

A Review

Study on the In-situ Bioremediation Techniques Applicable for Soils Contaminated with Petroleum Products

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Abstract

In this paper is made a study on the in situ bioremediation methods in order to establish an optimal method of bioremediation of soils contaminated with petroleum products. Crude oil consists of a complex mixture of hydrocarbons (acyclic saturated, cyclic and aromatic saturated) representing an important energy source, but also one of the significant soil pollution sources. For in situ bioremediation soil is not excavated, thus eliminating costs of excavation and transportation of contaminated soil to treatment facilities.

Keywords: bioremediation, petroleum products, soil.

1.Introduction

Soil is the surface layer of the Earth's crust, composed of mineral particles, organic matter, water, air and living organisms. Soil formation process is influenced by pedogenic factors such as: climate, microorganisms, vegetation and relief [1]. Soil is a physical, chemical and biological environment which ensures the necessary condition for the growth and development of both natural and cultivated vegetation [2], is a heterogeneous and tri-phase system (solid, liquid and gaseous phase) [3]. The solid part consists of 45% mineral particles and 5% organic matter, and the porous part consist of 25% water and 25% air with CO₂ (fig. 1) [3, 4].

A healthy soil has the ability to function as a vital system with a role in supporting the plant and animal productivity, improving and maintaining the quality of air, water and the health of plants and animals [5].

Soil composition

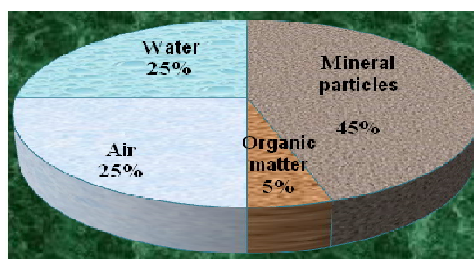


Figure 1. Soil composition

Fauna and microorganisms present in the soil, represented by protozoa, algae, fungi, actinomycetes and bacteria, have an important role in the soil's biological activity [3]. Microorganisms in the soil are engaged in a multiple activity on the soils, thus we can distinguish the enzymatic and symbiotic activities. Autotrophic bacteria synthesize food from inorganic matter, they can convert poisonous carbon oxide into useful carbon dioxide, nitrify ammonium into nitrates; heterotrophic bacteria and

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actinomycetes destroy organic matter including organic pollutants [3].

Environmental contamination with materials which interfere with human health, quality of life or with the natural function of the ecosystem is called pollution [6]. The main sources contributing to soil contamination in Europe are presented in figure 2, petroleum industry occupying an important place in soil contamination, respectively 14.10% [7].

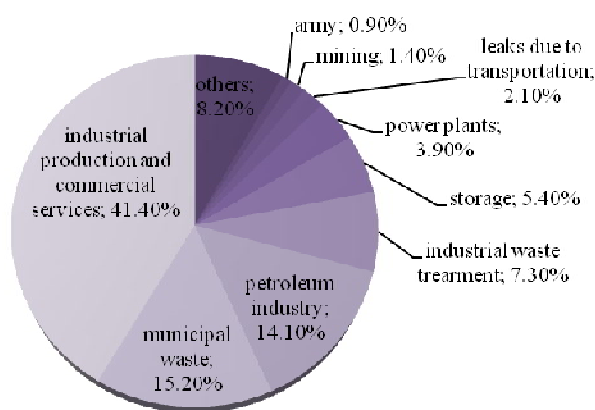


Figure 2. Causes of soil contamination [7]

Causes of soil contamination with petroleum products include: moral and physical wear of the used installations and equipment, improper use of materials during specific technological processes, irrational use of some facilities, processing of crude oil with high content of sulfur and use of the resulting fuels; incomplete combustion of fuels in old facilities, damage to storage tanks or pipes that transport oil and oil products, breaking of pipes for gasoline theft [8]. In the petroleum, chemical and petrochemical industry, one of the major problems is the loss by evaporation, thus in our country it was estimated that in one day, after handling and storage, a major quantity of petroleum products is evaporated [9].

Crude oil and petroleum products are composed of a complex mixture of hydrocarbons and other organic compounds [10].

Petroleum hydrocarbons are organic compounds present in bitumen, oil and coal. Crude oil is a mixture of thousands of organic compounds formed from various organic materials that have undergone chemical modifications under the influence of different geologic conditions that occur

over time [11]. In terms of chemical composition, oil is a very complicated mixture of hydrocarbons with molecules of different sizes, from methane to hydrocarbons with very high molecular masses; oil composition varies from one reservoir to another [12]. Crude oil is a mixture of three classes of hydrocarbons, namely [13]: acyclic saturated hydrocarbons (alkanes); cyclic saturated hydrocarbons (cycloalkanes; oil cycloalkanes are also called naphthenes); aromatic hydrocarbons.

Crude oils also contain small quantities of organic acids (naphthenic acids, less than 1%), some contain sulphur (up to 3%) that must be removed during processing as it burns to sulphur dioxide (a corrosive gas) [12]. The chemical structure of oil hydrocarbons is shown in figure 3 [11].

In this paper is made a study on the in situ bioremediation methods for choosing the optimal remediation method of soil contaminated with petroleum hydrocarbons.

To decontaminate soil polluted with petroleum hydrocarbons were developed and tested multiple techniques of soil remediation, such as: physical degradation, chemical degradation, photodegradation.

Most of these methods have some drawbacks in the remediation of soil contaminated with petroleum hydrocarbons. Bioremediation offers the best method in petroleum hydrocarbon contaminated soil remediation because it harnesses the capacity of indigenous microorganisms in the soil [14].

2. In-situ bioremediation methods

When remediation is performed in situ soil is not excavated, leading to important cost savings due to the elimination of costs of excavation and transportation of the contaminated soil to the treatment facilities [15].

In-situ bioremediation also presents some limitations, such as: it is not suitable for all soils, complete degradation is difficult to achieve and natural conditions (temperature) are difficult to control [16].

Some of the in situ treatment biotechnologies of soil contaminated with petroleum hydrocarbons are: bioventing, biosparging, in situ decontamination, application of biologic amendments due to soil tillage and phytoremediation.

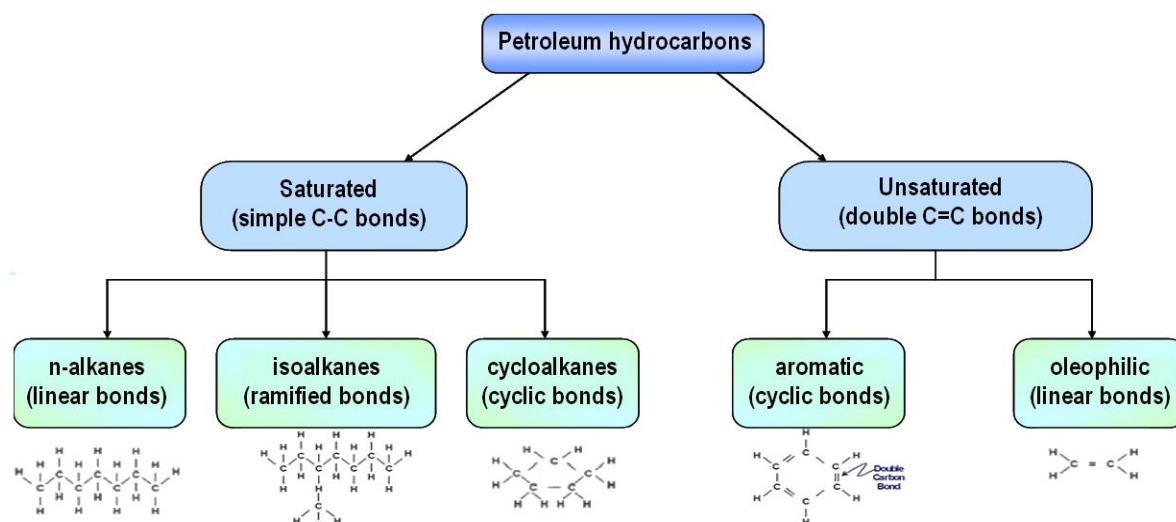


Figure 3. Structure of petroleum hydrocarbons [11]

Bioventing is an in situ remediation technology that uses microorganisms to decompose organic components absorbed in soil in the unsaturated area. Bioventing improves the activity of indigenous bacteria and naturally stimulates in situ biodegradation of hydrocarbons in the soil by inducing air or oxygen flow into the unsaturated area and, if necessary, by adding nutrients. Oxygen can be provided by direct injection of air into the soil.

Bioventing helps primarily in the degradation of absorbed fuel residues, but it also helps in degradation of volatile organic compounds (VOC). The natural degradation rate is generally limited by the lack of oxygen and electron acceptor, rather than the lack of nutrients (for example, electron donors). In bioventing, small quantities of air are used to offer only the needed amount of oxygen to sustain microbial activity [17].

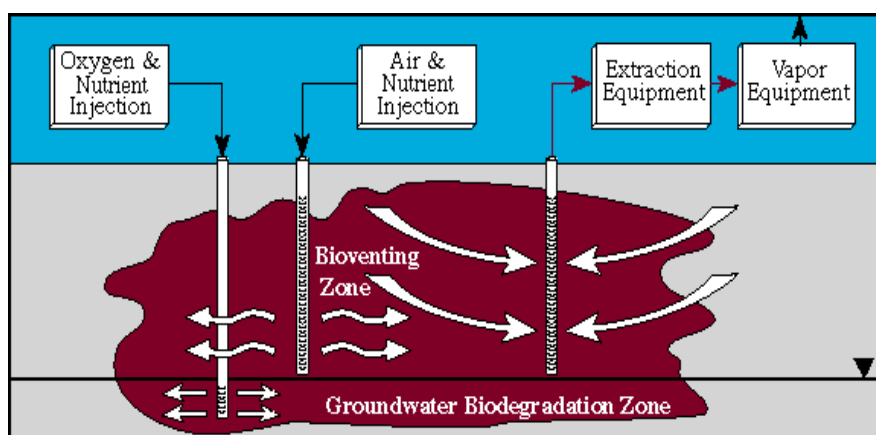


Figure 4. Bioventing [18]

Biosparging is an in situ remediation technology that uses indigenous microorganisms in the biodegradation of organic components in the saturated area. In biosparging, air (or oxygen) and nutrients (if needed) are injected into the saturated zone to increase the biological activity of the indigenous microorganisms [19].

In situ decontamination. For in situ bio-decontamination practice there are several applicable options that have as a basis the introduction of

nutrients and oxygen inside the contaminated area, in order to create favorable conditions for organic pollutants biodegradation.

The process involves the injection into the soil of water in which are dissolved phosphorous, nitrogen and oxygen, which accelerates the aerobic reaction intended for the annihilation of pollutants. The native bacterial flora, specific to the contaminated area, is used for in situ bio-decontamination [3, 4].

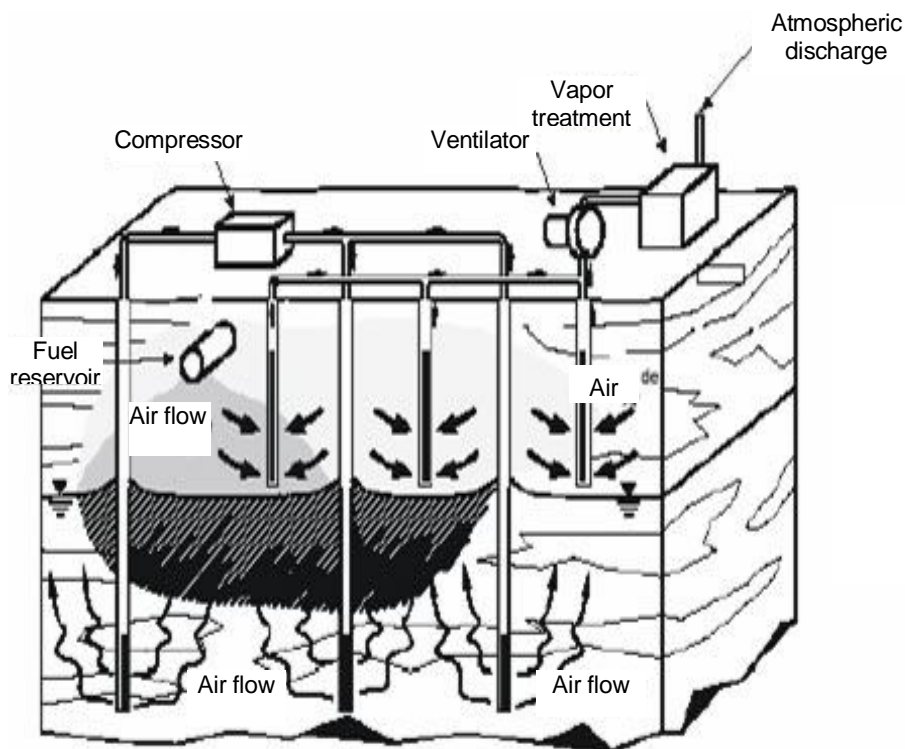


Figure 5. Biosparging [20]

Phytoremediation is an emerging technology that uses plants to eliminate contaminants from soil and water [15]. Lately, biological techniques such as phytoremediation are evaluated for remediation of sites contaminated with oil, but plants used must be suitable for the climate and soil conditions of the contaminated sites [21]. Physical and chemical methods are adequate for decontamination of relatively small areas, they are too expensive to be used on large areas such as those contaminated with industrial substances, petroleum products; this is why, nowadays, many developing countries (such as Iran) have abandoned almost completely the idea of decontaminating oil polluted soils by physical or chemical methods due to high remediation costs [22]. Phytoremediation is a relatively new technology, effective, ecological and promising for remediation of soil contaminated with petroleum hydrocarbons [22]. Phytoremediation presents a series of advantages, such as: relatively low cost, easy to implement and maintain, 10 - 20% costs of mechanical treatment, it's faster compared to natural attenuation. The method also has disadvantages, such as: a longer period of time is required; it is influenced by soil and climate conditions [14]. In table 1 are presented a series of plants, species capable to degrade a variety of

petroleum hydrocarbons and which may have potential in the phytoremediation process [23].

Application of biological amendments when tilling. Bioremediation techniques aim to modify the availability of pollutants and their concentration, as well as the speed of biodegradation reactions. By tilling and applied amendments, normally in the superficial layer, is aimed the modification of properties so that de microbial degradation of pollutants is activated. This technique requires the control of the main environmental characteristics, such as pH, water content, temperature, oxygen and nutrient concentration [3, 4]. Manure represents a valuable resource for the environment and it can be used in soil bioremediation. Manure is an important source of nutrients for cultures and has the ability to improve soil productivity [24]. Manure is a mixture of feces, urine, bedding and forage residues coming from mixed farms or farms with only one breed maintained on permanent or temporary bedding [25, 26]. The quantity of manure obtained from a farm varies and is influenced by a series of factors, such as: breed, type of bedding, age of the animals, etc. The quantity of fresh dejections obtained from different species and categories of animals in permanent stabulation is presented in table 2 [26].

Table 1. Species of plants used in phytoremediation [23]

Scientific name	Family	Form
<i>Agropyron smithii</i>	Gramineae	Grass
<i>Andropogon gerardi</i>	Gramineae	Grass
<i>Bouteloua curtipendula</i>	Gramineae	
<i>Bouteloua gracilis</i>	Gramineae	Grass
<i>Buchloe dactyloides</i>	Gramineae	Grass
<i>Buchloe dactyloides</i> var. <i>Prairie</i>	Gramineae	Grass
<i>Elymus canadensis</i>	Gramineae	Grass
<i>Festuca rubra</i> var. <i>Arctared</i>	Gramineae	Grass
<i>Populus deltoides</i> x <i>Nigra</i>	Salicaceae	Deciduous tree
<i>Sorghastrum nutans</i>	Gramineae	Grass

Table 2. Quantity of dejections obtained from different species and categories of animals [26]

Breed and category of animals	Dejections kg/head/day		
	Feces	Urine	Total
Horses	16-20	4-5	20-25
Milk cows	20-30	10-15	30-45
Feeding cattle	18-21	7-9	25-30
Calf	10-22	4-8	14-30
Adult sheep	0.7-3	0.7-1.5	1.4-4.5
Feeding pigs	2.5-3.5	3-4	5.5-7.5
Young pigs	1-1.5	0.7-1	1.7-2.5
Battery chickens	-	-	0.175

Manure has an average content of 20-25% solid substance (75 - 80% humidity) [28]. The main factor influencing the total amount of N and P from dejections is represented by alimentation; 55-90% of the N and P content in animal food is excreted in feces and urine. (www-pub.iaea.org) In table 3 are

presented the quantities (%) of N and P excreted in dejections from animal food [25].

The chemical composition of manure differs depending on the species from which it comes and in table 4 is presented the average values for different species [26].

Table 3. The quantity of N, P excreted in Alpha dejections [25]

Animal breed and category	N excreted (% of the ingested food)	P excreted (% of the ingested food)
Milk cows	65-80	65-80
Young bovine	75-80	70-85
Young pigs	75-80	75-85
Pigs	70-80	75-85
Egg laying chickens	65-80	85-90
Broiler chickens	55-65	50-65

Table 4. Composition of manure for different species [26]

Animal breed	Water %	Organic substance (%)	N %	P ₂ O ₅ %	K ₂ O %	Ca %
Horses	71.3	25.4	0.58	0.28	0.53	0.21
Cattle	77.5	20.3	0.34	0.16	0.40	0.31
Sheep	64.6	31.8	0.83	0.23	0.67	0.33
Swine	72.4	25.8	0.45	0.19	0.60	0.08
Chickens on bedding	35.0	-	1.76	1.70	1.00	-

3. Conclusions

Crude oil and petroleum products, made up of a complex mixture of hydrocarbons (alkanes, cycloalkanes and aromatics) and other organic compounds represent one of the main sources that contribute to soil contamination in Europe, being one of the main problems facing humanity adversely affecting plants, animals and human health.

Bioremediation, based on the presence of microorganisms in the soil, is an optimum method in remediation of soils contaminated with carbonate organic compounds, being successfully used in remediation of soils contaminated with crude oil and petroleum products. In-situ bioremediation presents a series of advantages, such as: soil is not excavated thus eliminating excavation and transportation costs.

Manure, a mixture of feces, urine, bedding and forage residues, is an important source of nutrients, representing a valuable resource for the environment and can be used in bioremediation of soil contaminated with petroleum hydrocarbons.

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