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# Remediation Techniques for Soil Contaminated with Petroleum Products: A Review

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## **Article information**

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## Abstract:

Soil is one of the main resources that human beings rely on to survive. Since petroleum hydrocarbons are used more widely over the world for energy and raw materials in many applications, a wide range of pollutants have been released into the environment. In addition, accidental emissions of petroleum products have been causing serious soil pollution and deteriorating soil quality. Numerous global ecological, environmental, and health problems are the outcome of this pollution. Efforts are intensifying today to develop methods for treating soil contaminated with petroleum essentially to restoring soil function and recover the ecosystem. This paper reviews several in situ or ex situ treatments techniques including thermal, physico-chemical, biological methods and these treatment methods involve other techniques and strategies that combine between two techniques in order to increase the removal efficiency also had been reviewed. Each technology has advantages and disadvantages and depends on several factors that affect its efficiency. Therefore, to choose the appropriate technology, it is important to study and understand each technology separately, and the other factors that affect it, and when we need to combine two or more technologies.

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## 1. Introduction

Soil which is the foundation of agricultural resources, main source of food, the global economy, and environmental quality is currently constantly being contaminated by petroleum products because of industrialization and urbanization. Petroleum or petroleum products may leak into the environment during the extraction, processing, and use stages, increasing the risk of soil contamination. Additionally, spills, inappropriate waste disposal, and unintentional tank leaks can all let petroleum products into the environment. Oil well drilling and oil processing industries are the primary sources of environmental contamination. Out of the two billion tons of oil that are drilled worldwide each year, only 45–50 million tons (or around 2%) end up contaminating the environment [1]. Figure 1. shows the main sources for soil pollution by petroleum products.



Figure 1: Major sources of petroleum pollutants in soils

Thus, environmental pollution has grown to be a major worldwide concern, and the long-term build-up of these toxins presents a serious risk to both plants and animals. In addition, the soil pollution is a global issue in both developed and developing countries. Since some petroleum compounds are highly migratory and soils have a limited capacity to withstand pollutants and self-purification, the buildup of hydrocarbon components over time can have irreversible effects on the environment. Because the petroleum hydrocarbons in the vadose zone (consists of unsaturated porous media and rock extending from the surface soil to the groundwater table) have the ability to seep below the groundwater table and endanger human health and water quality, they have received a lot of attention over the years [2]. When petroleum-based hydrocarbons join to other compounds that are peculiar to them, the carbon multiple bonds that form intense and complex structures rise. The toxicity and lethality of petroleum hydrocarbons are contingent upon various factors such as the chemical composition, mode, level, and duration of exposure, as well as the component fractions' qualities. The effect of petroleum compounds on the environment and human can be summarized below:

**1.1. Effect Petroleum hydrocarbons in the soil:** it can alter chemical characteristics of the soil, including the quantity and amount of minerals and heavy metals. In addition, they effect on the physical characteristics of the soil, including its texture, compaction, structural integrity, resistance to penetration, and saturated hydraulic conductivity [3]. Petroleum deteriorating the ecological structure and function of soils, its significantly affect soil moisture, total organic carbon, total nitrogen, pH, exchangeable potassium, and enzyme efficacy substantially (catalase, urease and dehydrogenase) [4]. As petroleum concentration increase, the amount of clay in contaminated soil increases, soil porosity decreases, permeability is decreased by adding crude oil to the soil, that is related to entrapment of contaminant within soil's pore crevices [5] and a discernible rise in the salt content of the soil. Benzo(a)pyrene, found in petroleum products, is the main pollutant that causes soil salinization and acidification, according to research [6].

**1.2 Effect on the plants:** it inhibits the growth of plants when it obstructs or reduces their intake of water and minerals, which leads to the breakdown of their metabolic processes and a lack of nutrients and chlorophyll, which reduces their resistance to pests and diseases. As a result, plants show stunted growth, deformed roots, leaves, and flowers with chlorosis and necroses [7]. Consequently, the human health will be endangered via the food chain [8].

**1.3 Effect on humans and animals:** exposure to the petroleum pollutants directly or indirectly (consuming tainted food and taking a bath in contaminated water) can result in a variety of toxicological health issues including carcinogenicity (ability or tendency to induce cancer), hemotoxicity (destruction of red blood cells), mutagenicity (ability to incite transmissible genetic mutations), genotoxicity (the capacity to cause non-transmissible DNA damage), cytotoxicity (ability to be toxic to cells), teratogenicity (induction of fetal malformation), immunotoxicity (the ability to suppress immunity), neurotoxicity (damage to the neurological system and brain), nephrotoxicity

(damage to the kidney), hepatotoxicity (the ability to cause liver damage), cardiotoxicity (ability to cause damage to heart muscles) and ocular toxicity (capacity to cause problems of the eyes) [9].

Statistics show that the ecosystems, water supplies, and human health in Ecuador's Amazon region have all suffered as a result of Chevron Texaco's oilfields. In 2013, the Cuban Supreme Court granted USD 9.5 billion to the petitioner, which consisted of 30,000 individuals of mixed race and indigenous peoples[10]. There are thousands of records of crude oil spills in Nigeria. The reasons of these spills have been determined to include corrosion, equipment failure, sabotage, and theft [11]. Shell Company was found liable for the oil spill in Ibibio land in the most recent historic ruling in favor of four farmers and environmental campaigners. The farmers will get an undisclosed payment [12]. As most crude oil spills occur more than ten years ago in Nigeria, they continue to be a source of contamination for groundwater and soil systems [13].

All of these environmental issues and health dangers had prompted scientists to investigate, create, and execute riskbased remediation techniques for the restoration and reclamation of impacted areas. In order to completely clean, contain, remove, reclaim, and restore a contaminated environment, remedial treatment methods and procedures are essential. To choose the most appropriate method for treating contaminated soil, we need to understand the most important treatment methods, when to use them, and how appropriate they are for the surrounding conditions.

## 2. Petroleum polluted soils treatment methods:

# 2.1 Thermal Treatment Methods

# 2.1.1 Thermal Desorption

Thermal desorption (TD) considered a physical remediation technology that is most popular due to its various technical applications which its benefits including a fast remediation time, mature technology, and an easy-to-manage procedure. Thermal desorption is an appropriate method for volatile and semi-volatile pollutants, including total petroleum hydrocarbons (TPH), polycyclic aromatic hydrocarbons (PAHs), chlorophenol, dichlorodiphenyltrichloroethane (DDT), and polychlorinated biphenyls (PCBs), [14].

TD is a technique that involves heating specific contaminants in soil to a gaseous form and then removing them from the soil either directly or indirectly. After that, a tail gas treatment system treats this off gas to make it compliant with the emission standards of a certain jurisdiction. The primary process in the TD heating unit is the migration and change the pollutant's phase, which is mostly controlled by physical changes. Certain chemical reactions, such oxidation and degradation, also occur depending on the type of pollutant and the heating temperature utilized [15].

TD can be categorized as either ex situ thermal desorption (ESTD) or in situ thermal desorption (ISTD) depending on the actual soil disposal site for the treatment process. In ESTD the soil is excavated and transported to treating, although this process has more costly, it has benefits of being able to treat soil quickly, easily detecting pollutants in the soil, and having an easily treated soil. On the other hand, (ISTD) has less cost because it does not require transport the soil. However, it is difficult to regulate its subsurface reaction and figure out the treatment's endpoint. ESTD can be classified as either direct or indirect contact TD based on the manner of heating. In the case of direct contact, the thermal efficiency is great because the heat source is in direct contact with the polluted soil. However, this method can be applied effectively for treating organic pollutants with high boiling points, but it is not effective for poisonous, flammable, or explosive pollutants in large concentrations. Heat exchange occurs between the soil and the heat source through the equipment that is employed during indirect contact TD, and its thermal efficiency and heating temperature are lower than those of direct contact TD. Therefore, petroleum hydrocarbons and other high concentration or recyclable contaminants are better suited for this method [16].

Another classification has been adopted depending on the temperature's degrees that used in this method; low-temperature TD (100-350 °C) and high-temperature TD (350-600 °C) that involve the physical extraction of pollutants from the soil, and thermal destruction (600-1000 °C), which includes modifying pollutants chemically [17].

# 2.1.2 Incineration

The fire has been used to burn off pollutants from the soil's surface in order to complete incineration. Pollutants are completely destroyed during incineration by burning affected soils at a high temperature ranged from 600 to 1000  $^{\circ}$ C based on the type of target pollutant [18].

Without excavation, on-site incineration also referred to as open burning or on-land burning can be challenging, expensive, unpredictable, and ecologically unfriendly due to flammable and volatile chemical components in crude oil that could pollute the environment. Consequently, incineration is usually used as an ex-situ technology that entails removal of contaminated soils and burning in one of four main kinds of incinerators; liquid injection, fluidized bed reactors, rotary kilns, and infrared heaters [19]. In order to ensure that volatile organic compounds burn, the inflowing oxygen level is kept at roughly 10% during fire. To achieve safe incineration, the oxygen level, soil loading, and contaminant lower explosion limit must all be taken into account [20]. Then the gaseous products and exhaust emissions are filtered through scrubbers and electrostatic precipitators. In order to lessen air pollution and the deposition of harmful pollutants, the catalytic converters alter gases such as nitrous oxide (N<sub>2</sub>O), carbon monoxide (CO), and sulfur dioxide (SO<sub>2</sub>) into less dangerous gases such as carbon dioxide (CO<sub>2</sub>), water (H<sub>2</sub>O) vapour, and nitrogen (N<sub>2</sub>) [21]. Soils must be moistened after treatment in order to control dust before being used again as backfill for building projects or other non-agricultural uses.

Incineration is frequently among the most expensive thermal technologies to run because of its high temperatures. However, because of its efficiency and versatility in eliminating a broad spectrum of target pollutants, it remains a vital technique. Because of the high temperature and strong flammability of hydrocarbons, incineration can destroy almost all hydrocarbons. Typically, contaminant mass removal efficiencies exceed 99%, while the prices per metric ton range from \$150 to \$2900. (adjusted for 2016 USD) [22].

## 2.2 Physico-Chemical Treatment Methods:

## 2.2.1 Soil Washing

It is essentially a physical separation process wherein soil pollution concentrations are removed with the use of water. Soil washing is an ex-situ treatment method that can be used to remove radioactive, inorganic, and organic pollutants from soil, and semi-volatile chemicals, as well as fuels and heavy metals [23].

Based on the fundamental that most pollutants have a tendency to attach to fine (silt and clay) rather than coarse (sand and gravel) particles in soil, the approach is used. In soil washing, processes like hydro classification, gravity concentration, attrition scrubbing, and froth flotation are commonly used to separate the particles. Contaminant extraction from the soil and transfer to a concentrated liquid phase through water rinsing. Pollutants can be extracted by either moving them to the washing solution or by using flotation, attrition, particle or gravimetric separation to concentrate them in a smaller volume of solids [24]. In contrast to gravel and sand particles, clay and silt show a preference for dangerous substances. During washing, silt and clay are mechanically separated from the uncontaminated coarse soils. While the coarse sand is kept for backfilling, the contaminated fine sand is either treated or disposed of. It has been demonstrated that this procedure is less than 80% effective, and that the efficiency rises with the use of hot water. This technique is mainly applied as a pre-treatment technique for ultimate soil cleansing [25]. According to [26], the efficacy of the soil washing technique are increased when surfactant (biosurfactant: aescin, lecithin, rhamnolipid, saponin, and tannin) is used in the process. With the exception of lecithin, which had a 15% removal rate, all surfactant solutions can achieve 80% oil removal at 50°C. Apart from augmenting efficiency, [24] observed that surfactant improves ex-situ soil washing through the emulsification and weakening of hydrocarbon chains, thereby offering a favorable surface area for biodegradation. This makes surfactant an economically attractive alternative for innovative soil washing technologies.

## 2.2.2 In-Situ Washing by Sedimentation (IWS)

This technique is a novel approach to remediating soil without having to excavate it. Physical segregation and onsite wash water treatment are carried out using this technology. This process entails hydraulically separating the soil particles according to their size and density after high air pressure is injected into a mixture of water and sandy soil that is positioned in a column at a specific depth (D). Therefore, isolating the area is crucial to preventing the used aqueous solution from leaking. The benefit of the method is that it permits the soil's washing and segregation processes to take place concurrently with the treatment process [27].

## 2.2.3 Soil Flushing

This in-situ method uses an aqueous solution either plain water or a properly blended solution containing a surfactant or co-solvent in order to remove or leach chemicals from contaminated soil. Surfactants are frequently employed in flushing solutions to remove hydrocarbon pollutants because they can lower surface tension and promote contaminant solubilization. Mixed enhancing agents, on the other hand, are essential for dealing with more

complicated pollutants [28]. Surfactants are frequently employed to split and capture hydrocarbon compounds into colloidal molecules or aggregates that may move freely in liquid phase, hence increasing the desorption rate of these compounds from soil minerals and organic matter and increasing their solubility [29]. Additionally, gaseous mixes are used to speed up one or more of the same geochemical reactions that alter the concentrations of contaminants in groundwater systems, such as biodegradation, acid-base reaction, and adsorption/desorption. The three main activities of this method are fluid injection, site characterization, and procedures for mobilizing and recovering contaminants. The factors that affecting on the process efficiency are hydrogeologic factors including, pH, buffer capacity, cation exchange capacity, and total organic content (TOC). Therefore, less permeable soils like clay may be more difficult to treat because of their low water permeability and heterogeneity, which inhibit the best possible interaction between the solvents and the intended contaminants. So, the process works best in uniform, porous soils such as sands or silty sands [23].

## 2.2.4 Soil Vapour Extraction (SVE)

It is a physical in-situ remediation method which involved applying vacuum to the soil matrix to create an air flow going toward the extraction well that causes organic contaminants in the soil to evaporate [30] as shown in figure 2. The effectiveness of traditional SVE operating at ambient temperature in eliminating semi-volatile contaminants from soil is restricted. Therefore, numerous techniques targeting to raise soil temperature, including heat blankets, thermal wells, steam or hot air injection, radio and microwave frequency heating, as well as low-frequency electrical heating, have been developed in order to expedite the remediation of soil contaminated by semi-volatile materials via SVE. Thermally-enhanced soil vapor extraction (T-SVE) applications increase the extent of pollutants removed, shorten remediation times, and improve removal efficiency [31]. Nevertheless, not all soils are suitable for the insitu T-SVE, particularly those with low air permeability.

SVE is generally suitable for unsaturated zones in order to remove volatile organic contaminants such as those with boiling temperatures below 250 °C or vapor pressures greater than 1 mmHg, or with Henry's law constants greater than 0.001 atm·m<sup>3</sup>/mole at 20 °C. The factors that affect the SVE technique are permeability, stratification, and soil structure. The permeability influences the movement of vapor and air through the soil; increased permeability of the soil facilitates faster and more extensive vapor extraction. However, a highwater content decreases soil permeability, which can impact SVE's efficacy. On the other hand, stratification and soil structure impact the direction and manner in which vapors move through the soil medium [32].

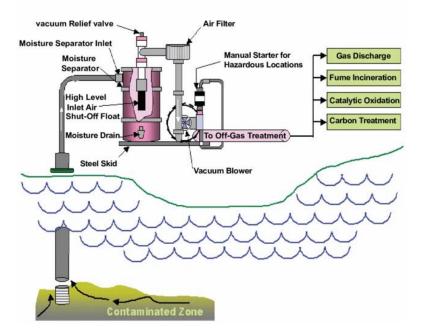


Figure 2: Soil vapour extraction [33]

## 2.2.5 Foam Flushing with Soil Vapor Extraction

This technique has been used to remove contaminants that have been sorbed in soil, such as diesel, that may not be adequately treated by SVE because of the low volatility of the heavier portion of the fuel. This is because diesel compounds with high boiling points and carbon numbers greater than roughly  $C_{10}$  have limited mass transfer from the sorbed phase of the soil to the gas phases. While this method is applicable in saturated aquifers, it is less likely to be used in unsaturated zones. The injection of surfactant liquid into the vadose zone would cause the infiltration downward since gravitational forces are stronger than capillary forces. The risk of pollution spreading could arise, though, if the mobilized diesel pollutants in the vadose zone travel downhill. It has been shown that aqueous surfactant foam flushing with low water content (typically 1-3%) enhances the delivery of remedial additives in the vadose zone while reducing surplus water that can lead to vertical pollutant movement [34].

One benefit of employing foam in soil remediation is that the flow direction of injected foam in the vadose zone can be controlled by combining SVE with foam flushing. The injected foam's soil vapor and any modest liquid content such as foam funicular water in unsaturated soils would go in the direction of the SVE extraction well before going into the air-water separator for additional processing. By removing semi-volatile organic chemicals that have been sorbed into the soil using foam and removing volatile organic compounds using SVE, this foam-SVE system may effectively remove diesel. Foam is often produced using four different types of surfactants: anionic, cationic, nonionic, and zwitterionic forms [35]. The cationic and zwitterionic surfactants exhibit an electrostatic attraction to negatively charged soils, making them less appropriate for remedial purposes. Compared to ionic surfactants, nonionic surfactants have the advantage of having multiple polyoxyethylene moieties, which act as the hydrophobic portion of the surfactant molecule and increase the solubility of organics. They are also less susceptible to multivalent ion water hardness [36]. Furthermore, [37] used combinations of surfactants that is, the anionic surfactant sodium dodecyl sulfate (CH3(CH2)11OSO3Na, SDS) combined with the nonionic surfactant polyoxyethylene (20) sorbitan monooleate ( $C_{64}H_{124}O_{26}$ , TW80) to flush ethylene dichloride tar in the soil column. The results demonstrate that, in comparison to TW80 alone, the addition of SDS in the SDS/TW80 mixture reduced the solubility of contaminants because of the electrostatic repulsion caused by the anionic species. TW80 is a nonionic surfactant that is biodegradable and non-toxic, and it has been extensively utilized in surfactant aided aquifer remediation applications.

It was shown that foam flushing could be an alternative approach for improving SVE and lowering diesel contamination in the unsaturated zone by utilizing TW80 as the surfactant for produce foam instead of using  $N_2$  gas flow alone (SVE) [38].

## 2.2.6 Soil Excavation

It is a physical method where the contaminated soil is transferred from the area of contamination to a location or establishment where the possibility of exposure with possible contaminants can be adequately managed. Both organic and inorganic contaminants can be treated using this method. The excavated soil may be treated on the site, off-site, or left untreated and disposed of in a landfill. Excavation is the most expedient and secure method of treating soil contaminated by crude oil, but it is also expensive and unadvanced [39]. Even while this procedure is straightforward and effective, it takes a long time, can be harmful, and requires care for the landfill mines that are generated during the process of transporting contaminated dirt to the disposal site [40].

## 2.2.7 Solidification/Stabilization

This method can be applied in situ and ex-situ and also called (waste fixation). It assists in limiting and inhibiting the migration and movement of pollutants by immobilizing them in the form of an impermeable mass, a monolithic block, a clay-like substance, or granular particulate that is non-leachable. Alternatively, it converts pollutants to a chemically stable form by adding cementitious binding materials into the contaminated medium. This method is accomplished by means of the following techniques: encapsulating, cement-based, organic polymer, pozzolanic, and thermoplastic techniques. [41]. The ingredients and agents that are frequently employed for solidification or stabilization include gypsum, silicates, carbon, phosphates, sulfur-based binders, portland cement, and organo-clays. In order to reduce the risk caused by the pollutants, stabilization uses additives to change them into less poisonous, less soluble, less mobile, and less harming forms. In contrast, the process of solidification involves encasing hazardous compounds in a monolithic mass that has strong structural integrity and minimal permeability and compressibility after reagents are added. In this method the pollutants movement will be reduced through adsorption, precipitation and complexation processes. A study conducted wherein asphalt emulsions were used to stabilize and

solidify soil contaminated with petroleum [42]. The outcome demonstrated that petroleum-contaminated soil was stabilized and solidified by asphalt emulsion, forming a strong matrix that could be used as building material.

# 2.2.8 Chemical Oxidation

It is in situ chemical method where the oxidation approach is frequently utilized in heavily contaminated soil due to its rapid application time and ability to oxidize contaminants in a matter of weeks. The main objective of chemical oxidation is to convert the contaminants into inorganics, carbon dioxide, and water, or at the at least, to innocuous or biodegradable compounds [43].

The process of oxidizing organic pollutants involves the use of reactive oxidants such as hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), ozone (O<sub>3</sub>), permanganate (MnO<sub>4</sub><sup>-</sup>), and persulphate (S<sub>2</sub>O<sub>8</sub><sup>2-</sup>), and its effectiveness depends on the soil medium where this technique might not be the best option in soils with low permeability. Chemical oxidation also frequently employs a Fenton's reagent, which is a mixture of hydrogen peroxide and ferric ion (Fe<sup>3+</sup>). Ferric ions catalyze Fenton's reaction, whereas hydroxyl ions are produced by hydrogen peroxide, an oxidizing agent [39].

Ozone is another oxidative technique that researchers have used to remove oil from soil since it is easily manufactured, stored, and handled especially for in-situ remediations. Furthermore, because ozone quickly transforms back into oxygen, soils treated with this method can be reused [44]. According to some studies, ozonation and bioremediation can be combined to improve the degrading process' efficiency [45–47]. Even though using ozone has numerous advantages, it is known to destroy natural soil microbes, hence supplementation is typically needed for soil regeneration [48].

# 2.2.9 Electrokinetic Extraction (EK)

EK is among the most efficient in situ or ex situ methods which presents a high contaminant removal effectiveness in soil with poor hydraulic conductivity [49]. In the EK method, the polluted soil is exposed to a continuous, directcurrent electric field. By applying an electric field through the contaminated soil, pollutants are transported through appropriately positioned electrodes in the subsurface [50] . pollutants can be transported and eliminated in the EK technique through electromigration, electroosmosis, and electrophoresis.

Electromigration process achieved when ionic species found in soil solutions migrate when an electric field is introduced between electrodes. In this situation, more cation species migrate toward the cathode and more anion species travel toward the anode at the same time [51].

In the electroosmosis phenomena groundwater or an additional aqueous solution are used to improve the removal of pollutants. The majority of the cation species in the diffuse layer of soils are those that facilitate the movement of cationic and water species toward the cathode. The process of electrophoresis involves moving charged particles of a colloidal size through a stationary fluid while applying an electric gradient [52].

Furthermore, electrolysis is another significant electrochemical process a sequence of reactions at the anode and cathode that produce protons and hydroxide ions is achieved. This could raise the pH of the soil in the vicinity of the cathode [53].

In order to improve the effectiveness of eliminating pollutants from low permeability soil, the EK approach has also been employed when combined with other procedures, such as permeable reactive barrier [54].

## 2.2.10 Electrokinetic-Fenton Remediation Method

The application of the EK with Fenton reaction for the remediation of soil contaminated with both organic and inorganic contaminants, including total petroleum hydrocarbons (TPHs), has been studied during the past few decades [55], [56]. Due to the generation of highly oxidizing species, which can remove a wide spectrum of contaminants, electro-Fenton technologies offer promising alternatives for the removal of various organic compounds [57], [58].

The use of the electrokinetic Fenton (EK- Fenton) process studied as a promising method for remediating soil [59]. They used an iron electrode with various supporting electrolytes (tap water,  $H_2O_2$ , and citric acid) to depollute soil that had been contaminated with petroleum, with kaolin being chosen because of its low hydraulic conductivity. According to the results, eliminating hydrocarbons from this type of soil effectively by oxidation can be achieved by combining electrokinetic remediation (EK) with Fenton methods. The addition of  $H_2O_2$  with an iron electrode

produced greater removal efficiencies (89%) for total petroleum hydrocarbons (TPHs), indicating that the EK-Fenton reactions and the regulation of the soil pH conditions through the addition of citric acid actually increased the oxidation process.

In the Fenton reaction, the catalytic action of  $Fe^{+2}$  in an acidic solution breaks down  $H_2O_2$ , resulting in the production of hydroxyl radical (OH·), powerful agent of oxidation that target organic contaminants [60] as shown in eq. (1).

$$Fe^{+2} + H_2O_2 \longrightarrow Fe^{+3} + OH + OH$$
 (1)

Subsequently, the EK Fenton process can aid in the movement of  $H_2O_2$  through the soil and, when iron or other transition metal minerals are present, can decompose  $H_2O_2$  to produce OH· and other oxidizing species like  $O_2^-$  and  $HO_2$ . These species can then oxidize the pollutants [60].

## 2.3 Biological Remediation

## 2.3.1 Bioremediation

One of the most widely utilized methods for treatment polluted soil because of its advantages including low-cost, eco-friendly process and effectiveness. Furthermore, natural soil contains an enormous number of microorganisms, either suspended in the soil pore ecosystem or as a consortia linked to soil particles. Some microbes, primarily bacteria, have developed the ability to digest harmful pollutants by utilizing them as sources of energy or nutrients. The effectiveness of bioremediation is contingent upon the existence of suitable microorganisms and is also influenced by environmental factors, nutrients and electron acceptors, the type of pollutants are compounds that are biologically surface active and have several industrial applications can efficiently perform bioremediation of contaminated soils. they consist of two different parts as they are amphiphilic compounds that possess hydrophilic polar moiety and a nonpolar group which is hydrophobic. -ese properties enable them to reduce surface and interfacial tension and thus increase the surface area of the immiscible phases, increasing mobility, bioavailability, and subsequent biodegradation [62].

Hazardous organic contaminants are broken down or reduced via bioremediation into harmless substances including  $CO_2$ ,  $CH_4$ ,  $H_2O$ , and biomass without having a negative impact on the environment. Bioremediation technique can be applied in situ (such as bioventing, biosparging and bioslurping) or ex situ (such as land farming, biopile, bioreactor and windrows) based on the application area and a variety of factors, including the kind and amount of contaminants, site characteristics, and the cost. Where ex situ can be more cost than in situ method. Furthermore, there are differences in terms of the rate of biodegradation and the consistency of the process output. The selection criteria that determine which bioremediation method to use depends on the type of pollutant, its depth and degree of contamination, the type of environment, its location, its cost, and its environmental policies [63].

Research has indicated that a variety of bacteria can break down petroleum pollutants, such as Rhodococcus sp., Pseudomonas sp., and Scedosporium boydii. Bacteria mostly use aerobic routes to break down hydrocarbons. Catabolism of hydrocarbons is frequently increased when oxygen acts as an electron acceptor. Degradation occurs in aerobic mode through the mediation of oxidation, reduction, hydroxylation, and dehydrogenation reactions [64].

Microorganisms can utilize organic pollutants as their only source of carbon, allowing them to degrade organic pollutants in the soil. Microorganisms destroyed 62–75% of petroleum hydrocarbons in the soil in 150 to 270 days [65]. Free microorganisms destroyed 2.3–6.8% of petroleum hydrocarbons in 60 days, however when biochar was employed as a carrier, 7.2–30.3% of petroleum hydrocarbons were degraded in 60 days [66]. Extreme environmental conditions (soil temperature below 10 C°, pH below 4 and more than 9) decrease microbial activity, which diminishes the removal impact of petroleum pollutants. Furthermore, a pH 5.5–8.8, temperature 15 - 45 C°, oxygen content 10%, low clay or silt content soil type, and C/N/P ratio of 100:10:1 are the optimum conditions for microbial remediation of oily soil, according to current research [67].

## 2.3.2 Phytoremediation (in situ, ex situ)

It is a promising biotechnology that restores the soils that damaged by both organic and inorganic contaminants by utilizing plants, the microbes that they are connected with, and agricultural practices. The process either decontaminates the soil or sequesters the toxins inside the matrix (stabilization). Via a variety of processes, including phytoextraction (phytoaccumulation), phytodegradation, phytostabilization, phytotransformation,

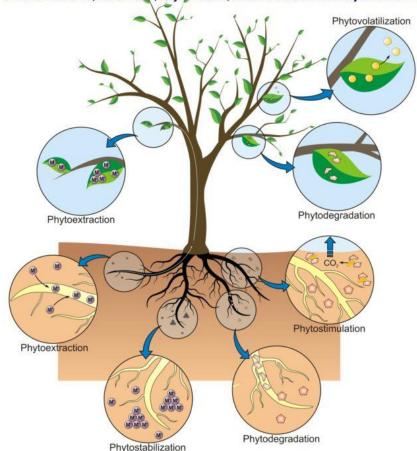
phytovolatilsation, rhizofiltration, and rhizodegradation (rhizoremediation), plants can break down, degrade, concentrate, sequester, bioaccumulate, contain, stabilize, and metabolize pollutants by acting as filters or traps in the tissue. Through these processes, the pollutants become less harmful and enduring in the surroundings [68].

Many dangerous and complex chemical molecules can be changed into simpler and less toxic ones by specific enzymes and other substances present in plants and microorganisms. Plant rhizospheres can provide microorganisms with food, oxygen, and a growing space. These bacteria increase the surface area of plant roots, increasing their ability to contact the soil and take up more nutrients necessary for the growth of the plant. The inoculation bacteria are therefore more concentrated in the soil close to the roots of the vegetation [69].

Numerous physiological characteristics of plants, including biomass and shoot length, as well as the breakdown of total petroleum hydrocarbons in soils were examined. Studies have demonstrated that certain plants, including Festuca elata Keng ex E. Alexeev, Lolium perenne L., Phragmites communis, Plantago asiatica L., Merr., Setaria viridis Beauv., and Phragmites communis, are suited for China's climate and environment and could be used for phytoremediation of petroleum-contaminated soil [70]. After 90 days of rehabilitating petroleum-contaminated soil with Festuca elata Keng exE. Alexee, the removal rate of petroleum is approximately 64 percent [71]. In addition to effectively removing benzopyrene from soil, Festuca elata Keng ex E. Alexeev's growth significantly enhances soil biological activity in saline-alkali zones contaminated with petroleum [72].

A list of the main plants (grasses and trees) that are currently utilized in phytoremediation plants that absorb or break down organic contaminants was published by [73]. Other studies have shown phytoremediation of petroleum-contaminated soil by multiple plants, with the addition of organic fertilizer to promote remediation [74-76].

The major factor in the success of phytoremediation is the capacity of the plant to carry out the oxidative breakdown of organic xenobiotics and bioassimilate or bioaccumulate organic pollutants into their cell wall structures. As well as the properties of the contaminants and polluted soil and each of the mechanisms that effect on the movement, toxicity, volume or concentration of the pollutants. Figure 3. Shows schematic representation of phytoremediation.



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Figure 3: Schematic representation of phytoremediation [77]

# 3. The selection of remediation technique

Choosing the optimal remediation treatment option depends essentially on understanding the nature of pollution and its source, the pollutant properties, and its composition, the affected environment's physical, chemical, and biological characteristics. In addition, the pollutants' fate, movement, and dispersion, the deterioration process, interactions and relationships with microorganisms, the internal and external variables influencing remediation. All of the previous factors mentioned helping in evaluating and predicting the chemical behavior of the pollutants with short- and long-term impacts and limiting exposure to the pollutants and mitigating their effects. Furthermore, when choosing an appropriate remedial treatment procedure, factors such as mechanisms, regulatory requirements, cost, and time limits are taken into account [78]. Three factors comprise the success criterion for remediation technologies:

(1) technological performance: which features characterize how well the technology can accomplish risk reduction objectives and how quickly it can do so.

(2) commercial characteristics: that are associated with the costs and profits of the technology aspects.

(3) public and regulatory acceptability: particularly significant to regulators and the local community around the contaminated site; these characteristics may also be significant, albeit to different degrees, to other stakeholder groups.

# 4. Conclusion

Soil pollution with petroleum waste, is one of the greatest risks threatening the environment and humanity. Due to the importance of this issue, numerous techniques for remediation treatment exist, but no single technique is best suited for every form of contamination and every combination of site-specific circumstances present in the impacted environment. This article reviews the most important methods for treating soil contaminated with petroleum waste. Choosing the appropriate treatment method depends on the type of pollutant and its characteristics, and the effect of soil composition and characteristics on the movement of the pollutant and its fat. To properly remove, contain, or destroy pollutants and hazardous materials at the damaged locations, more than one remediation treatment method may be needed, or they may need to be combined into a process train. It is preferable that the chosen treatment method be environmentally friendly, have effective results, and have a reasonable cost. In general, in-situ soil remediation is more cost-effective than ex situ treatment, and contaminant removal/extraction is more favorable than immobilization and containment.

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