

A REVIEW ON DIFFERENT BIOREMEDIATION TECHNOLOGIES FOR SOIL POLLUTED WITH PETROLEUM HYDROCARBONS

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Abstract

Crude oil and its derivatives now has become a threat to environment due to extraction and transportation. Accidental oil spills occur regularly at many locations throughout the world. Contamination / pollution of soil with petroleum hydrocarbons has become a serious problem. Various physical, chemical and biological remediation strategies have been used to restore polluted soils. For bioremediation technology application, it is necessary to know the optimizing ways of the biodegradation process. Even though cost of soil decontamination is roughly similar in many ways, more and more of pollution research is directed to biotechnological methods based on the ability of microorganisms to degrade certain pollutants under both natural conditions and through anthropogenic intervention meant to shorten the time of ecological reconstruction of polluted sites. Bioremediation can be divided into two basic types: natural attenuation, which can be applied when the natural conditions are suitable for the performance of bioremediation without human intervention, and engineered bioremediation, which is used when it is necessary to add substances that stimulate microorganisms. Soil bioremediation technologies could be in situ or ex situ. As bioremediation technologies in situ can be applied: biostimulation, bioaugmentation, bioventing, stimulation with surfactants, phytoremediation, use of agricultural land, natural attenuation, biobubbling, cometabolism. Ex situ bioremediation technologies could be achieved by bioreactors, hovering the land, biopile, composting.

Key words: bioremediation technologies, soil pollution, petroleum hydrocarbons

Petroleum products including gasoline, diesel or lubricants can be released to the environment through accidents, managed spills, or as unintended by-products of industrial, commercial or private actions; causing local and diffuse pollution to the environment (Park and Park, 2011).

MATERIALS AND METHODS

Soil bioremediation technologies could be in situ or ex situ. As bioremediation technologies in situ can be applied: biostimulation, bioaugmentation, bioventing, stimulation with surfactants, phytoremediation, use of agricultural land, natural attenuation, biobubbling, cometabolism. Ex situ bioremediation technologies could be achieved by bioreactors, hovering the land, biopile, composting (static / mechanical stirring).

RESULTS AND DISCUSSIONS

In situ bioremediation technologies

In situ biodegradation of petroleum hydrocarbons is one of the most cost-effective

means of site remediation. This method has proven successful in soils, ground water, and slurries.

Biostimulation

Biostimulation, also known as improved bioremediation, is achieved by increasing the nutrient content, involving the application of selected microorganisms, nutrients, oxygen donors, so on, to accelerate natural biodegradation processes. It is the process by which the development of soil degradation biofuel bacteria is stimulated by the addition of nutrients, so that the carbon to other nutrients ratio (NPK) is only affected by carbon excess (Lee and Levy, 1987, 1989, 1991).

Biostimulation is a relatively new method. In the tropical area, bioremediation represents an ecological rehabilitation of crude oil pollution. Ecological rehabilitation involves the reappearance of vegetation on affected areas. The objective of this study was to evaluate combinations: biostimulation, inoculation with selected microorganisms, hot water flushing, mixing of contaminated soil and soil tillage for the remediation of crude oil contaminated tropical soils.

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Odokuma and Dickson (2003) conducted a study on the bioremediation of a tropical-wet soil polluted with crude oil. Bioremediation is closely related to ecological rehabilitation by washing the soil. Ecological rehabilitation involves the return of the soil to arable land. The objective of the study was to evaluate various decontamination methods of soils polluted with crude oil: biostimulation, inoculation with selected microorganisms, washing with hot water and mixing with uncontaminated soil in various combinations. Thus, the experimental variants were:

- ✓ Experimental variant O – no treatment applied;
- ✓ Experimental variant A - washing with hot water, fertilization, biostimulation, inoculation with selected microorganisms and cultivation;
- ✓ Experimental variant B - mixing with uncontaminated soil, fertilization, biostimulation and cultivation;
- ✓ Experimental variant C - biostimulation, fertilization and cultivation;
- ✓ Experimental variant D - inoculation with selected microorganisms and cultivation;
- ✓ Experimental variant D1 - fertilization and cultivation.

All the experimental variants were polluted with 10% crude oil, and after 9 weeks, the total oil hydrocarbon concentration decreased by 2%, 73%, 82%, 84%, 88% and 89% for the experimental variants O, B, D, A, D1 and C.

An in situ bioremediation study of soils polluted with petroleum hydrocarbons using biostimulation was conducted by Menendez-Vega et al. (2007). Biostimulation was performed by the addition of fertilizer, surfactant and hydrogen peroxide. The results have led to the conclusion that the biostimulation method is effective and has led to the disappearance of pollutants.

Adesodun and Mbagwu (2008) achieved a comparative study on a tropical alfisol polluted with petroleum residues by adding manure (CD), poultry manure (PM) and pig manure (PW). The addition of the three types of organic fertilizers is meant to increase the nutrient content and, implicitly, the biodegradability rate. The soil was polluted with 5000 mg kg⁻¹ (0.5% SP), 25000 mg kg⁻¹ (2.5% SP) and 50000 mg kg⁻¹ (5% SP) petroleum hydrocarbons. Following the experiment, the decrease in total petroleum hydrocarbon were registered, depending on the treatment applied, thus the best yield was recorded in poultry manure, then manure and pig manure (Figure 1).

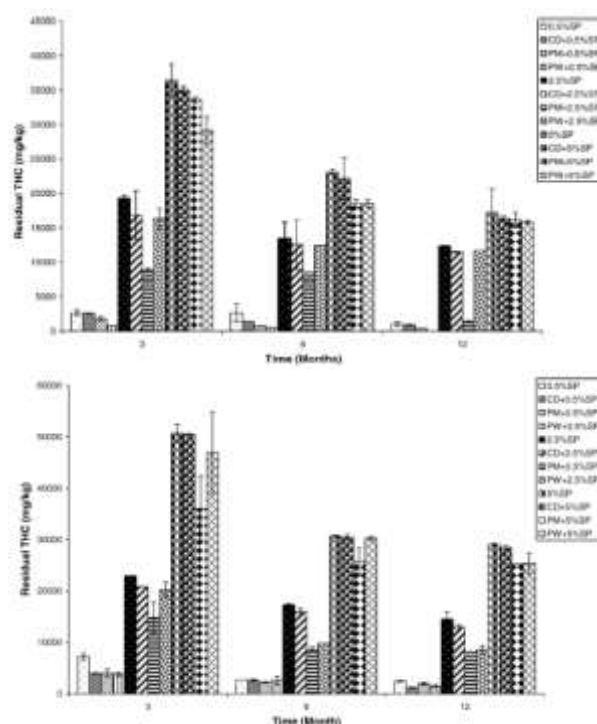


Figure 1. Total hydrocarbon concentration decrease during A) the first experimental year; B) the second experimental year (Adeson și Mbagwu, 2008)

Radwan et al. (2000) studied biostimulation mechanisms with the help of easily accessible peptone carbon and observed significant increases in total bacterial counts, leading to a higher biodegradability rate. Also, Radwan and Al-Muteirie (2001) have demonstrated the importance of vitamins in stimulating the biodegradation process. The development of two degrading bacteria, especially n-octadecane and phenanthrene, was achieved by adding folic acid (vitamin C), pyridoxine (vitamin B6), vitamin B12, vitamin B7, etc. These have also been confirmed by a field study conducted by vitamin fertilization on sandy soils polluted with petroleum hydrocarbons. The glucose and amino acid modifications are carbon sources for increasing the activity of soil microorganisms (Swindoll et al., 1988).

Another carbon source can be straw which, in dry form, contains lactic acid (66%), amino acids (24%) and lactose (5%). Thus, this straw can be used in the bioremediation process of soils polluted with petroleum hydrocarbons (Östberg et al., 2007).

Bioaugmentation (Inoculation with selected microorganisms)

Inoculation with selected microorganisms is used when soil bacteria are unable to respond to the need to initiate and carry out the biodegradation process, selected microorganisms with high degradation capacities of petroleum

hydrocarbons are inoculated into the soil (Thomassin-Lacroix et al., 2002).

Bioaugmentation and biostimulation are biodegradation methods (bioremediation) used today and whose speed is higher compared to natural attenuation (Lee et al., 1993). This method involves the addition of microbial populations. Sometimes these populations are obtained in the laboratory (Okpokwasili et al., 1986).

Bioremediation of soils contaminated by biostimulation, inoculation with selected microorganisms is a biotechnology to increase the biodegradation rate of contaminated soil by nutrient and oxygen intake dissolved in injection water, microbial activity is stimulated by water circulation supplemented with inoculum (Lee and et al., 1993).

Inoculation with selected microorganisms is a technique by which microbial cultures are added to the soil to repair and restore the soil into the soil (D'Annibale et al., 2006; Ruberto et al., 2003). Microbial cultures must have the ability to adapt to environmental conditions and survive in the presence of other microorganisms (Riser-Roberts, 1998).

Liu et al. (2008) carried out a comparative study on 10300 mg kg^{-1} soil polluted with crude oil with four different treatments: inoculation with selected microorganisms – bioaugmentation (BA), biostimulating with biosurfactants (BS), nutrient addition (NE) and a control with sterilized soil (SS). The experiment was carried out over a period of 330 days and a biodegradation of petroleum hydrocarbons by 66% in nutrient treatment (NE), 36% in biostimulating treatment (BS), and 81% in bioaugmentation. The results obtained in the experiment are shown in Figure 2.

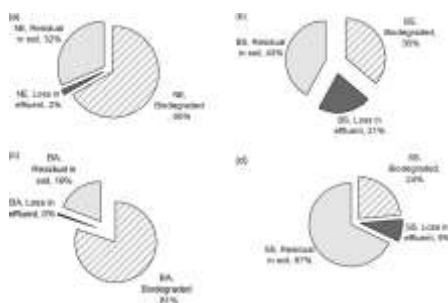


Figure 2 Biodegradation of petroleum hydrocarbons in a soil polluted with 10300 mg kg^{-1} THP in for different treatments: bioaugmentation (BA), biostimulation with biosurfactants (BS), nutrients addition (NE) and a control (SS) (Liu et al., 2008)

Bioventing

Bioventing is a technology that stimulates naturally occurring microorganisms in the soil to degrade some pollutants from the soil by providing the necessary oxygen. Biotechnology based on

stimulating the soil contaminants degradation process by injecting air, nutrients (nitrogen and phosphorus) to decontaminate in situ contaminated soils with crude oil or lubricants (Pepper et al., 1996).

Limiting factors: poor aeration of the soil, saturation with soil water, reduced nutrients (nitrogen and phosphorus), reduced aerobic biodegradation through cometabolism or anaerobiosis, low temperature.

Effects: stimulation of the existing microbiota, increasing bioremediation speed through water circulation in the soil, aerobic metabolism of contaminants through O_2 intake.

Biostimulation with biosurfactants

Synthetic surfactants can be used in bioremediation technologies, while biosurfactants (surfactants with microbial growth properties) present superior characteristics to synthetic surfactants such as: absence of toxicity, biodegradability and efficacy at extreme temperature, pH and salinity (Fiechter, 1992; Rosenberg, 1993; Mulligan et al., 2001).

Generally, the crude oil transfer rate is lower than the oxygen transfer rate or biodegradability rate and is the way to control the biodegradation of contaminated soils. The application of surfactants or emulsifying agents may result in a decrease in interphase stress and an increase in hydrocarbon solubility (Vardor-Suhan and Kosaric, 2000). Sorption of surfactants by soil particles depends on the type of surfactant, the soil properties, the amount and structure of the clay in the soil. Anionic surfactants are usually used in remediation procedures due to the high degree of adsorption on soil particles compared to cationic and non-ionic surfactants (Selberg and Tenno, 2002).

Biosurfactants have gained attention due to their biodegradability, low toxicity, ability to be produced from cheap raw materials and efficiency under extreme temperature, pH and salinity conditions (Kosaric, 2000). These substances have the ability to increase the hydrocarbon solubility and therefore have a very high applicability potential. They have been used in the last period more and more because they do not have a negative impact on the environment (Banat et al., 2000; Ron and Rosenberg, 2002).

A study by Plaza et al. (2006) on different culture media measured the surfactant surface to determine the biosurfactant capacity. The emulsion activity was tested for xylene, toluene, crude oil and mineral oils.

Cubitto et al. (2004) conducted a study of the biosurfactant influence *Bacillus subtilis* 09 on aliphatic and aromatic hydrocarbons. According to

the results obtained, this inoculation led to an increase in the bacterial population and, at the same time, to the acceleration of the biodegradation process in the case of aliphatic hydrocarbons. However, the degradation of aromatic hydrocarbons has not been stimulated.

Figure 3 shows the mechanism of hydrocarbon absorption by the involvement of a biosurfactant (Fritsche and Hofrichter, 2008).

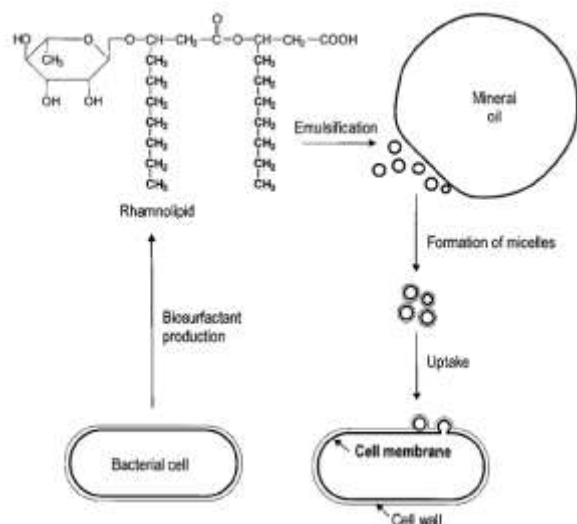


Figura 3. Involment of biosurfactants in the up-take of hydrocarbons (Fritsche și Hofrichter, 2008)

Phytoremediation

Phytoremediation is a technique that uses plants to remove, transfer, stabilize or destroy contaminants in the soil (Anderson et al., 1993). Surface contaminated sites with organic pollutants is best suited to applying one of the existing phytoremediation methods: phytotransformation, rhizosphere bioremediation, phytostabilization, phytoextraction or rhizofiltration (Burken and Schnoor, 1996; Schwab and Banks, 1999). Baud-Grasset et al. (1993) used phytotoxicity endpoints in the evaluation of the bioremediation process.

Plants have the role of increasing the activity of microorganisms in the rhizosphere by optimizing some environment parameters, such as humidity, pH. In addition, the roots development involves the oxygen penetration necessary for contaminants oxidation process (Lin and Mendelsohn, 1998; Joner and Leyval, 2003). Although the biodegradation of hydrocarbons in the rhizosphere is known, the mechanisms by which the rhizosphere influences the growth and activity of microorganisms is not yet clarified (Wiltse et al., 1998; Hutchinson et al., 2001).

The degradation processes in the rhizosphere area appear as an effect, the plants excrete organic compounds through the roots, which results in an increase in the density,

diversity and activity of the biodegradable microorganisms (Cunningham et al., 1996; Siciliano and Germida, 1998).

Yateem et al. (1999) determined a large number of microorganisms (bacteria, fungi and actinomycetes) in rhizosphere area compared to the area where the soil was uncultivated. Thus, on a cultivated soil there is a higher degradation of petroleum hydrocarbons compared to uncultivated soil.

Use of agricultural land

Contaminated soils are mixed with soil amendments such as reduction agents of bulk density and nutrients, applied to clean agricultural land incorporated into the soil; periodically, soil tillage are performed to improve aeration and homogenization. Can be applied on large surfaces with land reserved for non-agricultural purposes. The method consists in the application of polluted soil in thin layers on unpolluted soil, the mixing of layers by dilution and biostimulation treatments of degradation (Creangă et al., 2005).

Natural attenuation

Natural attenuation is a passive bioremediation process involving the process of biodegradation, evaporation, sorption, chemical degradation (photooxidation, autooxidation), dispersion, dissolution without human intervention. Biodegradation by natural microorganisms, surnamed and in situ attenuation, is the primary mechanism by which petroleum hydrocarbons can be removed from the environment (Margesin and Schinner, 2001).

Ex-situ bioremediation technologies

Ex-situ bioremediation technologies of contaminated / polluted soils require their treatment in bioreactors, biopiles or incinerators. Such treatments involve high costs (Amatya et al., 2002). An alternative to the listed methods is ground clearance or composting with or without injection of air to facilitate oxygenation (Catalan et al., 2004).

Bioreactors

Bioreactors are engineering systems where contaminants are degraded in a specific environment by microorganisms. The bioreactor is an independent plant for the treatment of small volumes of polluted soil where the environmental parameters are very well controlled: temperature, nutrient concentration, mixing time, microbiological activity, redistribution of oxygen, so on. (Creangă et al., 2005).

It is possible to achieve a biodegradability rate of up to 50% of initial pollution in 200 days by simply aerating the soil layer. By measuring the volume of carbon dioxide, degradation rates can be assessed (Lotter et al., 2001). The biodegradability

rate is controlled by the transfer of oxygen from the gaseous phase to the liquid phase.

Soil landing

Ex situ biotechnology of contaminated soil by soaking, aeration, nutrient intake and swelling agents to promote aeration and fluid circulation in order to increase the microbial degradation rate of contaminants (Creangă et al., 2005).

Biopiles

Biotechnology derived from the land-loosening method, based on soil contaminated soil lifting in mounds a few meters tall, ensuring aeration, moisture and nutrient intake. Contaminants are reduced to CO₂ and H₂O within 3-6 months (Rojas-Avelizapa et al., 2007).

Composting

Composting - a biologically controlled process by which organic soil contaminants are converted by microorganisms under aerobic conditions into stabilized byproducts. The composting of soil polluted with crude oil or oil sludge consists in depositing it in heaps specially arranged to allow for conditions of temperature, aeration, addition of nutrients, wetting so on (Creangă et al., 2005).

CONCLUSIONS

Bioremediation technologies can be in-situ and ex-situ. Bioremediation is based on the ability of microorganisms to use petroleum hydrocarbons as a source of carbon and energy. It is considered to be most effective because, in addition to the lower cost, it does not have irreversible effects on the pedogenic characteristics of the affected soil.

Depending on the degree of pollution, the appropriate soil bioremediation technology is chosen: biostimulation; bioaugmentation (inoculation with selected microorganisms); bioventing; biostimulation with surfactants; phytoremediation; use of agricultural land; natural attenuation; biobubbling; cometabolism; bioreactors; land loosening; biopiles; composting (static / mechanical stirring).

ACKNOWLEDGMENTS

The financial support provided by Ministry of Education and Research – project no. PN 16 07 03 08Bioremediation of an crudeoilpollutedsoil by using β-cyclodextrin.

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