

Review

# Bioremediation of Soil from Petroleum Contamination

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**Abstract:** Petroleum is the most common global fossil fuel. It is a complex multi-component system mainly composed of various hydrocarbons such as alkanes, cycloalkanes, mono-, bi- and polyaromatic compounds, resins and asphaltenes. In spite of humanity's need for petroleum, it negatively affects the environment due to its toxicity. The ecological problem is especially serious at petroleum mining sites or during petroleum transportation. Since it is not possible to replace petroleum with less toxic fuel, ways to reduce the toxic impact of petroleum hydrocarbons on the environment need to be developed. This review addresses bioremediation, a biological approach to petroleum degradation, which is mainly performed by microbes. The pathways of degradation of alkanes, alkenes and aromatic hydrocarbons are presented in detail. The effects of temperature, aeration and the presence of biogenic elements on microbial degradation of petroleum are discussed. Plant–microbe interactions involved with the bioremediation of petroleum-polluted soils are specifically addressed. The data presented in this review point to the great potential of bioremediation practices for cleaning soils of petroleum.

**Keywords:** rhizodegradation; microbial bioremediation; biodegradation; biosurfactants



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## 1. Introduction

Environmental pollution by petroleum and its products has an anthropogenic origin. The main losses of petroleum occur during mining, transportation and storage and amount to millions of tons per year [1–4]. Currently, 1.2 million hectares of land in Russia are contaminated to various extents and need re-cultivation [5].

The petroleum toxicity to all life forms is long-known and is usually attributed to softening of the plasma membrane lipid bilayer in the presence of petroleum [6]. In addition to membranes, petroleum can also impair the genetic processes in a cell [7,8]. With the above in mind, petroleum is considered to be one of the most dangerous pollutants of the environment due to its high toxicity and presence in the biosphere in vast amounts. In terms of its negative impact, petroleum, its products and wastes are ranked second after radioactivity. Petroleum spills from mining and processing accidents do significant harm to the ecosystems. In such cases, soil is mainly affected, because it is able to accumulate large amounts of pollutants due to its enormous adsorbing surface area. Petroleum pollution negatively affects soil biocenosis, seriously changes the chemical composition, structure and properties of soil, and reduces soil fertility and arable value. The petroleum spills may turn soils into typical technogenic deserts that are practically absent of biological processes. Petroleum-polluted soils are not suitable for agricultural and recreational uses and are potential sources of contamination of surface and ground waters.

Self-restoration of soils may take a long period, of 10 to 30 years or longer, depending on the soil type [9,10]. Remediation of petroleum-contaminated land requires a series of measures to clean up and restore soil as a natural environment. The most common of these measures are currently classified as physical, physicochemical, chemical and biological

measures. Sometimes, mechanical measures are used. Depending on the mechanism of action on the soil, the measures can be subdivided further (Table 1). In this review, we discuss only some of them.

**Table 1.** Soil cleanup methods' classification.

	Methods of Cleanup	Mode of Action (Examples)
Mechanical	Mechanical	Mechanical removal
Physical	Hydrodynamic	Flushing, filtering
	Aerodynamic	Vacuuming, purging, extraction
	Thermal	Thermos-osmosis
	Electrical	Electrochemical bleaching, electric osmosis, electrophoresis, electromigration, electro dialysis
	Electromagnetic	Magnetic separation
Physico-chemical	Volatilization	Removal of volatile petroleum products
	Dissolution, diffusion	Dissolution, leaching, diffusiophoresis
	Ion exchange	
	Adsorption	
Chemical	Hydrolysis	
	Photolysis	
	Neutralization	Reagent leaching
	Oxidation	Oxidation
Biological	Phytoremediation	Phytodegradation, rhizodegradation, phytovolatilization, phytoextraction, rhizofiltration, phytostabilization
	Bioremediation	Oxidation, biosurfactant

The strategy for the cleanup of petroleum-contaminated soil is influenced by the scale of the particular spill, by the landscape and geographical zone of the spill, and by the cleanup measures available. However, many researchers note that the traditional recultivation measures used for restoration of petroleum-polluted soil ecosystems have a number of flaws; specifically, they do not always facilitate the soil and flora restoration and often do long-lasting harm to the environment [11]. Soil recultivation reduces the rates of petroleum decomposition. Removal of a contaminated soil layer produces new spots of secondary pollution. It is therefore advisable to finish soil recultivation by application of biological cleanup methods, that is, by bioremediation and phytoremediation. These methods are discussed here in detail.

Therefore, the goal of this work is to discuss the potential of bioremediation for cleaning up petroleum-polluted soil.

## 2. Petroleum Composition and Its Effects on Soil

Petroleum is a complex multi-component system mainly composed of diversely structured hydrocarbons such as alkanes, cycloalkanes, aromatic compounds (benzene, toluene, ethylbenzene, xylene), polycyclic aromatics (naphthalene, phenanthrene, anthracene, benzo(a)pyrene), resins, asphaltenes and, in minor amounts, oxygen-, sulfur- and nitrogen-containing compounds. Depending on the source, crude oil consists of 82–85% carbon, 10–14% hydrogen, 0.01–7% sulfur, 0.02–2% nitrogen and 0.1–1% oxygen [2,12]. In terms of the petroleum composition, it can be classified as light (density 0.65–0.87 g/cm<sup>3</sup>), intermediate (density 0.87–0.91 g/cm<sup>3</sup>) or heavy (0.91–1.05 g/cm<sup>3</sup>) [13]. This is an important parameter, which influences the impact of petroleum on the environment [14,15].

According to the literature, the major mechanisms of the negative effects of petroleum on living organisms are the direct toxicity of hydrocarbons from the light oil fractions, and the altered hydrophobicity and the other physical and chemical properties of soil, caused by heavy oil fractions [16–19]. The light oil effects on plants are stronger, but short-lived relative to the effects of heavy oil [20,21]. The light fractions of petroleum, however, are quickly degraded by microbial destructors or rapidly migrate from the soil; therefore, it is mainly the heavy fractions that negatively affect living beings, such as plants, animals and microbes, when the contamination is serious [22].

Soil contamination by petroleum and its products changes more or less all soil properties, including its physical, physicochemical and chemical properties [23,24]. The extent of such changes depends on the soil type, the soil's initial condition, and the type and concentration of contaminant. As a result of contamination and the petroleum film coating of soil particles, the color of the soil profile changes to grey and dark brown [25,26]. The soil surface color changes result in lower light reflective properties of soil [27]. The light reflective ability of polluted soil was found to proportionally grow with time because of the petroleum transformation. This effect facilitates more efficient heating of such soils. The soil particles coated by hydrophobic films of high molecular weight petroleum components lose their ability to absorb and retain moisture. This leads to a considerable loss of water conductivity and capacity. As a result of greatly increased hydrophobicity, the upper contaminated layers dry out, whereas the cleaner lower layers suffer from excessive moisture, leading to incorrect air and water conditions and the development of anaerobic processes [28,29]. The abnormal water conditions lower solubility and availability of micronutrients to plants, hence inhibiting nitrification and ammonification. The waters adjacent to petroleum were reported to be high in sodium. Sodium ions reach the soil sorption complex and replace its pH-balancing cations, thus elevating the soil pH [30,31]. Petroleum and its products change the redox properties of soil. Ineffective aeration and anaerobic conditions in the soil depth lower its redox potential and may result in pasting and even surface waterlogging. The petroleum contamination also changes soil chemical properties. Humus becomes poorer in humic and fulvic acids, and its organic carbon grows by 2–10 times. The higher carbon elevates the C:N ratio, and the concentrations of important elements such as phosphorus and potassium drop. In addition, all of the above factors adversely affect microbes and plants [9]. Petroleum products are bound by upper soil layers and extrude air from the soil, leading to incorrect air conditions in soil and plant hypoxia. Thus, petroleum and its products mainly cause negative changes in all soil properties, from the soil layer morphology to humic acid chemistry.

### 3. Phytoremediation of Oil-Polluted Soils

Bioremediation uses live organisms for detoxification or lowering the content of pollutants in the environment. Microbes and plants play leading roles in bioremediation and phytoremediation, respectively. Phytoremediation, defined by Ilya Raskin in 1991 [32], is viewed as using plants for the accumulation, removal or degradation of organic or inorganic pollutants from soils, aquifers and underground waters. In 1998, the US EPA officially named six types of phytoremediation mechanisms: phytodegradation, rhizodegradation, phytovolatilization, phytoextraction, rhizofiltration and phytostabilization [33]. This classification is still in use, although some sources combine hydraulic control into a single type [34]. It has been shown that plant cover leads to a significant acceleration in oil degradation processes [35]. All phytoremediation mechanisms can be used for petroleum-polluted territories, but the main ones are phyto- and rhizodegradation and phytovolatilization. Rhizodegradation is based on plant–microbe interactions and is the most common way to clean up petroleum from soil [36–39]. Studies of rhizodegradation are focused on the analysis of plant–microbe associations, and the mechanisms of the plant–microbe interactions [40,41]. Regarding the plant–microbe associations, most researchers view the microbes as playing the main role in petroleum degradation, and plants stimulating microbial growth and ameliorating the soil. For example, Gunther et al. [42] showed that ryegrass increases the

microbe count and the petroleum degradation in soil [42]. The authors hypothesized that the plants stimulate growth of petroleum-degrading microbes. Epuri and Sorensen [43] detected more intense [ $^{14}\text{C}$ ]-benzopyrene mineralization and a higher count of microbes in the soil in which tall fescue was growing. Jordahl et al. [44] also reported higher numbers of microbes capable of degrading benzene, tolyene and xylene in the rhizosphere of poplar (*Populus deltoides* × *nigra* DN-4) versus the number of microbes in empty soil. Another study reported higher counts of microbial destructors in rhizospheres of alfalfa 2,2-dimethylpropylbenzene, benzoic acid, pyrene, decahydronaphthalene and phenanthrene compared to the microbe counts outside of rhizosphere and in unpolluted soil [45]. In our work, the best option for cleaning the soil from oil also used the plant–microorganism complex (*Medicago sativa* and *Candida maltosa*), which indirectly indicates the stimulation of microorganisms by root excretions of plants [39]. The roots of some plant species growing in the Kuwaiti desert (*Senecio glaucus*, *Cyperus conglomeratus*, *Launaea mucronata*, *Picris babylonica*, *Salsola imbricata*) and the cultivated legumes *Vicia faba* and *Lupinus albus* are closely associated with microbial petroleum destructors [46] and bluegrass grown in the soil laden with petroleum products. These plants' rhizospheres have more microbe density than the soil alone.

Plants act on microbes via their root system, first, by releasing root exudates with organic compounds (for instance, sugars and amino acids) that are metabolized by microbes and help to degrade the pollutants [47]. Plant roots loosen the soil and release oxygen into the soil, thus stimulating microbial bioenergetics and increasing the number of aerobic microbes [48]. Plants may increase the availability of hydrophobic compounds by selectively releasing organic acids to different organic pollutants [49,50]. A study of biodegradation of polycyclic aromatics and diesel fuel showed that alfalfa is more effective than ryegrass in degrading polycyclic aromatics, whereas ryegrass helps degrade diesel fuel better than alfalfa [51]. Microbes are stimulated by plant root exudates containing a variety of organic compounds (enzymes, carbohydrates, organic acids, etc.) that are released in the vicinity of the roots and rhizosphere [52–57]. Annually, the root exudates may comprise 10–20% of the total products of photosynthesis [50] and this may suffice for significant growth in microbes in the rhizosphere, of up to  $10^8$  to  $10^9$  microbes per gram of soil [58]. The microbes actively interact at distances from 1.5 to 9 mm from the root surface [59]. More developed root systems undoubtedly have more influence on the soil microbes. The individual roots of pasture ryegrass are measured to be spaced 3 mm apart, and the rhizospheres of the adjacent plants overlap [60]. In such conditions, the rhizosphere is essentially continuous.

The quantities and contents of root exudates depend on the plant species, its developmental stage and the environmental conditions: the soil type, nutrients content, pH, moisture level, temperature and aeration [47,61]. For example, apple, orange and black mulberry trees release flavonoids and coumaric acid, which stimulate degradation of polychlorinated biphenyls (PCBs) [62]. Gramss and Rudeschko [63] studied root exudates of alfalfa *M. sativa* L., white mustard *Sinapis alba* L. and cress salad *Lepidium sativum* L., and discovered over 20 different oxidoreductases: laccase, ascorbate oxidase, monophenol mono oxygenase, phenol 2-monooxygenase, guaiacol peroxidase, catechol 2,3-dioxygenase, and others [63]. Often, rhizodegradation is preferred to microbial bioremediation [64].

Nevertheless, in a few works, plants have been reported to have no effect on petroleum degradation in soil. Thus, crested wheatgrass (*Agropyron desertorum*) had no effect on the  $^{14}\text{C}$ -phenanthrene mineralization rate [65]. In this study, the authors hypothesized that phenanthrene was rapidly mineralized by microbes before any plant root–microbe interaction could be established. In 1997, the same authors reported that alfalfa did not affect the rate of benzene removal [66], but noticed that the pollutant content was low, and that benzene was also rapidly metabolized by microbes.

Phytoremediation is currently regarded to be the cheapest technology for large areas. In addition to the costs of preparing a territory for seeding, the costs of process maintenance are minimal. Phytoremediation technology is rather simple and results in a stable and long-lasting cleanup of the soil layer. The advantages of these processes are the supply

of oxygen and organics to soil, which help improve the quality and structure of the land. The plant growth diminishes erosion. It is worth noting that the use of phytoremediation systems is welcomed by society. Therefore, phytoremediation is the most ecological approach to petroleum contamination cleanup. Like any other technology, it, however, has its disadvantages. First, it is not suitable at high contamination rates (Table 2). Some authors used cell selection for improving plants' phytoremediation potential or tolerance to petroleum [67,68].

**Table 2.** Advantages and disadvantages of phytoremediation.

Advantages	Disadvantages
Relatively low cost	Takes a long time
Simple	Affected by seasons
Diverse decontamination mechanisms	Not possible to use at high contamination rates Not able to assimilate PCBs
Ecologically friendly	
Aesthetics	

#### 4. Microbial Bioremediation

##### 4.1. Bioremediation by Heterotrophic Microbes

Biodegradation of petroleum hydrocarbons is a complex process influenced mainly by the hydrocarbon's composition [69,70]. The petroleum ingredients can be classified into the following groups: saturated branched and unbranched hydrocarbons, cyclic alkanes, alkenes, aromatics, asphaltenes (fatty acids, ethers, porphyrins) and resins (pyridines, quinolines, carbosols, sulfoxides, amides) [12,13].

The efficiency of the microbial degradation of hydrocarbons depends on their structure, with the intensity of biodegradation decreasing in the following series: n-alkanes → branched alkanes → low molecular weight aromatics → cycloalkanes → polycyclic aromatics [71–73]. Aliphatic hydrocarbons are partially oxidized by many microbes, but can be fully metabolized by only a few species (*Pseudomonas*, *Nocardia*, *Xanthomonas*, *Bacterium*, *Corynebacterium*, *Mycobacterium*, *Acinetobacter*) [72,74]. Biodegradation of aromatic hydrocarbons depends on their number of benzene rings and their structural complexity [75].

Over 100 genera of bacteria, yeast and mycelial fungi are currently known to be able to degrade hydrocarbons (Table 3). According to the literature data, the proportion of petroleum subject to biodegradation varies from 6% [76] to 82% [77] for soil fungi, and from 0.13% [76] to 100% [73,78] for bacteria. High molecular weight polycyclic aromatics can be degraded, albeit rather inefficiently, by specific microbes, with some compounds not being prone to degradation at all [52,79–81].

Since microbes selectively oxidize petroleum components, a mix of microbes, including not only different bacteria but also fungi, is needed for a more complete cleanup. The microbial cultures are quite often isolated from petroleum-polluted soils. For instance, two bacterial strains, *Bacillus thuringiensis* B3 и *B. cereus* B6, and two fungal strains, *Geomyces pannorum* HR and *Geomyces*. sp. strain HV, isolated from a northwestern Ecuador oil mine, may be effectively used for the large-scale bioremediation of crude oil-polluted land [82].

Both abiotic (temperature, water availability, aeration, pH, presence of biogenic minerals) and biotic (microbial species) factors affect the biodegradation efficiency [83–87]. Temperature is a key factor for microbial life and for microbes' ability to degrade petroleum. The research points to the range of 30–40 °C as the optimal temperature for petroleum biodestruction in the soil. This is higher than summer soil temperatures at moderate latitudes, which spanning from 25 to 30 °C [83,88]. At elevated temperatures, the vitality of many bacterial species drops due to damage to their cellular structures. Temperatures below optimum, by comparison, lead to slowing cellular metabolism. Thus, any deviation from the optimal temperature results in reduction in petroleum biodegradation [89].

**Table 3.** Petroleum hydrocarbon-degrading microorganisms.

<b>Mycelia Fungi</b>	<b>Yeasts</b>	<b>Bacteria</b>
<i>Acremonium</i> sp.		<i>Acinetobacter calcoaceticus</i>
<i>Aspergillus fumigatus</i>		<i>Acinetobacter cerificans</i>
<i>Aspergillus</i> spp.		<i>Alcaligenes</i> spp.
<i>Cephalosporium roseum</i>		<i>Arthrobacter paraffineus</i>
<i>Cladosporium cladosporoides</i>		<i>Arthrobacter simplex</i>
<i>Fusarium</i> sp.	<i>Candida fumata</i>	<i>Bacillus</i> sp.
<i>Fusarium moniliforme</i>	<i>Candida guilliermondii</i>	<i>Corynebacterium glutamicum</i>
<i>Fusarium oxysporum</i>	<i>Candida lipolytica</i>	<i>Desulfovibrio desulfuricans</i>
<i>Hormoconis resiniae</i>	<i>Candida rugosa</i>	<i>Nocardia petroleophilia</i>
<i>Mucor</i> sp.	<i>Candida tropicalis</i>	<i>Mycobacterium smegmatis</i>
<i>Paecilomyces</i> sp.	<i>Rhodotorula</i> sp.	<i>Pseudomonas aeruginosa</i>
<i>Paecilomyces variotii</i>	<i>Torulopsis colliculosa</i>	<i>Pseudomonas fluorescens</i>
<i>Penicillium</i> spp.	<i>Yarrowia tropicalis</i>	<i>Pseudomonas oleovorans</i>
<i>Penicillium corylophilum</i>		<i>Pseudomonas putida</i>
<i>Penicillium cyclophilum</i>		<i>Pseudomonas</i> sp.
<i>Phialophora</i> sp.		<i>Rhodococcus</i> sp.
<i>Rhinoctadiella</i> sp.		
<i>Trichoderma viride</i>		
<i>Trichosporon</i> sp.		

Hydrocarbons generally degrade in aerobic conditions, since the initial step of the process is their enzymatic oxidation by oxygenases [90,91]. However, the degradation was recently shown to also proceed in anaerobic conditions [92]. In this case, nitrate or ferric ions may serve as terminal electron acceptors. A number of studies reported successful bioremediation of soils from petroleum [93], even at low temperatures [94], including of fuel oil [95] and toluene [96]. Hence, microbial bioremediation is a complex process influenced by many factors. Nevertheless, the diversity of microbes and their different mechanisms of detoxification of hydrocarbons present several advantages, as discussed below.

#### 4.2. Soil Bioremediation by Phototrophic Microbes (Microalgae)

Microalgae is the collective name for either prokaryotic or eukaryotic phototrophic microbes. Microalgae include unicellular microscopic phytoplankton such as cyanobacteria, diatoms, dinoflagellates and green algae [97]. These ubiquitous microbes comprise a substantial share of the soil microbial biomass and can be an alternative to fungal and bacterial bioremediation.

About 50 years ago, the feasibility of using microalgae, namely, the cyanobacteria *Oscillatoria*, to rid the environment of aromatic hydrocarbons such as naphthalene was shown [98]. Removal of pyrene by various microalgae was reported relatively recently, with 7 days of treatment being 34–100% effective [99].

Removal of petroleum and its products has been performed with the use of cyanobacteria (*Spirulina*, *Spirogyra*, *Oscillatoria*, *Synechocystis*) or unicellular algae (*Chlorella*, *Scenedesmus*, *Chlorococcum*, *Nannochloropsis*, *Selenastrum*) [100]. Green algae (*Chlorella* and *Scenedesmus*) are the most important for removal of petroleum, and were demonstrated to effectively degrade crude oil and polycyclic aromatics such as naphthalene, phenanthrene and pyrene [101–103]. For example, Lei et al. [103] studied different species of microalgae (*Chlorella vulgaris*, *Scenedesmus platydiscus*, *Scenedesmus quadricauda* and *Raphidocolis capricornutum*) for removal of either or both of fluoranthene and pyrene. *Scenedesmus* spp. were superior to *Chlorella*, having results of 78% and 48%, correspondingly [103]. Interestingly, the microalgae removed the mixture of fluoranthene and pyrene more effectively than when only one contaminant was present. However, most works report that *Chlorella* has a high bioremediation potential. It can remove up to 94% of contaminating petroleum and its products from soils [102]. Many authors point to the promising combinations of microalgae with bacteria. Algae will, first, supply oxygen and stimulate the oxidation of hydrocarbons

by bacteria. Microalgal exudates may promote bacterial growth and the bioavailability of hydrocarbons [100]. Overall, many studies have used microalgae for the cleanup of petroleum and its products from aquatic environments. A few works have nevertheless tried to address the use of microalgae for soil cleanup [104–107].

## 5. The Mechanisms of the Microbial Degradation of Hydrocarbons

### 5.1. Degradation of Alkanes and Alkenes

Alkanes are easily degraded by a wide range of microbes, including bacteria, yeast and molds [108,109]. Nevertheless, microbes degrade alkanes differently depending on the carbon chain length and branching. Depending on the study, alkanes having 10 to 18 [110], 20 [111], 22 [112] or 24 [113] carbon atoms are the easiest to degrade. The longer alkanes (C18 to C24) degrade slower [114,115]. Alkanes having short (C5–C9) carbon chains are often toxic, since they can dissolve microbial cell membranes; hence, they are metabolized by a limited number of bacterial and fungal species, including yeast [89,112]. The concurrent presence of microbes enhances the biodegradation [116–118].

Microbes degrade alkanes via the oxidation pathway, which includes the following steps (Figure 1):

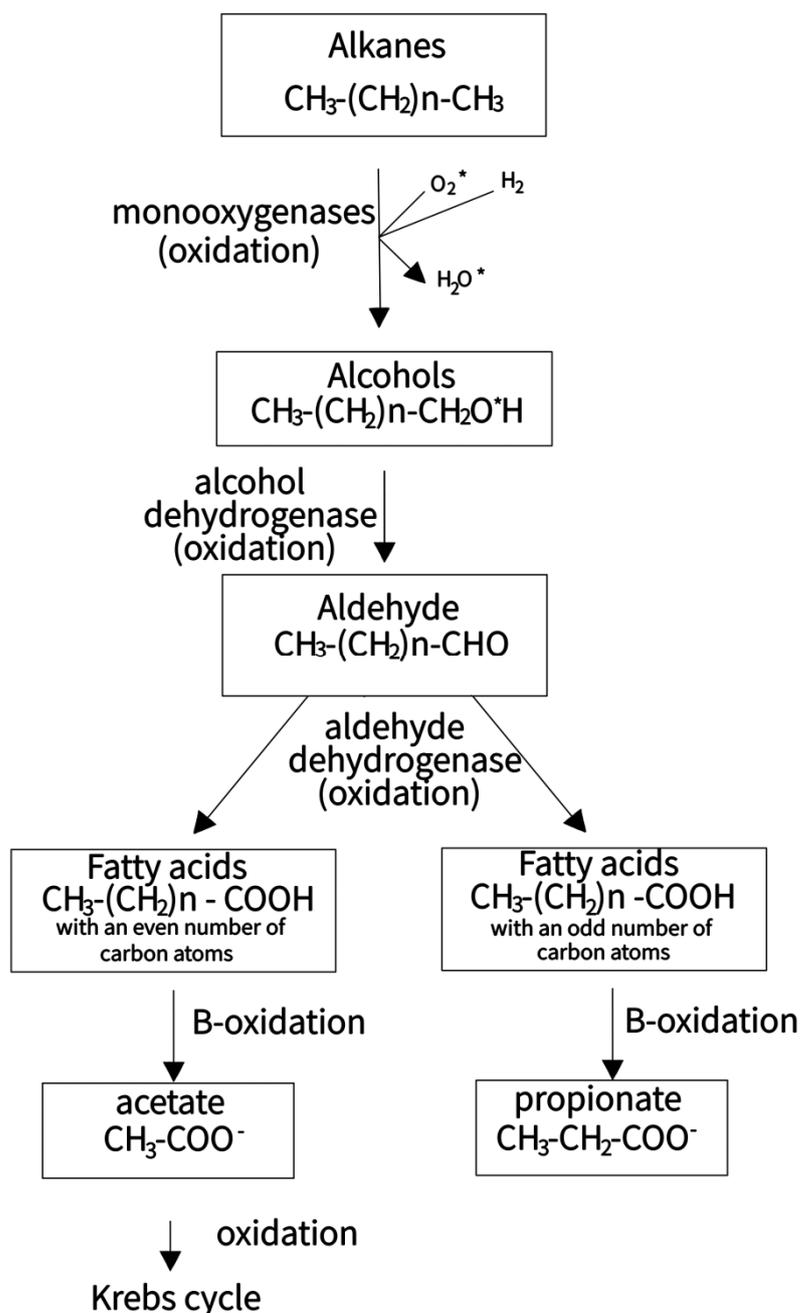
1. Oxidation of alkanes to a respective alcohol by monooxygenases. Some microbes can oxidize hydrocarbons to secondary alcohols, which are further oxidized to ketones and ethers.
2. Oxidation of the alcohol obtained in step 1 to a respective aldehyde by alcohol dehydrogenase.
3. The oxidation of the aldehyde to a respective fatty acid.

The even fatty acids are further beta-oxidized to acetate, which is further converted to acetyl coenzyme A entering the tricarboxylic acid cycle (TCA cycle). The odd fatty acids are beta-oxidized to propionate in the monoterminial pathway. The subterminal pathway of oxidation of a secondary rather than a primary alcohol also exists [72,119]. The latter pathway is less common, and was discovered in fungi and mixed cultures. The monoterminial oxidation pathway works faster compared to the subterminal pathway.

Branched alkanes are less prone to degradation in comparison with n-alkanes [120]. However, some bacterial strains were reported to degrade both simple (isooctane) [74] and more complex (pristane and phytane) [121,122] branched alkanes. Metabolic assimilation pathways of the branched alkanes are less understood than those of n-alkanes, but they are known to include omega- and beta-oxidation of their carbon atoms.

With the exception of methane-oxidizing microbes, the microbes that metabolize alkanes are not specific; rather, they are ubiquitous and typical of uncontaminated ecosystems. It is this lack of specificity of the alkane-oxidizing microbes that gives soil and water biocenoses the ability to self-clean when contaminated by alkanes.

In spite of the considerable number of reports on the degradation of alkanes, few researchers have described the microbial degradation of alkenes. This pathway generally involves the alkenes' oxidation to acetate, which then enters the TCA cycle. Terminal alkenes are subject to biodegradation. Monooxygenase oxidizes it to epoxide, which is converted to diol. The alpha hydroxyl is further oxidized to carboxyl, and this saturated fatty acid is beta-oxidized [123].

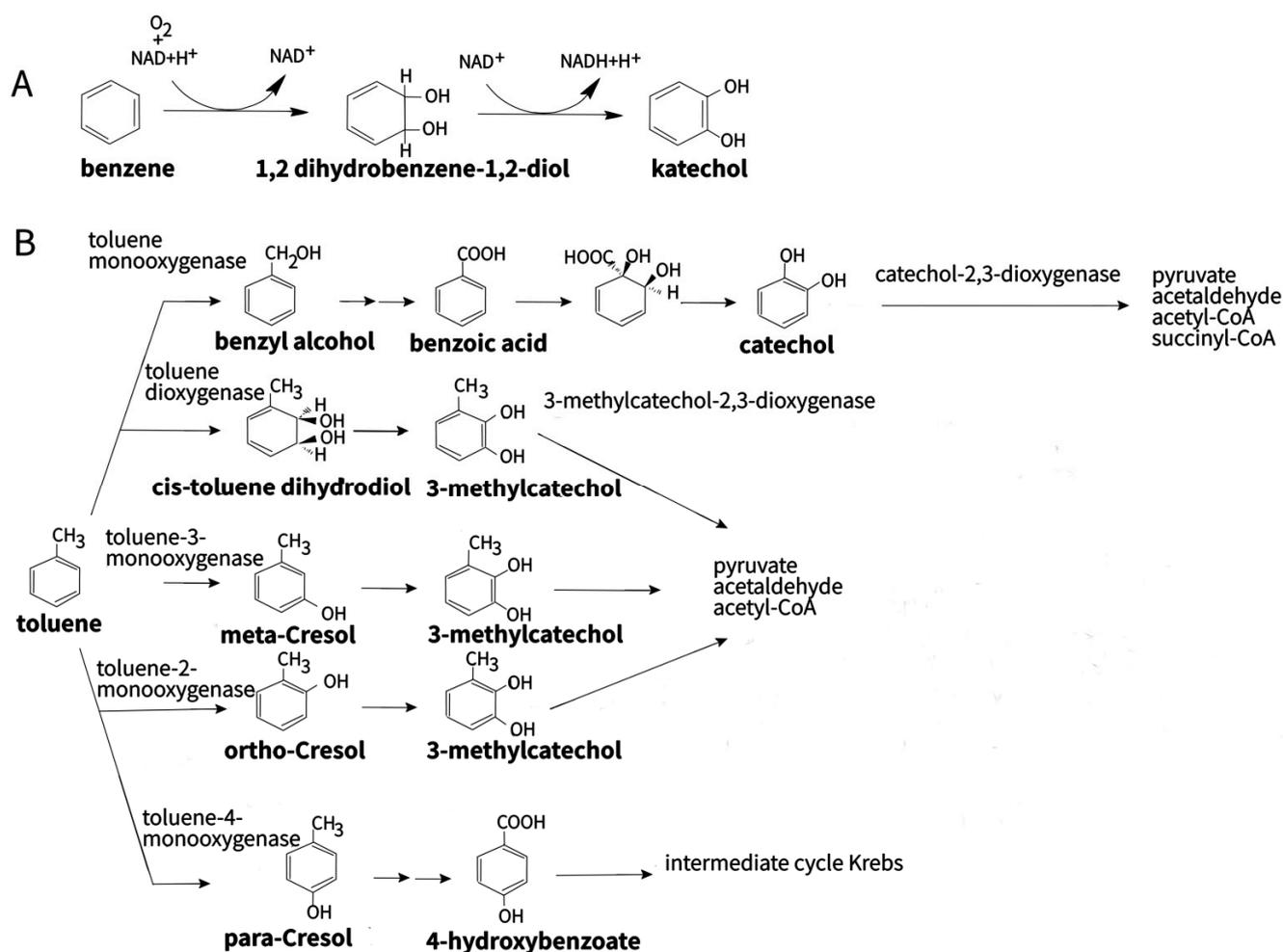


**Figure 1.** Oxidation of alkanes by microorganisms.

### 5.2. Aromatic Hydrocarbons

Aromatics may comprise 5 to 35% of petroleum products. They may have one (benzene, toluene, xylene, phenol), two (naphthalene) or several (anthracene, phenanthrene, pyrene) benzene rings. A number of current works report the degradation of aromatics in different media [124–127].

The microbial metabolism of monocyclic aromatic hydrocarbons has been studied for over 80 years. Toluene degradation pathways have been most studied. In 1928, Grey and Thornton described a bacterium, *Mycobacterium agreste*, which is able to grow on toluene as a single carbon source [128]. Subsequently, Gram-positive bacteria participating in the biodegradation of monoaromatic hydrocarbons were rarely studied, and this research was only resumed at the end of the last century [129,130]. Five pathways of toluene degradation are currently known (Figure 2).



**Figure 2.** Pathways of oxidation of aromatic compounds using benzene (A) and toluene (B) as examples.

The degradation pathway of simple aromatics depends on the presence of a side group [131]. Biodegradation is always based on enzymatic oxidation by monooxygenases, dioxygenases, peroxidases, tyrosinases and dehydrogenases [71], with its products including catechin, epoxide, phenolics, cis- and trans-dehydrodiol, and benzoquinone. However, the main product is catechol [71], which is further metabolized to acetate and succinate, and to acetaldehyde and pyruvate, by meta and ortho pathways, respectively. The produced intermediates enter the TCA cycle [81].

Using GC-MS, the toluene biotransformation was shown to involve not only the familiar pathways, such as toluene-3-monooxygenase, toluene-2-monooxygenase, toluene-4-monooxygenase, toluene methyl monooxygenase, and meta- and ortho-ring degradation pathways, but a specific metabolic pathway was also confirmed. The latter includes conversion of toluene to intermediates such as cyclohexene, cyclohexane, cyclohexanone and cyclohexanol. LC-MS analysis detected fatty acid amides, stigmin, emmotin A and 2,2-dinitro propanol in supernatants of the bacterial cultures [125].

Polycyclic aromatics are degraded to a lesser extent compared to the other hydrocarbons because of their higher hydrophobicity. They are biodegraded by the double hydroxylation and subsequent opening of a benzene ring. The next steps of aromatic degradation are extremely diverse and are catalyzed by a number of enzymes [132].

A number of either mesophilic or thermotolerant bacterial species are now known to be able to degrade aromatic and polyaromatic hydrocarbons, thus suggesting their use in the cleanup of petroleum from soil.

### 5.3. Biosurfactants Use for Bioremediation

Hydrocarbons, such as high molecular weight paraffins and polycyclic aromatics, bind to soil particles and become less available to microbes, and their biodegradation is slowed [133–136]. One strategy to increase the bioavailability of these substrates is the production of surfactants by hydrocarbon-destroying microbes. Biosurfactants are used to increase their availability. Surfactants are amphiphathic molecules with both polar (hydrophilic) and non-polar (lipophylic) moieties [136]. The surfactant properties are determined by the balance of their hydrophilic and lipophilic moieties. Surfactants are characterized by their ability to lower interphase surface tension, by the critical micelle concentration (CMC) and by the hydrophilic–lipophilic balance. CMC is the lowest surfactant concentration at and above which the micelles of ramnolipids are formed [137–139].

There are currently two classes of surfactants: chemically synthesized surfactants and biosurfactants [140–142]. Synthetic surfactants are more widely used, but, in most cases, they are highly toxic and resistant to degradation [142,143]. With this in mind, biosurfactants are more advantageous than chemically synthesized surfactants, because they are less toxic [142,144,145], easier to degrade [146], selective and easy to foam [147]. Therefore, biosurfactants are increasingly used as biodegradable and ecologically safe alternatives to synthetic surfactants [148,149]. A disadvantage of using biosurfactants for bioremediation is their high production cost. Nevertheless, the right choice of microbes with high product yield and the use of a cheap substrate may significantly reduce the expenses [150].

The biosurfactants are classified as follows: glycolipids, lipopeptides, fatty acids, neutral lipids, phospholipids, polymeric surfactants (emulsan) and particulate biosurfactants (vesicles). Glycolipids are the most common and studied biosurfactants. They contain carbohydrate moieties linked to long chain aliphatic or hydroxy aliphatic fatty acids.

Dozens of biosurfactant-producing microbes, mostly bacteria and micromycetes, are now known. Bacteria of genera *Bacillus*, *Lactobacillus*, *Pseudomonas*, *Burkholderia*, *Mycobacterium*, *Rhodococcus*, *Arthrobacter*, *Nocardia*, *Gordonia* and *Acinetobacter* are the most common, as are micromycetes of genera *Candida*, *Starmerella*, *Trichosporon*, *Saccharomyces*, *Pseudozyma*, and *Ustilago*. To grow their cultures, sugars, petroleum, alkanes, and various agricultural and food industry wastes are being used. The microbes can be classified into groups according to the biosurfactants they produce. For instance, lipopeptides are produced by *B. subtilis*, *B. pumilus*, *B. licheniformis*, *Serratia marcescens*, *Pseudomonas fluorescens*, *Aspergillus* sp., *Arthrobacter* sp., etc. Glicolipids are produced by *P. aeruginosa*, *Rhodococcus* sp., *Candida antarctica*, *Ustilago* sp., and *Pseudozyma* sp., among others, and polymeric surfactants are produced by *Arthrobacter calcoaceticus*, *Candida tropicalis*, and *Candida lipolytica*. [141,151,152].

Ramnolipids are biosurfactants produced by many microbe species grown on various substrates such as sugars, petroleum and food industry wastes. They are extracellular or membrane-associated amphiphathic molecules [153,154]. The ramnolipids were discovered in 1946 by Bergstrom et al. [154]. They were isolated in an oily glycolipid from glucose-grown *Pseudomonas aeruginosa* that was later named ramnolipid R<sub>3</sub> (L-ramnosyl-L-ramnosyl-beta-hydroxydecanoyl-beta-hydroxydecanoate R<sub>2</sub>C<sub>10</sub>C<sub>10</sub>) [155,156]. By now, over 60 ramnolipid structures have been identified. These vary with respect to the number of ramnose residues (mono- or diramnolipids) and the aglycone structure, which may comprise one, two or, in rare instances, three beta-hydroxy fatty acids which, in turn, may be saturated, or mono- or polyunsaturated, and have aliphatic chains from C<sub>8</sub> to C<sub>16</sub>.

Depending on the strain and carbon source, *P. aeruginosa* strains can produce mixtures containing from 2 to 28 ramnolipids [157]. Its major ramnolipids are monoramnolipid R<sub>1</sub> (L-ramnosyl-beta-hydroxydecanoyl-beta-hydroxydecanoate R<sub>1</sub>C<sub>10</sub>C<sub>10</sub>) and two ramnolipids containing a single residue of beta-hydroxydecanoic acid (R<sub>2</sub>: R<sub>1</sub>C<sub>10</sub>; R<sub>4</sub>: R<sub>2</sub>C<sub>10</sub>) [155,156]. The ramnolipids' biosynthesis includes the following steps: the first step is the synthesis of beta-hydroxydecanoyl-beta-hydroxydecanoate from its precursors catalyzed by RhIA (which is encoded by *rhlA*); the second step is the monoramnolipid synthesis from TDP-L-ramnose and beta-hydroxydecanoyl-beta-hydroxydecanoate catalyzed by RhIB (which is

encoded by *rhlB*); the third step is the RhlC (which is encoded by *rhlC*) catalyzed transfer of the second TDP-L-rhamnose residue, which produces a dirhamnolipid [157].

Rhamnolipids increase the pollutants' bioavailability, leading to their faster degradation. They can be more effective than the chemical surfactants such as SDS and Tween 80 [138]. The mechanism of rhamnolipid-assisted degradation of polycyclic aromatics includes several steps. It starts with polycyclic aromatic-containing micelles formed by biosurfactants; then, biosurfactants solubilize the hydrophobic components inside micelles and make them available to cells. In addition, micelles interact with membranes and increase their porosity, thus facilitating the polycyclic aromatics' transport inside the cells, where they are attacked by the proper enzymes [136,158]. In another mechanism, biosurfactants increase the membrane hydrophobicity, thus helping the cell to directly contact polycyclic aromatics.

The successful applications of biosurfactants for the degradation of pyrene [159], kerosene and diesel fuel [160], crude oil in soil [161], liquid media [162] and polyaromatic hydrocarbons such as naphthalene and phenanthrene have been reported [159].

## 6. Conclusions

Bioremediation is used to clean various contaminants from soils. The removal from soils of contamination by petroleum and its products is important for environmental protection. In this review, we demonstrated the effectiveness and the great potential of the bioremediation of petroleum-polluted soils. Although alkanes can be effectively degraded by a wide range of microbes, this process is greatly affected by the length and branch structures of their carbon chains. Degradation of alkenes and aromatics needs to be studied further. Bioremediation with the help of biosurfactants is of great practical interest. The combined use of microbes and plants has high potential. However, many research results are not used in practice due to the complexity of microbial bioremediation, and the effects of environmental factors and the nature of contamination on the efficacy of the process. This challenge needs to be overcome. It is clear that the study of petroleum bioremediation and its practical applications are the key directions in applied ecology (environmental science).

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