediation of total petroleum hydrocarbon (TPH) contaminated soil reported the use of grasses (Poaceae) and legumes (*Leguminosae*).^{119,120} It has been assumed that the main advantage of grass species is their extensive fibrous root systems, which have significantly greater root surface area (per m³ of soil) than do other species and may penetrate the soil to the depth of up to 3 m.¹²¹

Some authors reported a higher degradation of petroleum contaminants in soil vegetated with tall fescue, sorghum, cowpea, alfalfa, and black rush compared to unvegetated soil.¹²² Leguminous plants such as *P. vulgaris* capable of fixing nitrogen may have had advantage in the remediation of oil contaminated soil because of their ability to provide their own nitrogen fertilizer via nitrogen fixation to correct imbalance in C:N ratio.⁷ Legumes such as white clover (*Trifolium repens*) and alfalfa (*Medicago sativa*) were effective for petroleum degradation in soil.¹²³ Likewise, ryegrass (*Lolium perenne* L.) accelerated the disappearance of aliphatic hydrocarbons in soil,¹²⁴ and Verde Kleingrass removed PAHs from the rhizosphere in contaminated clay soils by virtue of its deep and dense root system. Prairie Buffalograss was also used to remediate PAHs in clay soil.¹²⁵ Mixtures of tall fescue/western wheatgrass and tall fescue/red clover, and birdsfoot trefoil and yellow sweet clover were used for remediation of oily sediments in a vehicle wash facility in Kansas.¹²⁶ Other commercial plant species can tolerate significant amounts of petroleum hydrocarbons; for example, tomatoes, kale, and leaf lettuce.¹²⁷ Legumes occurring naturally in oil contaminated areas have the potential to clean up petroleum hydrocarbons.¹²⁸

The degradation of phenanthrene and pyrene can be promoted by four different plant species, including two grasses and two legumes.¹²⁹ Study of the capability of nine plant species to promote the degradation of pyrene in soil and higher degradation rates in vegetated soil.¹³⁰

In a study on alfalfa showed the highest root concentrations of phenanthrene (5.25 mg /kg) and pyrene (40.90 mg/ kg), while tall fescue and ryegrass contained the lowest portion of these compounds.¹³¹ Finding that more than 99% degradation of phenanthrene and 77–94% degradation of pyrene were observed in soil after 80 days of treatment by the native Korean grass species *Panicum bisulcatum* and *Echinogalus crus-galli*.⁹⁴

Seepweed showed a potential for high rhizodegradation of TPH in the soil, which could be due to its fibrous root system providing a large specific surface area and root volume and a high number of root tips to interplay with microorganisms in the rhizosphere. Root growth promote soil aeration, which could enhance oxidative degradation of organic compounds, and this may also widen the way for trapping contaminants to become accessible to degrading bacteria^{1,132} also reported that Seepweed increased the amount of organic matter and total nitrogen in the soil, helping to stimulate the survival and action of the rhizosphere microorganisms.

In the phytoremediation of organics which is based on a stimulated microbial degradation in the rhizosphere, fertilization is essential for success. Adequate fertilizer applications may reduce competition between plants and microorganisms for limited nutrients in oil polluted soil, resulting in enhanced total petroleum hydrocarbon (TPH) degradation rates.¹³³ Plants have capacity to resist relative high concentrations of organic chemicals, such as oil, without toxic effect and they can uptake and convert this contaminates quickly to less toxic metabolites in some cases by rhizodegradation.⁷ This is achieved by the release of root exudates, enzymes that stimulate mineralization of the oil contaminant.

Variety of contaminant-degrading enzymes can be found in plants. These include peroxidases, dioxygenases, P450 monooxygenases, laccases, phosphatases, dehalogenases, nitrilases, flavonoids and nitroreductases.¹³⁴⁻¹³⁶

Microbial populations benefit the plant through recycling and solubilization of mineral nutrients as well as by supplying vitamins, amino acids, auxins, cytokinins, and gibberellins, which stimulate plant growth.¹³⁷ One study indicates that over 90 times population of microorganisms in rhizosphere than that of non-rhizosphere soil.¹³⁸ Also, another study showed that the population of hydrocarbon degrading bacteria was five times more abundant in the rhizosphere of hybrid poplar trees relative to an unplanted reference site.¹³⁹ Additionally, fluorescence microscopy was used to show that the microflora in the rhizosphere of bitumen contaminated soil was greater than in unplanted soil, and that the community structure was also different.¹⁴⁰

Finding that, when fertilizer was not applied, the clover, wheat/oats, and sunflower/mustard contained lower levels of oil/grease after 150 days, that is, 100, 77 and 67% reductions, respectively, compared with the control (47% reduction).⁴ When fertilizer was added to the treatments, the residual oil/grease typically disappeared more rapidly. After 100 days, the sunflower/mustard reduced the oil/grease content by 68% and at 150 days all extractable oil/grease was removed. Also, a

study showed that in a soil contaminated with used motor oil, soybean, maize (*Zea mays L.*) and peanuts (*Arachis hypogaea L.*) grew better when fertilizer, particularly N-based, was applied.¹⁴¹

In a greenhouse experiment, tall fescue (*Festuca arundinacea Schreber*) degraded benzo[a]pyrene in soil contaminated with crude oil, and resulted in an increase in microbial populations.¹⁴² Benzotriazoles appear to be actively taken up and then incorporated into plant tissue by sunflowers (*Helianthus annuus L.*) grown in hydroponic solution.¹⁴³

Using ¹⁴C-labeled pyrene, Pyrene mineralization is seen in 38% and 30% in tall grass (*Festuca arundinacea*) and switchgrass (*Panicum virgatum L.*), respectively, compared with 4.3% in the uncultivated control.¹⁴⁴ Also, using mangrove (*Kandeliacandel* and *Bruguiera gymnorrhiza*) wetland systems to treat pyrene-contaminated sediments.¹⁴⁵ After six months, pyrene concentrations decreased in the mangrove treatments relative to the controls.

In the evaluation of leguminous plants in diesel-contaminated soil, finding that contaminated soil had fewer nodules, but these nodules were more developed.¹⁴⁶

An increased deterioration of crude oil under the influence of tropical grass was observed only a few months later.¹²² A study showed that 30%, 16.8% and 13.8% reduction of TPH in rhizosphere soil of broad bean, corn and wheat, respectively.¹⁴⁷ In addition, another study showed that 41.61-63.2% removal of TPH by *Mirabilis jalapa*.¹⁴⁸

The decrease of soil micropore surface area and volume was probably due to the organic acids released from plant roots.¹ Seepweed could exudate organic acids, dominated by oxalic acid. These low molecular weight organic acids (LMWOA) can chelate soil cations, resulting in localized soil aggregate destruction which subsequently accelerates pollutant desorption and increases its solubility, mobility and bioavailability.

In a study, it was found that 67.6% and 56.6% biodegradation in 1% and 2.5% used lubricating oil contaminated soil using *Jatropha curcas* after 180 days.¹⁴⁹ In addition, another study found that star grass (*Melampodium palusodum*) reduced the initial TPH content in motor oil contaminated soil from 75.46 mg/g to 49.822 mg/g in two weeks after plant stabilization and to 30.07 mg/g after 16 weeks of plant stabilization.¹⁵⁰

According to ability of hydrocarbon fractions for biodegradation; aromatic and polar compounds are less biodegradable than aliphatic¹⁵¹ and asphaltene group is the least biodegradable of all.^{152,153}

5.2 Agricultural wastes as bulking agent and nutrients amendment.

Bulking agents are materials of low density that when added to soils, lower the soil's bulk density, increase porosity, may increase oxygen diffusion, and may help form water stable aggregates. Such changes to a soil increase aeration and microbial activity. Bulking agents and tillage enhanced bioremediation of crude oil spilled on soil and may reduce the time required to remediate oil contaminated soil. Apparently the bulking agents and tillage enhanced bioremediation possibly by reducing the size of oil-saturated aggregates, thereby exposing more of the oil to microbial active sites.¹⁶

There are many environmental parameters which have effect on bioremediation.¹⁵⁴ One of these parameters is aeration, which can be improved in bioremediation systems by the use of plant crop residues that act as bulking agents. Addition of bulking agents can also help the adaptation process for microbes by absorbing access to hydrocarbons in the soil when the concentration of crude oil is too high. The reason for differences in biodegradation between the bulking agents may have been from a priming effect on microbial populations.^{155,156} It has been noted previously that additions of organic materials to soil enhanced oil degradation. The significant reduction in TPH content in the amended soil may be attributed to the high nutrient level especially nitrogen and phosphorus which are essential in stimulating the proliferation of microbial population and activities in soil.¹⁵⁷

Bulking of contaminated soil with chopped wheat straw, hay, wood chips, pine bark, peat, and loam enhanced remediation of 3,4-dichloroaniline and benzo(a)pyrene,¹⁵⁸ and solid swine waste bulked with peat moss and sawdust decreased composting time.¹⁵⁹ Amending soil with maize straw significantly enhanced mineralization of methabenzthiazuron,¹⁶⁰ and in a laboratory investigation bermudagrass and alfalfa were found to enhance biodegradation of crude oil in the soil.¹⁵⁶

Spent mushroom bedding, cow dung, poultry droppings are effective nutrient sources in the degradation of TPH in the soil.¹⁶¹ All treatments reduced the level of the PAHs. The mushroom was most effective (98.93% reduction) than cowpea (97.90%), algae (97.07%), heat (97.81%) and the last dead vegetable cum live earthworms (89.99%).²⁵

A study showed that 23.86%, 84.22% and 87.44% of TPH were degraded in crude oil contaminated soil with control (without amendment), 400 g cocoa pod husk (CPH) and 500 g (CPH) amended soil, respectively, and 23.58%, 80.69%, 81.04% of TPH were degraded in control, 400 g plantain peels (PP) and 500 g (PP) amended soil, respectively, while 23.86%, 81.92%, 83.53% were degraded in control, 200 g (CPH) + 200 g (PP) and 250 g (CPH) + 250 g (PP) amended soil,

respectively.¹⁵⁷ Also, It can be concluded that cocoa pod husk, plantain peels and cocoa pod husk + plantain peels (1:1) possess the bio-utilizing potentials in enhancing the degradation of total petroleum hydrocarbon.

A study indicates that 60% loss of diesel fuel in 30 days in diesel-contaminated soil planted with pine tree and amended with NPK fertilizer.¹⁶² Also, A study showed that compost addition combined with phytoremediation, increases the rate of removal of diesel fuel in soil.¹⁶³ Appreciable degradation of used lubricating oil in soil when the growth of *Jatropha curcas* was enhanced with brewery spent grain.¹⁴⁹

Biodegradation of used oil was high (92–95%) in all the soil amended with different organic wastes: banana skin (BS), brewery spent grain (BSG), and spent mushroom compost (SMC) compared to the unamended soil (68%).²⁸ The kinetic parameters observed in this study showed that the rate of degradation of used oil in soil amended with BSG was higher than other treatments; this may be due to high percentage of nitrogen present in BSG compared to other organic wastes and bioavailability of the nutrients in BSG to bacterial species in the oil-polluted soil.

Using sawdust exhibit consistent removal of oil from contaminated soil up to 50% till day 60.¹⁵⁴ Additionally, it was suggested that an organic bulking agent such as sawdust or bagasse would be a better prospect than a mineral bulking agent like sand or gravel for bioremediation of oil contaminated soil. In another study showed that coconut shell always led to higher removals of TPH than rice husks especially in the tests with higher diesel percentage (9%).¹⁶⁴

Contaminated soil is always poor in organic matter and thus has low microbial activity.⁹³ Addition of NPK fertilizer and empty fruit bunch of oil palm (EFB) as inorganic and organic nutrient enhanced the microbial growth and thus concurrently increased the degradation of TPH. EFB can improve the soil structure by adding porosity. This is because the availability of oxygen in soil is important for the microbial enzymes to degrade the hydrocarbon.¹⁶⁵

A study showed that 3% corn-crop residue (CR) with 100:30 C:N ratio and 30% moisture microcosm removed 67% of the diesel added by the end of the process, as compared with the control sterile microcosm.²⁶ the sugar cane crop residue removed only 24% of the contaminant. It was also observed that crop residues and moisture alone increased 35% and 43% diesel removal, respectively. A study showed that addition of bulking agent, 180.7 mg/kg sugarcane bagasse to the soil contaminated with 10000 mg/g Maya heavy crude oil, achieved 40% of TPH degradation in 15 days of treatment.¹⁶⁶⁻²²²

6. Conclusions

Hydrocarbon pollutants in the ecosystem are the greatest important environmental problems in the world. The study exposed that there has been an overuse of hydrocarbon pollutants which has led to a significant threat to the environment. The study highlights the removal of hydrocarbon pollutants using remediation technology of various chemical, physical and natural types. Clearly, the data studied in this review define the great potential of remediation technology. This recommends that this technique can be efficiently used to remove this kind of contaminants.

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