

Bioremediation of Hydrocarbon Contaminated Soil Using Selected Organic Wastes

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1. Theme description

The large increase in the past century of industrial development, population growth and urbanization favoured the release of hazardous chemicals in the environment and a general global pollution. Several chemicals, including heavy metals and radionuclides, but also organic compounds such as pesticides, dyes, Polycyclic Aromatic Hydrocarbons (PAHs), may persistently accumulate in soils and sediments, thus potentially menacing human health and environment quality, due to their carcinogenic and mutagenic effects, and ability to bioconcentrate throughout the trophic chain^[1].

The concern on toxicity risk and environmental pollution associated with chemical contaminants has called for the development and application of remediation techniques. In fact, a large effort has been devoted to find ways to remove contaminants from ecosystems. In particular, several strategies were devised to remediate and restored polluted soils, based on physical, chemical and biological methods. These techniques may be applied in situ, i.e. in the very contaminated soil, thus offering numerous advantages over ex situ technologies, whereby the soil is removed to be treated elsewhere. Thus, in situ remediation techniques do not require soil transportation costs and can be applied to diluted and

widely diffused contaminations, thus minimizing dangerous intensive environmental manipulation. Conversely, ex situ processes imply the excavation of polluted soil and their decontamination to be conducted in a separate processing plant[2]. Table 1 summarizes the main technologies for cleaning up polluted soils and the estimated costs for each treatment.

Depending on contaminants characteristics and soil properties, different soil remediation technologies can be applied with variable success. However, effective eco-friendly biological, physical and chemical remediation practices are being today preferred over the techniques which imply larger biotic and abiotic environmental impacts.

Table 1. Main technologies for cleaning up of polluted soils and the estimated costs of each treatment.

Treatment	Approximate remediation cost (£/tonne)
Removal to landfill	Up to 100
<i>Solidification</i>	
Cement and Pozzolan based	25-175
Lime based	25-50
Vitrification	50-525
<i>Physical processes</i>	
Soil washing	25-150
Physico-chemical washing	50-175
Vapour extraction	75
<i>Chemical Processes</i>	
Solvent extraction	50-600
Chemical dehalogenation	175-450
In situ flushing	25-80
Surface amendments	10-25

<i>Thermal treatment</i>	
Thermal desorption	25-225
Incineration	50-1200
<i>Biological treatment</i>	
Windrow turning	10-50
Land farming	10-90
Bioventing	15-75
Bioslurry	50-85
Biopiles	15-35
In situ bioremediation	175

2. Bioremediation Methods

Bioremediation, either as a spontaneous or as a managed strategy, involves the application of biological agents to clean-up environmental compartments polluted by hazardous chemicals. Plants, microorganisms and plant-microorganism associations, either naturally occurring or tailor-made for the specific purpose, represent the main bioremediation active factors.

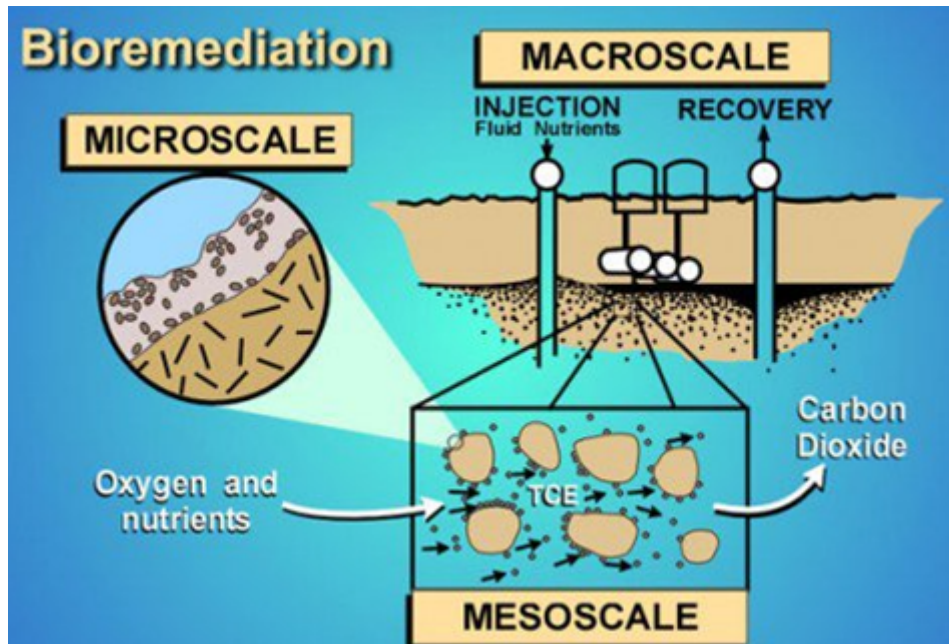


Figure 1- Bioremediation scheme.

2.1 Microorganisms

In contaminated soils, aromatic Anthropogenic Organic Pollutants (AOPs) can be degraded by bacteria or fungi via an aerobic or anaerobic metabolism or both. In aerobic metabolism, molecular oxygen is incorporated into the aromatic ring prior to dehydrogenation and subsequent aromatic ring cleavage. In anaerobic metabolic processes molecular oxygen is absent, and alternative electron acceptors, such as nitrate, ferrous iron, and sulfate, are necessary to oxidize aromatic compounds.

The effective agents in the transformation of organic pollutants are the microbial enzymatic system that, as powerful catalysts, extensively modify the structure and toxicological properties of contaminants or completely mineralize the organic molecule into innocuous inorganic end products. However, in order to be biodegraded, contaminants must interact with the enzymatic system within the biodegrading organisms. If soluble, they can easily enter cells, but, if insoluble, they must be transformed into soluble or more easily cell-available products.

Their main sources of these enzymes are fungi, such as wood-degrading basidiomycetes, terricolous basidiomycetes, ectomycorrhizal fungi, soil-borne microfungi, and actinomycetes. Most fungi are robust organisms and may tolerate larger concentrations of pollutants than bacteria. In particular, white-rot fungi appear unique and attractive organisms for the bioremediation of polluted sites. A possible alternative to the bioremediation of polluted sites by microbial activity may be the direct application of cell-free enzymes after their isolation from microbial cultures.

Bioremediation of contaminants can be more rapidly accomplished by two methods, bioaugmentation and/or biostimulation[3]. The process of bioaugmentation, as it applies to remediation of petroleum hydrocarbon contaminated soils, involves the introduction in a contaminated system of microorganisms that have been exogenously cultured with the aim to degrade specific chains of hydrocarbons. These microbial cultures may be derived from the very same contaminated soil or obtained from a stock of microbes that have been previously proven to degrade hydrocarbons. On the other hand, the biostimulation process implies the addition to polluted soils of nutrients in the form of organic and/or inorganic fertilizers, in order to stimulate the activity and proliferation of indigenous microbes. These may or may not be proved to aim the polluting hydrocarbons as a primary food source. However, the hydrocarbons are assumed to be degraded more rapidly in comparison to natural attenuation processes, probably because of the increased number of microorganisms induced by the greater amount of nutrients provided to the contaminated soil.

2.2 Plants

Phytoremediation of organic and inorganic contaminants involves either a physical removal of pollutants or their bioconversion (biodegradation or biotransformation) into

biologically inactive forms. The conversion of metals into inactive forms can be enhanced by external conditioning of soils: enhancement of soil pH (e.g. through liming), addition of organic matter (e.g. sewage sludge, compost etc.), inorganic anions (e.g. phosphates) and metal oxides and hydroxides (e.g. iron oxides). Concomitantly, plants can play a role here in transforming contaminants in inactive forms by releasing different anionic species in soil and altering soil redox conditions[4].

The uptake of AOPs by plants occurs through two pathways. One pathway is the soil-water-plant cycle in which pollutants are uptaken from the soil solution and then transported up plant shoots within the xylem transpiration system. A second pathway involves the soil-air-plant cycle, in which AOPs are uptaken by aerial parts of plants either from soil particles adsorbed on plant leaves or directly as gaseous forms of AOPs after their volatilization from soil. Following plant uptake, AOPs are further translocated, sequestered, and degraded in plant tissues by other processes. The key parameters which influence the translocation of contaminants from soil to plant include the content of contaminants in soil (or water), their physical-chemical properties, the plant species, the soil types, and the time of exposure to plant[5].

The advantages of phytoremediation over other approaches is due to the inherent preservation of soil natural structure and to the free sunlight energy involved in the process, that enhances the content of degrading microbial biomass in soil.

2.3 Compost and Biochar

The composting process is the biological decomposition of organic wastes under controlled aerobic conditions. In contrast to uncontrolled natural decomposition of organic compounds, the temperature in composting waste heaps can increase by self heating to the ranges which are typical of mesophilic (25-40 °C) and termophilic microorganisms (50-70

°C). The end product of composting is a biologically stable humus-like product that can be employed in several applications, e.g.: soil conditioner, fertilizer, biofiltering material, fuel. The composting process can concomitantly reach different objectives, such as the volume and mass reduction of biomasses, their stabilization and drying, and the elimination of phytotoxic substances and pathogens[6].

Composting is also a method to be employed in the decontamination of polluted soils, because compost is capable of sustaining various microbial populations potentially hydrocarbons' degraders, such as bacteria, including bacilli, pseudomonas, mesophilic and thermophilic actinomycetes, and lignin-degrading fungi. Compost can also improve the chemical and physical properties of soil to be decontaminated, since it affects soil pH, nutrients and moisture content, soil structure, and microbial biomass population.

Unless coupled with more bioactive compost materials, the possible use of biochar in the remediation of contaminated soil appears limited by its inherent biological recalcitrance that depresses the activity of pollutants microbial degraders[7].

3. Case Study: Bioremediation by selected organic wastes

Inadequate mineral nutrient, especially nitrogen, and phosphorus, often limits the growth of hydrocarbon utilizing bacteria in water and soil. Addition of nitrogen and phosphorus to an oil polluted soil has been shown to accelerate the biodegradation of the petroleum in soil. It was reported that 18.7% and 31.2% higher crude oil biodegradation in soil amended with chicken droppings and fertilizer, respectively, compared to un-amended control soil after 10 weeks while degradation of crude oil in soil amended with

melon shells as source of nutrients was 30% higher than those of un-amended polluted soil after 28 days[8].

Addition of a carbon source as a nutrient in contaminated soil is known to enhance the rate of pollutant degradation by stimulating the growth of microorganisms responsible for biodegradation of the pollutant.

It has been suggested that the addition of carbon in the form of pyruvate stimulates the microbial growth and enhances the rate of Polycyclic Aromatic Hydrocarbons (PAHs) degradation. Mushroom compost and spent mushroom compost (SMC) are also applied in treating organo-pollutant contaminated sites. Addition of SMC results in enhanced PAH-degrading efficiency (82%) as compared to the removal by sorption on immobilized SMC (46%). It is observed that the addition of SMC to the contaminated medium reduced the toxicity, added enzymes, microorganisms, and nutrients for the microorganisms involved in degradation of PAHs[9].

Therefore, utilization of organic waste in the bioremediation of soil seems a highly potential area. This will reduce the amount of organic waste sent to landfill, thus reduce the emission of landfill gases and also provide a cheap source of organic additive for the remediation purpose.

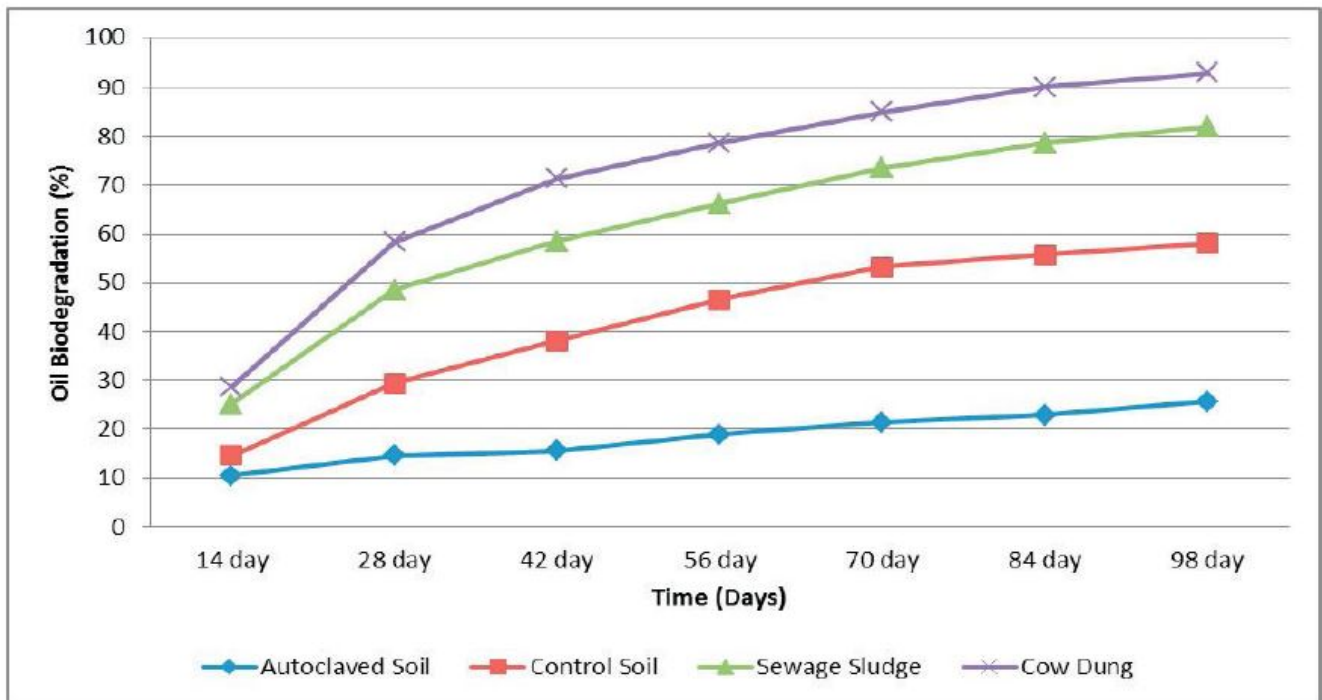


Figure 2 – Percentage biodegradation of petroleum hydrocarbon in soil contaminated with used lubricating oil and amended with organic wastes.

Figure 3 shows the biodegradation of a lubricating oil in soil (throughout the period of 98 days) are reported in Agamuthu et al. 2013[10]. The results showed high biodegradation of used lubricating oil at the end of 98 days with soil amended with organic wastes compared to the control soil treatment. At the end of 98 days, used lubricating oil contaminated soil amended with cow dung showed the highest percentage of oil biodegradation with 94%, followed by soil amended with sewage sludge which is 82% compared to the un-amended control soil that showed 66% of biodegradation of oil at the end of 98 days. Used lubricating oil contaminated soil amended with organic wastes have greater oil biodegradability compared to un-amended control soil in this study.

The main difference of oil biodegradation between the soil amended with organic wastes and unamended soil treatment occurred during the 14-28 days, where biostimulation resulted in significant increase of oil biodegradation. The addition of

nutrients stimulates the degradative capabilities of the indigenous microorganisms thus allowing the microorganisms to break down the organic pollutants at a faster rate.

In conclusion, bioremediation can be a viable and effective response to soil contamination with petroleum hydrocarbons and can be positively enhanced by the use of organic wastes.

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