Advanced Studies in Biology, Vol. 16, 2024, no. 1, 175 - 186
HIKARI Ltd, www.m-hikari.com
https://doi.org/10.12988/asb.2024.91935

Methods Used in Remediation of Oil Contaminated Soils

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Abstract

Both in the world and in our republic, sufficient methods are used for the treatment of oil-contaminated soils, and the search for new methods and technologies is focused on as a priority direction. It is clear that when considering each method, its advantages and disadvantages are discussed. At this time, aspects such as environmental safety, economic efficiency, impact on human health and the environment, practicality and ease of purchase are taken into account during the use of that method. In this review article, the purpose of determining the advantages and disadvantages of the use of physical, chemical and biological recovery methods, guided by the world practice, was chosen as the goal of eliminating the problem. At this time, the main attention was focused on ecological safety and improving the state of the environment, for this purpose it was determined that bioremediation, especially the use of micromycetes in remediation, is more suitable for the purpose.

Keywords: Physical remediation; chemical remediation; bioremediation; micromycetes; lipolytic enzymes

Introductıon

Oil pollution is the most serious problem of the soil ecosystem. Physical, chemical and biological (bioremediation) solutions are proposed to solve this problem. Although physical and chemical solutions are superior to bioremediation in terms of less time to eliminate the problem and accuracy, biological remedia-tion due to greater capital investment, secondary pollution during their application, destruction of existing microbiota in the area and reset of soil biological indicators lags behind the methods [38].

In this case, mechanical cleaning as a physical solution (transportation and cleaning of the contaminated area with devices such as bulldozers during local pollution), thermal cleaning (due to high heat), electrokinetic cleaning (based on the movement of pollutants towards the electrodes through electric current), chemical cleaning as a chemical solution from oxidation (the neutralization of pollutants in the soil based on the oxidizing ability of chemical reagents), chemical sorbents (based on the adsorption capacity of substances such as coal, etc.), soil washing (the washing of petroleum hydrocarbons from the soil surface with chemicals) and finally phytoremediation as a bioremediation solution (where plants the ability of the roots to adsorb pollutants and the ability of some plants to keep the pollution in a stable state are used), with microorganisms (by injecting biopreparations from some bacteria and fungi into the polluted areas or by using enzymes obtained from them) methods are widely used. [2, 13, 20, 22, 25].

1. Physical cleaning methods

1.1. ***Mechanical remediation***. This method is included in the physical methods of local cleaning of contaminated soils and previously contaminated soils, which are created during the drilling of oil wells, and at this time it involves the transportation of these soils and their cleaning or destruction. As it is usually not economically viable to build a new landfill for this purpose, it is often considered more appropriate to use that area as a landfill. Although this method is effective, the problems it causes from an ecological point of view are that their use is not suitable for the purpose. So, the risks of transporting those soils are the most serious environmental problem caused by them. For all these reasons (ecological, economic, health), this method is considered as a temporary solution to the problem, and solving the problem in the next stages requires more costs [35].

1.2. Thermal desorption. Thermal desorption is a technology capable of cleaning the soil from various types of hydrocarbons using high temperature, which is distinguished by its efficiency and high accuracy in a short time, regardless of the physico-chemical properties of hydrocarbons. This technology is capable of purifying even polluted soils from chlorine organic compounds and mercury and is applied in this direction as well. Also, this technology is sufficiently applied in the cleaning of oil and oil solutions from the soil that in studies it is noted that thermal desorption at a temperature of 380^0C was used in concentrations between 2000-10000 mg/kg and good results were obtained. At the same time, excessive temperature in the used method leads to serious changes in the structure of the soil and the destruction of the biota there, which disrupts the natural balance of the ecosystem and makes its restoration impossible in the long term [15, 31].

1.3. Electrokinetic remediation. Electrokinetic remediation is a method based on the movement of pollutants towards electrodes in-situ, planning an environmentally friendly solution of oil-contaminated soils. According to this method, an electric current passes through the ground. Two electrodes, cathode and anode, are used in the process. Based on the electric charge, ions, colloids and suspended particles move towards the electrodes through the electric current and the pollutants are collected. Co-solvents and surfactants are used to accelerate the desorption of hydrocarbons. Currently, a number of electrodes are used, including a number of Ti/RuO_2, graphite, Ti/RuO_2/Iro_2 alloy. This process is simply explained by the presence of H^+ at the anode and OH^- at the cathode because of the hydrolysis of water and the ability of these ions to decompose polycyclic aromatic hydrocarbons. Citric acid, Tween 20, and other oxidants are used to speed up the process [5, 9, 29].

Although the mentioned method is chosen as an environmentally friendly, innovative and accurate method, it has a number of disadvantages during its use, for example - high energy costs in long-term projects aimed at cleaning large areas, additional costs caused by their restoration and installation of new ones when the electrodes wear out, long cleaning time it is not considered economically viable due to time consuming, high initial costs, limited usage conditions (depending on soil type and climate). On the other hand, although the method is considered environmentally friendly, it is known to change the physical and chemical properties of the soil during long-term use and to have a negative effect on the soil biota [11, 19, 21].

2. Chemical cleaning methods

2.1. Chemical oxidation. The last product of the oxidation (decomposition) of all organic products is carbon dioxide and water. The chemical oxidation method belongs to the chemical cleaning methods, which involves breaking down the aromatic hydrocarbons in the oil into simpler organic compounds by oxidizing them. These oxidizers are widely used in the treatment of both oil-contaminated soils and wastewater. This method is highly effective, accurate and provides the desired results in a short time, easy to apply, neutralizes a wide range of pollutants and is usually harmless (because the last product is usually water and carbon dioxide, which in turn is harmless to the environment). Although it is widely used, this method also has several disadvantages. These include the toxic effect of the used oxidants (for example, high doses of potassium permanganate, hydrogen peroxide and ozone can have a toxic effect and negatively affect the biological activity of the soil); generation of intermediate pollutants as a result of incomplete oxidation; economic inefficiency due to the high cost of some reagents; environmental risks (these oxidants can adversely affect natural water bodies and soil). Oxidizers such as Hydrogen Peroxide (H_2O_2), Ozone (O_3), Potassium Permanganate ($KMnO_4$), Sodium Persulfate, $Na_2S_2O_8$, Fenton's Reagent (Hydrogen Peroxide and Iron (II) Sulfate) are the most widely used oxidants during chemical oxidation [10, 20, 38].

2.2. Chemical adsorption. This method is a relatively ecologically clean technology carried out by adsorption of pollutants in oil-contaminated soils (as well as water, atmosphere) using chemical substances with adsorption capacity. Thus, secondary pollution is rarely observed in the chemical adsorption method. This method has its advantages and disadvantages. Advantages - rarely causing secondary pollution (environmentally friendly); high efficiency and high selectivity (usually adsorbents have high selectivity against a group of pollutants, which makes their use more efficient in cleaning those pollutants); variety of adsorbent substances (enables the cleaning of various pollutants); durability, and negative features - saturation of adsorbent substances (after long-term use); some adsorbents are expensive; difficulties and costs of reuse; sensitivity of adsorbent substances to changes in various environmental factors (pH, temperature); because saturated adsorbents themselves are potentially saturated with pollutants, the problem of their management, etc. belongs to. Activated carbon, resin, CaO, zeolites, silica gel (porous silicon oxide), aluminum oxide, biochar, etc. are used as adsorbent [13, 14, p19-21, 19].

2.3. Washing the soil with chemicals. Aqueous soil washing technology, which belongs to the chemical methods widely used in the treatment of oil-contaminated soils, is an in-situ method of cleaning the slurry using surfactants or complex solvents. Solvents desorb contaminants from the surface of the aggregate. This method also involves using gaseous mixtures to accelerate geochemical reactions (adsorption/desorption, acid/base reactions, biodegradation). The method is more effective in sandy and sandy soils with high permeability, because in clayey and gravelly soils with low permeability, water permeability is poor, so washing does not show its result at the required level (the contact between reagents and pollutants is weak). This method removes 97% of petroleum hydrocarbons and 73% of benzo(a)priene from the soil [7, 32].

3. Biological cleaning methods

3.1. Bioremediation with microorganisms. Among the microorganisms, bacteria and micromycetes are widely used in the treatment of oil-contaminated soils due to their properties. The process itself consists of several stages, including bioaugmentation (introduction of microbes capable of biodegradation to the area), biostimulation (providing fertilizers such as nitrogen and phosphorus to increase the activity of microorganisms and improving the oxygen regime) [23] and finally controlling environmental factors as much as possible. These organisms are irreplaceable alternatives in bioremediation due to their high biomass formation in a short period of time and their powerful enzyme apparatus. As with other methods, bioremediation with microorganisms has its advantages and a number of disadvantages. So, the short vegetation period mentioned above, having a well-developed enzyme system, and ecologically clean, wide application area, adaptive to different soil types, economically (much lower costs than physical and chemical methods), low costs, repeated Usability and sustainability (because microorganisms can multiply in that area for a long time and continue the process) and harmlessness for human health are their positive features. In addition, the cleaning of pollutants takes a long time; conducting constant control to ensure effectiveness; sensitivity to environmental factors (pH, temperature, humidity, oxygen, etc.), etc. such properties refer to the negative properties of the use of microorganisms as bioremediators [8, 18, 24, 25].

Bacteria are capable of generating large biomass in a short time, synthesizing a wide variety of enzymes, clean use in ecological processes, etc. is one of the best alternatives used in remediation of oil-contaminated soils. A number of bacteria *Microbacterium deserti*, *M. barkeri* [27], *Bacillus*, *Acinetobacter*, *Sphingobium*, *Rhodococcus*, a number of species belonging to the genus *Pseudomonas* [33], *Mycolicibacterium frederiksbergense*, *Rhodococcus erythropolis*, *Rhodococcus* sp. [8], *Bacillus aerius*, *Psuedomonas stutzeri*, *Ochrobactrum intermedium*, *Micrococcus lylae*, *Acinetobacter calcoaceticus* [12] are used in this process.

Fungi are widely used in bioremediation for a number of reasons. First, enzyme synthesis in fungi is extracellular, which makes the acquisition of the enzyme more practical (making these fungi superior to bacteria), and among them there are species with a high lipolytic activity. Second, fungi, like bacteria, have a short growing season. Third, a number of fungi are widely distributed in soils contaminated with oil to varying degrees [2]. Among the micromycetes, there are several species used in bioremediation and biodegradation of oil- contaminated soils, such as *Curvularia brachyspora*, *Penicillium chrysogenum*, *Scopulariopsis brevicaulis*, *Cladosporium sphaerospermum*, *Alternaria alternata*, *Stemphylium botryosum* [6], *Purpureocillium lilacinum*, *Aspergillus ustus* [3], *Cladosporium herbarum*, *C. macrocarpum*, *C. sphaerospermum and C. cladosporioides* [26].

3.2. Phytoremediation. Phytoremediation includes methods of biological remediation of lightly oil-contaminated soils and water bodies using plants. This method combines several directions, i.e. methods, as an environmentally friendly and economically efficient cleaning method. These methods include pollutant degradation (rhizo-degradation, phytodegradation), accumulation (phytoextraction, rhizofiltration), immobilization (hydraulic control and phytostabilization). Depending on the classification and concentration of pollutants, it is possible to use one or several of these methods together [4, 34].

A number of plants are used as phytoremediators, the most widely used of which are the following: Fenugreek (*Festuca arundinacea*) - this plant has the ability to biodegrade hydrocarbons in oil-contaminated soils with its strong root system, and this plant with high biological valence is a resistant species that grows in contaminated soils. This plant is also widely used in the bioremediation of soils contaminated with heavy metals due to its ability to accumulate metals such as Cd, Ni, and Pb in its roots [36]. Among wetland plants, Typha latifolia provides root filtration by growing in polluted environments [1], common reed (*Phragmites australis*) provides a surface for microorganisms to live in its roots as a plant resistant to high levels of pollution [39], and grass oats (*Lolium perenne*) , Alfalfa (Medicago sativa) from leguminous plants, and Poplar (*Populus spp*.), Willow (*Salix spp.*) from woody plants are widely used plants in biological remediation of oil-contaminated soils as phytoremediators [16, 17, 28, 30].

Results and their discussion

As a result of the analysis of the literature data, we have concluded that there is a large amount of oil-contaminated land on the Absheron peninsula, and that land restoration is not carried out at the required level. The physico-chemical properties of Absheron's oil-contaminated soils, the uniqueness of the soil type, climate, physical-geographical and ecological conditions create conditions for carrying out physical, chemical and biological restoration works in the region. If so, a few factors should be considered to select the appropriate method. These are the following:

Soil properties. The type of soil, its physical and chemical properties, its permeability, water capacity, oxygen regime, environmental conditions, the composition of rocks in the soil, as well as the species diversity and biomass of the biota there are the main factors during the choice of the method. So, many of the methods listed above depend on the properties of the soil. Of course, dependence mostly refers to biological remediation methods, physical and chemical remediation methods are not so dependent on the factors listed above.

Characteristics of the pollutant. Of course, soil properties alone are not conducive to choosing a suitable method, so the concentration and chemical composition of the pollutant in the soil should also be considered when choosing a method. Because, while bioremedial plants can be used in lightly oil-contaminated soils, and microorganisms can be used in the remediation of weakly and moderately contaminated soils, this is not so important for physical and chemical methods.

Environmental safety. In modern times, both in our republic and in the world, environmental safety and improvement of the environment is an urgent issue. In solving any problem, scientists and researchers first focus on the environment. When considering the methods of oil pollution elimination, the main issue is to determine how these methods will affect the biota (plant, animal, microorganism) and human health. Thus, during the use of the appropriate method, the creation of secondary pollution centers, the destruction of the existing biota, and potential risks to human health after use are undesirable consequences. Therefore, physical and chemical solutions are not favorable from an ecological point of view. Bioremediation methods are the best alternative as an "environmentally friendly" technology.

Economic efficiency. In a market economy, capital preservation is the main condition that the good gained from a product exceeds the lost. However, oil pollution is a problem that often requires high capital investment to solve. Physical and chemical recovery methods are not effective in this direction either. Because they require more capital investment than bioremediation and have more costs.

Legal issues. At this time, the existing legislation should be reviewed, standards and protocols accepted around the world should be reviewed.

Time and accuracy. In accordance with the time allotted for the project, it should be taken into account that biological recovery methods take longer than physical and chemical methods and are less accurate because they are directly dependent on other sharia.

To sum up the above, bioremediation is superior to physico-chemical remediation because it is cheap from an economic point of view and efficient from an environmental point of view. Based on literature data, the conclusion we reached is that the use of physical and chemical solutions in the recovery of poorly, and in some cases medium (depending on the specific conditions) contaminated soils with oil is not suitable for the purpose, on the contrary, the application of bioremediation is more favorable. In most of the literature, it is noted that in the recovery of moderately and highly contaminated soils with oil, the selection of the less harmful for the environment from physical or chemical methods, and that it is more appropriate to stop these methods and apply bioremediation after the contamination has decreased to the level that will allow bioremediation to be carried out.

Among the bioremediation methods, since plants are more sensitive to microorganisms than water, microorganisms (bacteria and fungi) should be used first, and then plants appropriate to the area should be planted for both greening and plant-fungus, plant-bacteria association to accelerate the purification. Among the microorganisms, bacteria and fungi can be used together or alternately applied in separate stages. However, it is important to note that extracellular enzyme synthesis of fungi is the main factor that makes them superior to bacteria. Thus, in the bioremediation of oil-contaminated soils, it is possible to use both by injecting fungi into the soil and by applying enzymes dependent on them.

Conclusion

If we summarize the results based on the analysis of the literature data, we can say that there is enough oil-contaminated land on the Absheron peninsula that the remediation of those lands remains relevant for the modern era. Physical and chemical remediation methods used for the remediation of oil-contaminated soils lag behind bioremediation in terms of environmental safety and environmental protection. According to our conclusion, the use of lipolytic enzymes from micromycetes and active strains in this process will be more convenient. If we consider that the flora and fauna of the peninsula is kasad and this diversity is declining due to oil pollution, then bioremediation work should be accelerated. In order to achieve this goal, the search for new active strains adapted to local environmental conditions and the preservation of the obtained pure cultures should be the main goal of researchers conducting research in this direction, using local bioresources.

Acknowledgment. This work was supported by the Azerbaijan Science Foundation – Grant № AEF-GAT-7-2023-2(44)-10/04/3-M-04

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Received: November 21, 2024; Published: December 6, 2024