Chapter

Source and Control of Hydrocarbon Pollution

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Abstract

Hydrocarbon contamination is of great worry because of their widespread effect on all forms of life. Pollution caused by increasing the use of crude oil is ordinary because of its extensive application and its related transport and dumping problems. Crude oil contains a complex mixture of aliphatic, aromatic, and heterocyclic compounds. Soil naturally consists of heavy metals, and due to human action like refining of oil and use of pesticides, their concentration in soil is rising. Several areas have such high heavy metal and metalloid concentration that surrounding natural ecosystem has been badly affected. The reason is that heavy metals and metalloids limit microbe's activity rendering it unsuitable for hydrocarbon degradation, thus reducing its effectiveness. Environmental remediation is thus extremely necessary and involves with the elimination of pollutants from soil, air, and water. In the last several decades, different methods have been employed and applied for the cleanup of our environment which includes mechanical, chemical, and biochemical remediation methods. The hydrocarbon pollution consists of many aspects like oil spills, fossil fuels, organic pollutants like aromatics, etc. that are discussed below.

Keywords: aromatic hydrocarbons, organic and inorganic pollutants, bioremediation, chemical remediation

1. Introduction

Contamination of hydrocarbon occurs due to toxic organic substances, petroleum, and pesticides which is a serious concern for the environment. Contamination caused by petroleum hydrocarbon is a matter of worry because these are harmful for various life forms. Crude oil contamination is common due to its extensive use and its related dumping process and accidental spills. Complex mixture of a large range of high and low molecular weight hydrocarbons makes up the petroleum. The complex mixture of petroleum consists of saturated and branched alkanes, alkenes, and homo- and heterocyclic naphthenes; aromatics consisting of heteroatoms such as heavy metal complexes and N, S, and O; hydrocarbon consisting of different functional groups such as ethers, carboxylic acids, etc.; and large aromatic molecules such as asphaltenes, resins, and naptheno-aromatics.

Heavy metals are present in crude oil, and its heavy metal content is associated with porphyrins which is the pyrrolic structure. Lube oil waxes, light oil, asphaltenes, naphtha, diesel, kerosene, etc. are the several fractions in which the petroleum is refined. Light ends is the term that is used for the light fractions which are distilled at atmospheric pressure, and heavy ends is used for heavy fractions such as asphaltenes and lube oil. Due to different hydrocarbon compositions of light and heavy ends of petroleum, light ends consists of a lower percentage of aromatic compounds and lower molecular weight saturated and unsaturated hydrocarbons, while heavier ends consists of higher molecular weight saturated and unsaturated hydrocarbons, aromatic compounds with high molecular weight, and organometallic compounds. This part is relatively affluent in metals and nitrogen, sulfur, and oxygen-containing compounds [1].

Concentration of heavy metal is rising in the soil as a consequence of human action. There is a large impact of higher heavy metal and metalloid concentration in some areas [2].

2. Hydrocarbon pollution

This is caused mainly by accidents on oil platforms and ships used for hydrocarbon transportation but also by discharging water into the sea which is used to wash tanks of tanker vessels. Crude oil and petroleum products form a waterproof film on water that prevents the oxygen exchange between environment and water causing damages to plants, animals, and human beings. Nowadays during transport overseas, "double-hulled" tankers are used to avoid leaks in case of accidents. Best international practices are adopted with regard to oil platforms to face or eventually adequately deal with any type of inconvenience.

3. Organic pollutants

With the onset of industrialization, the use and buildup of organic compounds have increased. Major sources which are responsible for organic contaminants are anthropogenic activities including the use of fuels, solvents, and pesticides. Various organic compounds are harmful and are related to health concerns globally.

Diverse sources are responsible for the generation of hydrocarbons in sediments which are categorized below [3, 4]:

- Anthropogenic sources
- Petroleum inputs
- Partial burning of fuels
- Fires of forest and grass
- Biosynthesis of hydrocarbons by marine or terrestrial organisms
- Diffusing from the petroleum source rocks, reservoirs, or mantle

Organic pollutant is responsible for environmental and health-related problems; hence bioremediation provides an efficient explanation to this problem [5].

3.1 Polycyclic aromatic hydrocarbons (PAHs)

PAHs are considered to be ubiquitous contaminants. There are 100 diverse compounds of polycyclic aromatic hydrocarbons present. PAHs are seldom used for the industrial purpose, but only few are used for the manufacturing of pesticides, dyes, and plastics and for the production of medicines. Polycyclic aromatic hydrocarbons are produced on partial burning of organic matters [5]. PAHs due to carcinogenic and mutagenic nature are highly poisonous to organisms. The degradation of PAHs is predominantly slow with high molecular weights because due to low hydrophobicity and water solubility it has a tendency to accumulate in sediments [6]. PAHs have been classified as a priority pollutant by the USEPA which has classified 16 individual PAHs as pollutants due to its poisonous, carcinogenic, and mutagenic nature [7].

3.2 Polychlorinated biphenyls (PCBs)

Polychlorinated biphenyls (PCBs) due to carcinogenicity, toxicity, and slow biodegradation in the nature are well thought-out to be the worst pollutants [8] of commercial PCBs of about hundreds of thousands of metric tons are persevere in aquatic sediments [9]. In adhesives and lubricants, dielectric fluids in flame retardants, transformers, hydraulic fluids, and plasticizers, PCBs are widely used. PCBs are released from disposal and spillage [10].

3.3 Polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs)

Polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) are still present in deep sediment layers which are deposited decades ago. Toward biotic and abiotic degradation processes, PCDD/Fs are often well-thought-out to be recalcitrant [11]. PCDD/Fs are the most notorious pollutants present in nature [12].

Table 1 Microorganisms studied.

Pollutants	Organisms	Function	References
2,4,6-Trinitrotoluene (TNT)	*Methanococcus* sp.	Biotransformation	Boopathy and Kulpa [13]
Atrazine	*Pseudomonas* sp. (ADP)	Biodegradation	Newcombe and Crowley [14]
Chlorpyrifos	*Enterobacter* strain B-14	Biodegradation	Singh et al. [15]
Dibenzothiophene (DBT)	*Rhizobium meliloti*	Biodegradation	Frassinetti et al. [16]
Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)	*Acetobacterium paludosum*	Biodegradation	Sherburne et al. [17]
PAHs	*Clostridium acetobutylicum*	Biodegradation	Zhang and Hughes [18]
Phenanthrene, PAH	*Pseudomonas* sp., *Pycnoporus sanguineus*, *Coriolus versicolor*, *Pleurotus ostreatus*, *Fomitopsis palustris*, *Daedalea elegans*	Biodegradation	Arun et al. [19]
Polychlorinated biphenyl (PCB)	*Agrobacterium*, *Bacillus*, *Burkholderia*, *Pseudomonas*, and *Sphingomonas*	Biodegradation	Aitken et al. [20]
Polycyclic aromatic hydrocarbon (PAH)	*Rhodococcus erythropolis* TA421	Biodegradation	Chung et al. [21]
	Rhizobium sp.		Damaj and Ahmad [22]
	Fungi		Atagana [23]

Table 1.
Microorganisms studied or bioremediation function.

4. Inorganic pollutants

Human sources are mainly responsible for the heavy metal contamination, but contamination due to natural and biological processes are also common which includes:

1. Mineral weathering over time.

2. Erosion and volcanic actions.

3. Forest fires and biogenic resource.

4. Vegetation causes release of particles.

Cellular binding sites of microbes are responsible for the absorption of heavy metals. By various mechanisms, heavy metals can be complexed with extracellular polymers of microbes. Organic contaminants can be mineralized by these microorganisms and convert into metabolic intermediates which can be utilized as primary substrates for growth of the cell. Heavy metals can be eliminated from the metal-polluted soil by microbes which can change the heavy metal oxidation state by immobilizing them [24]. Research on bioremediation of heavy metals by microbes has not been carried out extensively due to metal adsorption and incomplete knowledge of the genetics of the microbes.

5. Sources and effects of hydrocarbon-contaminated wastewater effluents

Numerous sources such as pesticides, petroleum, or different harmful organic substances which are discharged into the water streams as effluents are responsible for the hydrocarbon pollution into the wastewater. Water contaminated with hydrocarbons is known to be carcinogenic, neurotoxin, and mutagenic to flora and fauna [25]. Contaminated lands, oil spillage, pesticides, automobile oils, and urban stormwater discharges are the major causes for the hydrocarbon contamination.

Oil spill is one of the major sources of hydrocarbon contamination. Oil spills caused mainly by accidents on oil platforms and ships are needed for transportation of hydrocarbon but also by disposal of water into the sea which is used to wash tanks of tanker vessels [2]. Underground oil storage tanks and leaking pipelines are also responsible for oil spilling in water [26, 27].

Increase use of vehicles and automobiles leads to increase in utilization of automobile oil, which is the major cause of hydrocarbon contamination in water. This type of contamination occurs when oil from the car drops onto the ground and leaks; it could be washed into water streams by runoffs [28].

Pesticides are another source of hydrocarbon contamination in water. Pesticides include herbicides, fungicides, and insecticides. Only small amount of pesticide is able to achieve the target, while the major proportion stays in the soil, and it can be washed away by the rain in the water stream [29]. Herbicides, out of all the pesticides, are most hazardous because it is directly applied on the soil in order to kill the weed and can be washed away during rainfall into the water streams.

Another source of hydrocarbon contamination in water is the land where some type of industrial action is being carried out. These lands contaminated by hydrocarbons or toxic organic compounds are washed due to rainfall into the water steams, thus causing pollution [30].

One of the main sources of hydrocarbon pollution is the discharge of urban stormwater. In urban communities, car parks and roads are frequently polluted by gasoline and oil from the vehicles, and during rainfall, these pollutants are washed into water streams and hence can contaminate them [30, 31].

Wastewater contaminated by hydrocarbons has an adverse effect in nature, animals, human beings, and plants. Lack of oxygen, decrease in crop yield, and effects on aquatic plants are various effects of hydrocarbon contamination in nature. There would be decrease in the crop yield and available food for household due to inappropriate crop's growth when the farmland is irrigated by water contaminated with hydrocarbon [32, 33]. Soil fertility can be decreased to an extent due to the presence of oil in water due to the reason that most of the vital nutrients are no longer accessible for crop consumption which results in the decrease of the crop yield. The reduction in the yield of crop results in the decrease of the farmer's earnings [34, 35].

Oxygen shortage is another environmental effect of hydrocarbon contamination. The main source of oxygen in nature is the economic trees which rely on rainfall or on the water steams for their growth. Oil spills can inhibit root penetration due to hydrocarbons which can block the pores of the soil, thereby removing water and air [36]. This results in the death of such plant or distortion in the growth and hence causes oxygen shortage for human utilization [37]. Hydrocarbon contamination in water avoids the penetration of light into the water and the exchange of gases for consumption by aquatic plants. This leads to the death of the plant because plant becomes incapable to photosynthesize and hence can affect the food chain. Plants consume the pollutants from the contaminated water which can be passed to humans and animals through the food chain [38].

Polycyclic hydrocarbons are toxic and found to have serious effects on human beings. The immune system, liver, respiratory system, reproductive system, circulatory system, kidney, etc. are the organs which are affected due to the hydrocarbon ingestion [33]. Individual's susceptibility and level of exposure are the factors on which the degree of damage depends [2]. Cancer risk and hormonal problems that can disturb developmental and reproductive processes are the other effects of effluents polluted by hydrocarbons on human beings [39–41].

Discharge of wastewater contaminated with hydrocarbon into the water streams poses risk to animals through absorption, breathing, and ingestion. Sea birds are the most exposed to the hydrocarbon pollutant because it spends majority of its time near the water bodies [42]. There is unusual decrease in the temperature due to the destruction of the protective layer of the feathers in sea birds as a result of the presence of oil in water [43]. Scavengers such as ravens and vultures are also in danger when they consume preys and contaminated fish [44]. Water contaminated with hydrocarbon is consumed through gills of the fish during the respiration and accumulates in the gall bladder, liver, and stomach, and thus the fish becomes unhealthy for human utilization [45].

6. Remediation

Polluted land or water systems have become a serious concern for human health. Over the past few decades, several methods have been developed and applied for the cleanups. The degradation either biological or chemical of petroleum which is a complex mixture of chemical substances is difficult because different treatments are required for different classes of compounds. Hence, remediation of oil-containing environment is not easy. Remediation strategies are decided after knowing the oil composition and physicochemical nature of the polluted site. Physical and chemical properties and pH of the polluted water/soil are the different factors on which the crude oil degradation depends. Oil-producing wells are generally situated near seashore, so due to this reason, water is contaminated mostly by oil spills during oil production operation. Oil spills are controlled by biological and chemical methods. Out of these two methods, chemical method is more frequently used. Bioremediation is gaining worldwide attention.

7. Remediation techniques for hydrocarbons

Contamination due to petroleum is widespread in the environment and contaminates surface and groundwater [46]. Several operations in petroleum exploration, leaking of underground storage tanks, and its production and transportation are responsible for affecting the environment [47]. Contamination causes threat to human health and safety and can affect nature by contaminating surface and groundwater [46].

Efforts are made both nationally and internationally in order to remediate the pollution caused by hydrocarbon contamination which can cause environmental and health risk. There are three methods involved in the remediation of sites contaminated due to hydrocarbon [2, 48]:

1. Phytoremediation

2. Bioremediation

3. Chemical remediation

7.1 Phytoremediation

Phytoremediation is the process which involves the use of plants for the degradation, extraction, and elimination of the contaminants from the air, water, and soil [40, 49–51]. It includes various mechanisms which can lead to degradation of contaminants, dissipation, immobilization, and accumulation [52, 53]. Various phytoremediation applications with examples are systematically given in **Table 2**.

7.1.1 Mechanisms of phytoremediation

Contaminated land and water are remediated more feasibly by using plants involving a variety of pollutant attenuation mechanisms than physical and chemical remediation techniques [54–58]. Plants due to their sedentary nature had developed various abilities for dealing with hazardous compounds. Plants serve as solar-driven pumping and filtering systems as they take up pollutants from the soil through the roots which is transported to various parts of the plant by the help of plant tissues where they can be volatilized, metabolized, or sequestered [57, 59]. Different types of mechanisms are used by the plant for removing the pollutants from the soil. They consist of biophysical and biochemical processes such as adsorption, translocation, and transport, as well as mineralization and transformation by plant enzymes are the mechanisms of phytoremediation [8]. Halogenated substances like TCE are degraded by plants using oxidative degradation pathways, and it includes plant-specific dehalogenases. After the death of the plant, the dehalogenase activity is still maintained [60]. Laccases, P450 monooxygenases, nitroreductases, dioxygenases, phosphatases, peroxidases, dehalogenases, and nitrilases are various contaminant-degrading enzymes which are present in plants [61–63]. The basic physiological mechanisms involved in phytoremediation in higher plants and related microorganisms, such as

Application	Media	Contaminants	Typical plants
Phytotransformation	Soil, groundwater, landfill leachate, land application of wastewater	Herbicides, aromatics, chlorinated aliphatics, nutrients, ammunition waste	Phreatophyte trees (popular, willow, cottonwood, aspen) Grasses (rye, Bermuda, sorghum, fescue) Legumes (clover, alfalfa, cowpeas)
Rhizosphere bioremediation	Soil, sediments, land application of wastewater	Organic contaminants (pesticides, aromatics, and polynuclear aromatic hydrocarbons)	Phenolic releasers (mulberry, apple, Osage orange) Grasses with fibrous roots (rye, fescue, Bermuda) for contaminants 0.3 ft deep Phreatophyte trees for 0.10 ft Aquatic plants for sediments
Phytostabilization	Soil, sediments	Metals (Pb, Cd, Zn, As, Cu, Cr, Se, U), hydrophobic organics (PAHs, PCNBs, dioxins, furans, pentachlorophenol, DDT, dieldrin)	Phreatophyte trees to transpire large amounts of water for hydraulic control Grasses with fibrous roots to stabilize soil erosion Dense root systems are needed to sorb/bind contaminants
Phytoextraction	Soil, brown fields, sediments	Metals (Pb, Cd, Zn, Ni, Cu) with EDTA addition for Pb selenium (volatilization)	Sunflowers Indian mustard Rape seed plants Barley Hops Crucifers Serpentine plants Nettles Dandelions
Rhizofiltration	Groundwater, water and wastewater in lagoons or created wetlands	Metals (Pb, Cd, Zn, Ni, Cu), radionuclides (137Cs, 90 Sr, U), hydrophobic organics	Aquatic plants: emergents (bulrush, cattail, coontail, pondweed, arrowroot, duckweed); submergents (algae, stonewort, parrot's feather, Eurasian watermilfoil, hydrilla)

Table 2.
Application of phytoremediation with examples.

mineral nutrition, photosynthesis, transpiration, and metabolism. The root of the plant is responsible for the uptake of the organic and inorganic compounds from the soil, and it can bind and stabilize substance on its external surfaces on interaction with microorganism in the rhizosphere. Uptake or release of molecules occurs through exchanging gases from the aerial plant's parts with the atmosphere [64]. For addressing different contaminants in different substrates, six phytotechnologies have been recognized by Interstate Technology and Regulatory Cooperation:

1. For organic contaminants, phytotransformation is ideal in all substrates.

2. Rhizosphere bioremediation is used in soil containing organic contaminants.

3. Phytostabilization is used in soil for organic and inorganic pollutants.

4. Phytoextraction is useful in substrates containing inorganic pollutants.

5. Phytovolatilization is used for volatile substances.

6. Hydraulic flow can be controlled in the contaminated environment by using evapotranspiration.

7.2 Bioremediation

Bioremediation is a cost-efficient method used for the treatment of soil polluted with oil and wastes of petroleum consisting of biodegradable hydrocarbons and indigenous microbes.

The management of suitable levels of nutrient fertilizer addition, moisture control to optimize soil degradation by microorganisms, aeration and mixing, and pH amendment are required for the process of land treatment [65].

Enzymes attack on some inorganic compounds and on most of the organic compounds through the activities of living organisms. Bioremediation is the technique which involves the productive use of the biodegradative process for the elimination or detoxification of pollutants from the environment.

Oil spill causes contamination of soil which is considered as the chief worldwide concern. Pollution of soil due to petroleum causes a serious effect to human being, affects the groundwater, decreases the agricultural production of the soil, and causes economic loss and ecological problems. Plants, animals, microorganisms, and humans are affected by the toxicity of the petroleum hydrocarbons. Oil spill and accidents occur due to the transportation of crude oil which is generally through tankers on water or through land pipeline. Problems of the oil contamination occur mostly due to the reason that the main oil-producing countries are not the chief oil clients; hence petroleum is transported to the consumption area. Certain microorganisms are accountable for the petroleum hydrocarbon degradation and are used as the resource of carbon and energy for growth and maintenance. Soil contamination can be remediated by many ways including both physicochemical and biological techniques.

Biological techniques are more economical and proficient than physicochemical techniques. The degradation rate of petroleum products is increased by developing several remediation methods. Bioremediation through microorganism is considered to be the most effective method in comparison to other biological methods, but the high molecular weight hydrocarbons with low adsorption and solubility limit their accessibility to microorganisms.

7.2.1 Principle of bioremediation

Composite mixture of diverse chemical substances makes up the crude oil. Oil and its component are recognized by microbes using bioemulsifiers and biosurfactants, and then they join themselves; hydrocarbon is used as the resource of carbon and energy. High molecular weight hydrocarbons due to their low adsorption and solubility limit their accessibility to microorganisms. Oil biodegradation rates are improved by the biosurfactant's addition which increases the elimination and solubility of these pollutants.

The oil constituents vary particularly in susceptibility, volatility, and volubility to biodegradation. A number of substances are easily degraded, some are nonbiodegradable, and some oppose degradation. Diverse species of microbes preferentially attack diverse compounds due to this biodegradation of petroleum that occurs at different rates but concurrently. Enzymes produced by microorganisms in the presence of sources of carbon are accountable for attacking the hydrocarbon molecules. Hydrocarbon present in the petroleum is degraded by different enzymes and metabolic pathways. Hydrocarbon degradation is prevented by the lack of suitable enzyme [66].

Bioremediation process involves the utilization of natural microorganisms for the decontamination of atmosphere [67]. This process converts pollutants into useful or nontoxic substances by using bacteria, fungi, and yeast which are the naturally occurring microorganisms [40]. This is also a process in which microorganisms restore the quality of the environment by degrading and metabolizing the chemical substances [48]. **Table 3** represents the main microorganisms which are included in the remediation of hydrocarbons.

7.2.2 Microorganisms

7.2.2.1 Bacteria

Microbial species has efficient hydrocarbon degradation capability in natural environments. Various microbial species have been isolated from heavily polluted coastal areas, variety of oil spill, or soil contaminated by petroleum. These are isolated on the basis of their capability to metabolize different sources of carbon such as aliphatic and aromatic compounds and their chlorinated derivate. Enrichment culture procedures were used for obtaining the microorganisms, and for the selection criterion, maximum final cell concentration or maximum specific growth rate was used. Various microorganisms such as fungi, microalgae, bacteria, and yeast [68] are used for degrading the petroleum hydrocarbons. Out of these microorganisms, bacteria play a significant role for hydrocarbon degradation. Rapid degradation of low molecular weight alkanes is reported by various studies. The capability of microorganisms to use hydrocarbons to assure the growth of cell and energy requirements by degrading hydrocarbon is the driving force for the petroleum biodegradation. Biodegradation of petroleum is carried out more extensively by mixed cultures in comparison to pure culture [69]. Adequate indigenous microbial community in many ecosystems is capable of biodegradation of oil, but for oil degradation metabolic activity, environmental conditions should be favorable. Indigenous microorganisms have several advantages than adding microorganisms for hydrocarbon degradation.

7.2.2.2 Fungi

For the biodegradation of hydrocarbons in soils, fungi play a more vital role than bacteria. Filamentous fungi which are found in aquatic structures are mostly related with surface films and sediments. The enzymatic processes used by mammalian organizations are also used by fungi in polycyclic aromatic hydrocarbons (PAHs).

Bacteria	**Yeast and fungi**
Achromobacter	*Aspergillus*
Acinetobacter	*Candida*
Alcaligenes	*Cladosporium*
Arthrobacter	*Penicillium*
Bacillus	*Rhodotorula*
Brevibacterium	*Sporobolomyces*
Corynebacterium	*Trichoderma*
Flavobacterium	*Fusarium*
Nocardia *Pseudomonas* *Vibrio*	*Trichoderma*

Table 3.
List of microorganisms for bioremediation.

Two major types of cytochrome P450 monooxygenases have been well characterized in yeasts and filamentous fungi. Several fungi have the ability to oxidize polycyclic aromatic hydrocarbons to phenols, dihydrodiols, and other metabolites and conjugates, but only some fungi such as *Phanerochaete chrysosporium* have the capability to catabolize them totally to CO_2.

Example:

i. *Mitosporic Ascomycota*

ii. *DothiorellaAureobasidium*

iii. *Saccharomycetales candida*

7.2.2.3 Yeast

The biodegradability of various yeasts decreases from n-alkanes > branched alkanes > low molecular weight aromatic hydrocarbons > cycloalkanes > high molecular weight aromatic and polar compounds.

Bioremediation process involves the detoxification of pollutants due to the various metabolic capabilities of microorganisms which is the developing method for elimination of contaminants from nature together with the yields of the petroleum industry [70]. Bioremediation technique is considered to be cost-effective and noninvasive. Petroleum and other hydrocarbon contaminants can be eliminated from the atmosphere by using microorganisms which is considered as primary mechanism, and it is the cheaper method in comparison to other remediation technologies. Microorganisms having suitable metabolic capabilities are the essential requirement.

Alkylaromatic degradation is carried out by various microorganisms such as *Arthrobacter*, *Mycobacterium*, *Sphingomonas*, *Burkholderia*, *Rhodococcus*, and *Pseudomonas*.

Fungi, bacteria, and yeast are accountable for the biodegradation of hydrocarbons in the environment. Six percent [71] to 82% [72] is the reported efficiency of biodegradation for soil fungi, 0.003–100% [73] for marine bacteria, and 0.13% [71] to 50% [72] for soil bacteria. Complex mixtures of hydrocarbons such as crude oil in freshwater, aquatic environments, and soil are degraded by mixed populations with overall wide enzymatic capacities [74].

Bioremediation involves two processes as follows:

1. Bioaugmentation

2. Biostimulation

7.2.2.3.1 Bioaugmentation

Bioaugmentation process involves the degradation of the harmful hydrocarbons by the addition of microorganisms in order to achieve the pollutant reduction [67]. It is also the injection of polluted water with microorganisms capable of hydrocarbon degradation [48]. This process sometimes involves biodegradation of the hydrocarbon pollutants by adding the genetically engineered microorganisms into the polluted water [75]. Bioaugmentation process is not often used for the hydrocarbon degradation because microorganisms responsible for hydrocarbon degradation naturally exist in the environment. Bioaugmentation process is not so much effective to be used in oil spill remediation sites, and nonindigenous microorganisms used in this process can cause competition with the microbes already present in the environment [76].

7.2.2.3.2 Biostimulation

Biostimulation is the process which involves degradation of the harmful compounds by adding the nutrients required by indigenous hydrocarbon-degrading microbes [67]. The growth of microorganisms responsible for the degradation of oil during oil spillage is activated by the increase in carbon. The tendency of the microorganisms to degrade the hydrocarbons is enhanced by addition of suitable concentration of supplemental nutrients. Due to this reason, microorganisms are competent of achieving their utmost rate of growth and consequently the utmost rate of contaminant uptake [77, 78]. The maximum biostimulation is achieved by obtaining the ideal nutrient concentration which is required for the utmost growth of the microorganisms and maintaining concentration as long as possible for microorganisms [79].

7.3 Chemical remediation

This process requires the use of chemicals. Contaminants can be treated by using various chemicals. Chemicals usually have the capability of altering the contaminant's chemical and physical properties [80]. Dispersants, solidifiers, and chemical oxidants are the three categories in which the chemical remediations are grouped [2, 48, 52].

7.3.1 Dispersants

Slick of oil can be broken down into smaller droplets by surfactants which are present in dispersants, and these droplets undergo rapid dilution by transferring it into the water and can be effortlessly degraded [81]. Chemical dispersants can raise the oil droplet surface area which results in an increased rate of natural biodegradation, and this process makes the oil less sticky to the surface by slowing down the development of oil-water emulsions and allows fast treatment [82]. This method makes oil spills less harmful for living organisms and the marine life. This is achieved by converting oil slicks into droplets which in turn can be degraded by bacteria [2, 81]. Nokomis 3-F4, Slickgone NS, Finasol OSR 52, SPC 1000™, Neon AB3000, ZI-400, Corexit 9500, Corexit 8667, and Saf-Ron Gold are some of the examples of chemical dispersants [83].

7.3.2 Solidifiers

In this method oil is removed by physical method which involves the interaction of dry granular materials with the oil and converts its liquid state into rubberlike solid state. Dry particulate and semisolid substances such as balls, pucks, sponge, etc. are the various forms in which the solidifiers can be applied. Solidification can be enhanced by using the solidifiers in the seas because mixing energy is provided by the seawater. Solidifiers are difficult to recover after solidification, and it is less efficient, which are the major drawbacks for the use of the solidifiers [82, 84].

7.3.3 Chemical oxidation

This technique involves the usage of chemical agents which are capable of oxidizing the organic pollutants [85]. These chemical agents are introduced by the help

Chemical treatment	Advantages	Disadvantages
Dispersants	Suitable in all weather condition and for wide range of oils	No oil recovery Not effective on highly viscous, non-spreading, and waxy oil
	Accelerates by degradation of the oil by natural processes Advanced formulations have reduced the previous concerns about toxicity Less man power needed Less expensive than mechanical methods	The localized and temporary increase in the amount of oil in water concentration that would have an effect on the surrounding marine life If dispersion is not achieved, other response method effectiveness may reduce on less disperse oil
Solidifiers	All weather conditions Quick	Lack of practical application Large amount required Selected oil Not effective No oil recovery

Table 4.
Advantages and disadvantages of chemical treatment.

of the mixing apparatus and injection in water or soil at the contaminated site. The usefulness of the process is found to depend upon oxidant quality, efficient contact between pollutant and oxidant, geological conditions, and oxidant's residence time [86]. This process is rapid and can be applied in all weather situations which are some of the advantages of this process. **Table 4** represents the details of other advantages and disadvantages.

8. Chemical and mechanical remediation methods

8.1 Oil spilled on the sea surface

There are various techniques involved for the elimination of oil from the surface of the sea and to avoid the oil to reach the shoreline. The widely used methods are mechanical recovery and the application of dispersants. The crude oil spreads over the sea surface because it is lighter than water and the thickness of the oil film becomes very thin in a small time. Type of oil, temperature of atmosphere, tide, temperature of water, and wind are the factors on which the velocity of oil spreading depends.

If oil spills accidentally, then the spreading of the oil can be prevented by using skimmers and booms which can control the spill to a short area, and finally the oil can be collected into the container. Oil can be solubilized by applying biosurfactants which are generally not detrimental to nature.

For oil spill remediation, at times in situ oil burning is also used as an optional method; but in situ method is useful only when the spilled layer of oil is floating on the surface of the water, oil spill is fresh, or after the oil has been converted into a smaller area by the booms. The above technique has some drawback that aquatic system gets polluted by the by-products and smoke generated as a result of burning of oil. Weather, tides, and ocean currents are the factors on which the usefulness of the cleaning method depends. If the oil reaches the shoreline, different methods are applied to clean up the gravels and sand. Oil is absorbed sometimes by oil sorbents similar to sponge. Oil is removed from the oiled vegetation by washing with water, but the plants damaged severely should be detached completely.

When the amount of contaminated water is less than ex situ, remediation method is applied by pumping the contaminated water to the processing site. The shore sand and gravels are removed and cleaned in a different place from the contaminated site.

8.2 Oil spilled on soil

Pollution of soil occurs due to leakages from pipes and wellheads during offshore oil production and drilling operations, leakage from underground storage tanks of petroleum, overflow from gathering stations, petroleum yields, and inappropriate dumping of waste of petroleum. During the excavation, transport, and handling of polluted material, significant risk may be created by this method. For the final disposal of the substance, it is very hard to locate new landfill sites. There is continuous requirement of monitoring and maintenance of separation barriers since the pollutant remains on the site, and hence cap and containment technique is the temporary solution.

Methods for the treatment of soil contamination are as follows:

1. In situ

2. Ex situ

8.2.1 In situ method

This method involves physicochemical processes including air sparging, soil air extraction, or by combinations of these two methods applied to the soil at the contaminated site. Vertical & horizontal fossil fuel drilling equipment's are used *in-situ* treatment. This technique is more efficient on sandy soil than on clay soils. Soil pollutant can be taken out by using air sparging which is also known as soil venting.

The growth of aerobic bacteria on oxygen feeding is accelerated by the help of this method. Air sparging can be also performed under the water table if the contamination takes place in the groundwater through extraction wells or to the surface by gravity segregation. The oil can be extracted from the oil saturated ground water or partially saturated soil by using a process called as slurping.

The volatile components which are trapped in the soil are extracted by injecting steam into the contaminated soil.

8.2.2 Ex situ

This technique involves the elimination and transportation of polluted soil to off-site remediation ability. Various processes are used to perform the ex situ remediation which is as follows:

Land farming process is used in which soil polluted with oil is excavated and spread above a bed where it once in a while is tilled until the contaminants are degraded. Fifteen to 35 cm of soil surface is treated with the help of this technique. Composting involves the increase in the development of the microbial species by mixing polluted soil with harmless organic compounds to contaminated soil. Bioreactors are used for the bioprocessing of polluted soil, sediment, and water in which the three phases, gas, soil, and liquid, are mixed continuously in order to enhance the biodegradation rate. Before loading the contaminated soil to the bioreactors, the soil is pretreated. Contaminants undergo chemical reaction and convert harmful compounds into nontoxic compounds. Dechlorination or UV is used for the catalyzation of the oxidation reactions. These techniques have a few limitations such as high cost due to the complication of the method required, while bioremediation due to natural biological action is a choice which provides the chance to degrade the hydrocarbon contaminants.

9. Application of bioremediation

1. Ecologically sound, natural process; there is an increase in the number of the existing microorganisms when the contaminants are present, and the microbial population decreases naturally when the contaminants are degraded. The residues such as water, carbon dioxide, and fatty acids obtained as a result of the biological treatment are usually nonhazardous product, and the obtained CO_2 can be used for the photosynthesis process by the plants.

2. Bioremediation is responsible for destroying the target chemicals in place of transferring the contaminants from one place to another.

3. Other techniques which are used for the cleanup of harmful waste are more costly than bioremediation. For example, through the cleanup of the Exxon Valdez spill, the cost of 1-day physical washing is more than bioremediating 120 km of shoreline.

4. Bioremediation deals with in situ treatment and does not involve the transfer of a large amount of the polluted wastes off-site, and the risk due to the transportation can be overcome.

5. Microbe efficiency can be enhanced by using nutrient formulation in the bioremediation process.

6. The residues such as CO_2, fatty acids, water, etc. obtained from the biological treatment are generally nonhazardous.

It is a less costly technique than other techniques which are used for cleaning up of the toxic waste.

Hydrocarbons due to their different solubility from polar compounds such as methanol have lower polarity and hence have low solubility. Degradation of hydrocarbons is not only determined by solubilization. Many microorganisms are responsible for increasing the surface area of the substrate by excreting emulsifiers including *Bacillus licheniformis*, *Pseudomonas putida*, *Bacillus cereus*, *Pseudomonas aeruginosa*, *Bacillus subtilis*, and *Bacillus laterosporus*. Absorption of hydrophobic substance is facilitated by change in the cell surface by microorganisms. The behavior of individual hydrocarbons as well as mixtures can be changed by changing the physicochemical character of hydrocarbons [74].

10. Conclusion

Hydrocarbon pollutants have a widely applicable consequence on land, aquatic, as well as atmospheric ecosystem. This has been a problem ever since the use of fossil fuels and industrial revolution started. The unparalleled growth in populations with frequent oil spills, leakages in pipelines, and rampant use of pesticides contribute to substantial increase in pollution. These together are threatening the lives of animals and native microbiological population in land, air, and water surfaces and subsurfaces. Thus environmental remediation is the most important aspect of human survival. This book not only highlights the causes but also explains the techniques used in pollution rectifications. The various remediations described in this chapter are (i) phytoremediation, (ii) bioremediation, and (iii) chemical remediation.

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