IN SITU BIOREMEDIATION TECHNOLOGIES OF POLLUTED SOILS

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Abstract
Bioremediation procedures are destructive procedures which stimulate the growth of microorganisms and polluting agents' consumption as a source of food and energy and create a favorable development environment for microorganisms. Bioremediation techniques are used in soils, mud and ground waters remediation polluted with oil hydrocarbon, solvents, pesticides, wood preservations compounds and other anorganic compounds.

1. General views on in situ bioremediation of polluted soils

Bioremediation procedures are destructive procedures which stimulate the growth of microorganisms and polluting agents' consumption as a source of food and energy and create a favorable development environment for microorganisms. Oxygen supply takes place, as well as nutrients and humidity, temperature and pH control. Adapted microorganisms can come from the already existent ones in the soil or they can be created special cultures from the genetic point of view able to degrade a certain type of polluting agent.

Biological processes have a low cost, as polluting agents are destroyed without being necessary to involve remediation processes for residual polluting agents. Final products are CO2, H2O and other intermediaries depending on the type of polluting agents, soil existent conditions and involved microorganism type. Bioremediation can take place in aerobe and anaerobe conditions in the presence of electron acceptors like NO_3^-, SO_4^{2-}, O_2.

Bioremediation techniques are used in soils, mud and ground waters remediation polluted with oil hydrocarbon, solvents, pesticides, wood preservations compounds and other anorganic compounds. Bioremediation does not apply for remediating soils polluted with anorganic compounds. Their presence on the soils where bioremediation techniques are used can have a negative impact upon the biologic activity.

The application of biologic remediation of soils polluted with aromatic polycyclic hydrocarbons (PAH) does not lead to their complete destroy, as in the soil there are still hard biodegradable PAH with big molecular weights, cancerigenic ones. Biodegradability is reduced if the number of halogen atoms in the molecule is higher. Some compounds' molecules can be divided into more toxic molecules than the initial ones (for example the vinyl chloride TCE). In situ bioremediation needs a monitoring of the soil polluting agent concentration and sometimes it is also necessary to clarify the water in the aquifer.

2. Factors influencing in situ bioremediation of polluted soils

Polluting agents' biodegradation velocity by bacteria is influenced by: soil type, oxygen concentration, humidity, temperature pH, nutrients, bacteria type and metabolism.

Soil type
- in situ bioremediation is efficiently carried out in well aired soils, easily permeable ones
- in saturated soils it is difficult to carry it, due to a weak weight transport of electron acceptors (usually oxygen)
- it is difficult to apply on clayey soils with low permeability

Oxygen concentration
- it can have higher values in unsaturated soils in water, high sand and gravel content soils and reduced in clay (weakly compacted soils), in low redox potential soils and low concentrations in biodegradable materials
- in order to achieve enough concentration of oxygen into the soil for reaching aerobe conditions, air or peroxide is injected under pressure

Humidity
- it has an important role as a transport environment for nutrients and organic cells to microbe cells and for metabolites from the cells to the soil solution

Temperature
- influences the microbial activity in the environment
- low biodegradation velocity at low temperatures, so that in cold climate areas bioremediation can be inefficient during the cold periods of the year if the bioremediation process is not carried in a controlled climate area
- microorganisms remain liable for temperatures below the freezing point and microbial activity begins again when temperature rises
- warming the bioremediated area by warm air injecting can speed the velocity of the bioremediation process
- soil temperature increase can cause desorption and polluting agents volatilization (polluting agents' solubility increases with the temperature increase)
- hydrocarbons are more soluble at low temperatures than at high temperatures
- oxygen solubility into the water decreases with the temperature increase

pH
- influences solubility, thus the availability of many constituents in the soil by affecting biologic activity
- many of potentially toxic metals for microorganisms are insoluble at high pH values, so that the risk of inhibiting the microorganisms at basic pH can be reduced in treatment systems

Nutrients
- they are nitrogen, phosphorus, potassium, sulphur, magnesium, calcium, manganese, ferrum, zinc, copper and other microelements
- if nutrients are not available in enough amounts the microbial activity can be reduced
- nitrogen and phosphorus are the most likely nutrients to be deficient in contaminated environments; they are added in bioremediation systems under the form of mineral fertilizers (ammonium salts for nitrogen and phosphates for phosphorus)

- in order for the biologic activity to be carried under optimum conditions and for supplying the necessary nutrients the C:N:P report has to be 100:10:1

Bacteria type and metabolism

Inoculation

- in some cases, indigene microorganisms cannot produce the necessary enzymes for polluting agents degrading, as it is necessary to introduce some microbial cultures into the soil, specially developed for degrading some polluting agents or groups of polluting agents sometimes for surviving under very severe environment conditions.
- microorganisms are collected from the areas that will be bioremediated, separated by cultures and reintroduced in the soil for a rapid development of the microorganism population (they are isolated and stimulated in increasing the natural microorganisms populations which are degraded, and especially the polluting agents in the area to be remediated)

Co-metabolism

- it is the simultaneous metabolism of two compounds, where degradation of the second compounds (secondary-polluting sub-layer) depends on the presence of the first compounds (primary sub-layer); oil hydrocarbons can be biodegraded only in the presence of additional amounts of organic compounds supplying the necessary energy for degradation, but they can serve as co-metabolisants when degrading polycyclic aromatic hydrocarbons with more that 4 aromatic rings
- co-metabolic inoculation uses microorganisms developed on a certain compounds for producing enzymes, which chemically transforms other compounds where they cannot grow

3. Bioventilation

- oxygen is forced (through injection or extraction) through the unsaturated soils for increasing the oxygen concentration necessary for in situ biodegradation
- uses low flows of air introduced through injective
- in the case of volatile compounds absorbed into the soil, they are desorbed so that polluting agents biodegradation take place under the form of steams (fig.1)

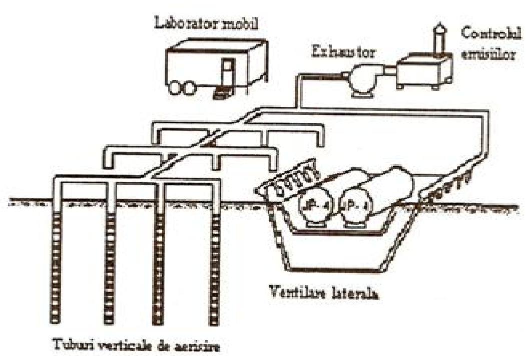

Fig. 1 Typical bioventilation system

- it is especially applied for remediating soils contaminated with oil hydrocarbons, non-halogenated solvents, some pesticides, wood preservation compounds and other organic compounds
- it does not degrade anorganic compounds, but it can change their oxidating status and favor absorption, radicular absorption, micro and macro organisms bioaccumulation
- the factors limiting the efficiency of bioventilation are:
    - o aquifer high level, saturated (lentils) or low permeability layers
    - o the possibility to accumulate steam in the neighbor buildings basements in the injection well (it can be remediated by extracting the air in the soil near the respective buildings)
    - o low humidity content
    - o low temperatures reduce the biologic processes velocity
- in order for a soil to be remediated by bioventilating it has to allow enough air for providing aerobe conditions and contain a numerous enough population of microorganisms for providing high biodegradation velocities
- before establishing technological parameters, some tests have to be carried related to the air permeability through the soil and in situ breathing process velocity
- the gas permeability through he soil is influenced by: *soil particles sizes* and *humidity* (high humidity, fine sizes of soil particles and high aquifer level very often make bioventilation unfeasible); optimum humidity value depends a lot of the soil type; a very high humidity reduces air permeability and oxygen transfer and a too low humidity inhibits the microbial activity (experiments have shown that biodegradation takes place under good humidity conditions between 2 and 5% weight); in very droughty areas it is necessary to increase humidity by irrigating or injecting wet air.

4. Accelerated bioremediation

- it is a technology that proposes degrading soil polluting agents to untoxic products by stimulating microbial processes (local or inoculated microorganisms) through forced water passing (or aqueous solutions) through the contaminated soil for accelerating biological processes for organic polluting agents degrading of in situ anorganic polluting agents immobilization (fig.2)

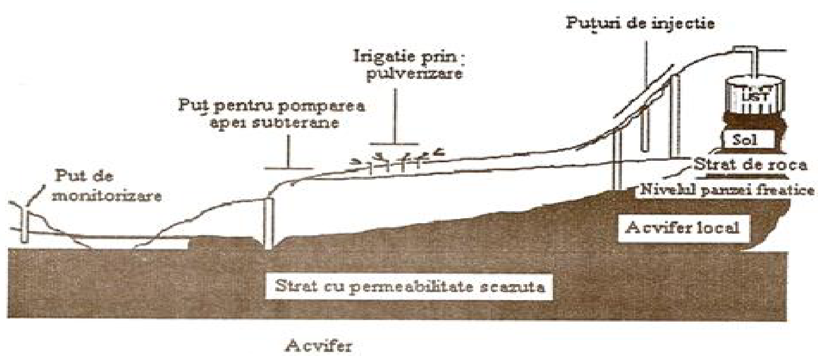

Fig. 2 Accelerated bioremediation system

- in the presence of enough oxygen amounts (aerobe conditions) and nutritive organic polluting agents are transformed at CO_2, H_2O and microbial weight

- in the absence of oxygen (anaerobe conditions) organic polluting agents are finally metabolized at CH_4, reduced amounts of carbon dioxide and hydrogen marks.
- under reducing conditions sulphate can be reduced to sulphur ions or elementary sulphur, and nitrate into molecular nitrogen
- low temperature slow the velocity of the bioremediation process; in the case of low temperature soils a protecting sheet is used for providing favorable temperatures for the biodegradation processes
- it is a long process that can last a few years; it is efficient for low contamination degree soils and can be applied for soils, mud and ground waters contaminated with oils hydrocarbons, solvents, pesticides, wood preservation compounds and other compounds.
- factors limiting the applicability of the method:
  - water circulation in the soil increases the mobility of contaminants and aquifer treatment is required
  - certain soil matrices do not allow a contact between polluting agents and microorganisms
  - preferential channels can be created for carrying injected fluids through the contaminated area (it does not apply for clayey soils, with many heterogeneous layers (horizons) due to the deficient transfer of oxygen of other electron acceptors
  - high concentrations of heavy metals, high chlorinated organic compounds, high carbon chains hydrocarbons or anorganic salts can be toxic for microorganisms
  - the biodegradation process is very slow at low temperatures
  - for establishing the process efficiency we have to know some polluting agents features for establishing the levigability potential (water solubility soil absorption coefficient), chemical reactivity (the tendency to take part in chemical reactions such as hydrolysis, oxidation, polymerization) and most importantly, biodegrability

The advantages of in situ bioremediation are:

- they are natural processes, in the presence of soil microorganisms which make immobilization or total or partial destroy of organic polluting agents;
- it allows soil treatment without digging and its transport which cause a more reduced contamination with polluting agents through generated dust, lower costs;
- operating costs are lower than in the case of other procedures applied in situ (washing, solidification, incineration); they are influenced by the type and amount of organic polluting agents, soil features, processed material volume, nature and depth of the polluting agents
- it is possible to use inoculation or/and peroxide for increasing the process efficiency
- big surfaces can be treated and they are enough for permeable, sandy or uncompacted soils
- problems related to waste storage are cancelled
- polluting agents spreading under water and wind pressure is reduced
- the increase of microorganisms number will reduce the soil permeability and polluting agents migration velocity

The disadvantages of in situ bioremediation are:

- they are slower than ex situ methods, requiring years to complete, in accordance with the degradation velocity of specific polluting agents, areas and climate features
- they are relatively non uniform processes due to the variation of soil and aquifer characteristics, the processes efficiency being difficult to verify

- they do not work well in clayey, compact soils, where oxygen or nutrients are difficult to introduce in the treatment area
- secondary products can be more mobile or more dangerous than initial polluting agents

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