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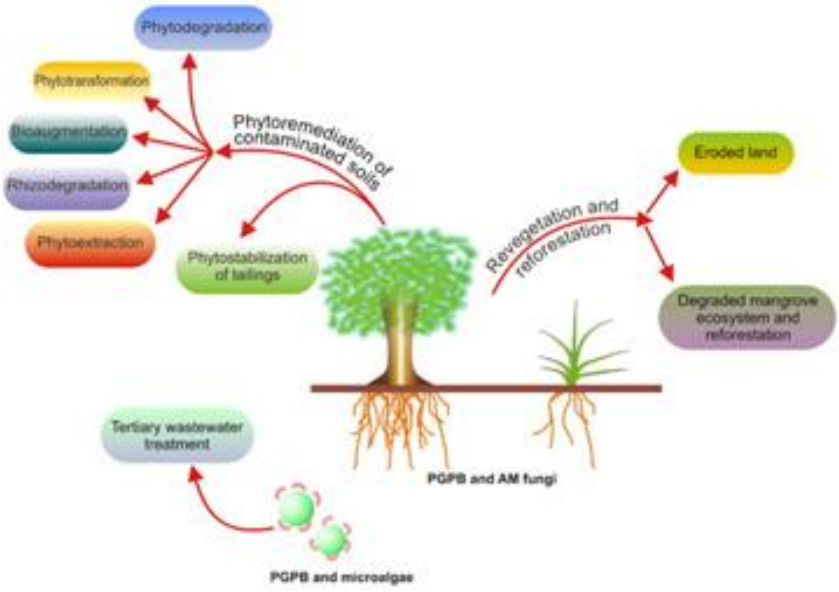

TOPIC VII: BIOLOGICAL TREATMENT OF SOLID AND HAZARDOUS WASTE

Content: Principles of biodegradation of hazardous wastes, composting, in-situ and ex-situ bioremediation

ABSTRACT

Continuing with the treatment of solid and hazardous wastes, this module looks at methods employed in biological treatment of these wastes.

IITM-EWRE

Solid and Hazardous Waste Management

Source for graphic above: *Cleaning up the mess with Bioremediation*
www.envirohealthmatters.org

TOPIC VII: BIOLOGICAL TREATMENT OF SOLID AND HAZARDOUS WASTE

Biological treatment of waste matter is the optimization of a natural biological process, which results in the treatment of waste. This mode of treatment makes use of micro-organisms (such as bacteria and fungi). The process may be aerobic or anaerobic, and requires control of nutrient concentration, temperature, moisture, pH, presence of inhibitors such as metals, and level of aeration. The factors influencing biological treatment of waste are the composition and nature of waste.

How is biological treatment of hazardous waste different from biological treatment of municipal solid waste?

- Hazardous waste may be present as complex mixtures – both low and high molecular weight compounds. These compounds will be toxic to micro-organisms, which makes their treatment a challenge.
- The microbes may not be sufficiently equipped to treat hazardous wastes (i.e., they may lack the appropriate enzyme). This is important as the reaction proceeds in accordance with the lock-and-key mechanism: Enzymes are specific. Only molecules with the exact shape can fit into the enzyme. This lock-and-key model plays a deciding role in the ability of micro-organisms to degrade certain contaminants.

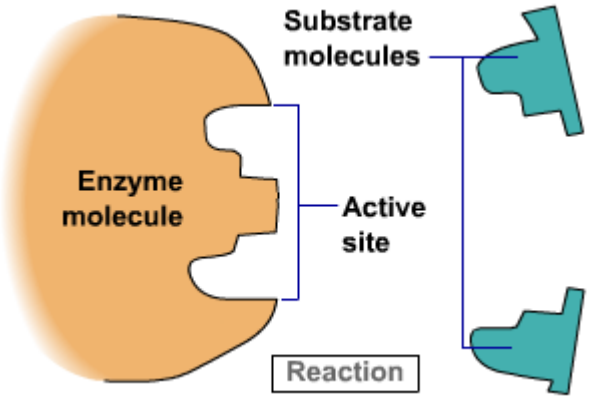

Fig. 1: Lock-and-key mechanism for enzyme activity in micro-organisms
Source: BBC Bitesize GCSE: Science. *Enzymes: The lock and key mechanism.*
http://www.bbc.co.uk/schools/gcsebitesize/science/add_edexcel/cells/enzymesrev2.shtml

- Acclimatization/ Adaptability: This refers to how well the microbial population can adapt to the presence of contaminants in their nutrient media. It depends on a "survival of the fittest" strategy. Only when the micro-organisms adapt to the contaminant, they start secreting enzymes which will eventually break down the contaminant. For e.g., microbes need to adapt to long chain polyaromatic hydrocarbons if they are to be used to break down crude oil in an oil spill site.

Steps for design of biological treatment

1. Identification of microbial consortium: This is carried out in laboratories. Soil samples from contaminated sites are collected, and the microbes existing in these environments are first isolated and observed. Some microbes may die and some may thrive. Microbes which thrive are those which have adapted to the contaminant. These microbes are then cultured repeatedly by increasing the dose of contaminant present in the nutrient broth. This is called enrichment.
2. Thermodynamic feasibility of reactions: Biological reactions are redox reactions, and their thermodynamic feasibility must be studied. Organic matter (waste) acts as electron donor, and electron acceptors are present in the environment. Most common electron acceptors in groundwater environment are O_2, NO_3^-, Fe, Mn, SO_4^{2-} and CO_2 (in decreasing order of reduction potential E^o). For e.g., O_2 is reduced to H_2O and HCHO is oxidized to CO_2 (if formaldehyde is the contaminant under consideration).

Composting

Composting is the controlled, aerobic, biological conversion of organic wastes into a more complex stable final product having a number of beneficial uses – most commonly for agriculture and landscaping.

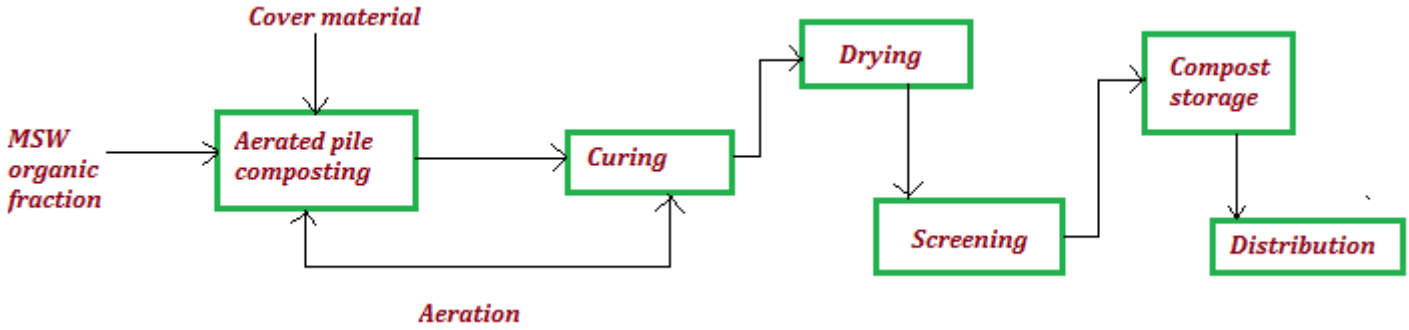

Fig. 2: Different phases in a composting operation for MSW

As an aerobic process, composting is dependent on the growth of microorganisms like bacteria, fungi, actinomycetes, protozoa. Bacteria have the most significant effect on decomposition – they are the first to form colonies in the pile, and begin to break down substances which can decompose readily (sugars, carbohydrates). Nitrogen fixing bacteria are also present in the pile, and these bacteria will fix atmospheric nitrogen for incorporation into cellular mass (during cell synthesis). Fungi play an important role in composting as the pile begins to dry up, as they can tolerate low moisture conditions and have lower nitrogen requirements than bacteria. Actinomycetes which are present in soil and sediments naturally can decompose aromatics, steroids, phenols, and slightly larger organic compounds. Macroorganisms such as earthworms, mites, nematodes, beetles move within the pile foraging for food and thus reduce the volume of the composting pile. Carbon and nitrogen are required for the metabolic processes of the microbes.

Carbon is available from the waste content, and nitrogen is made available to the bacterial population from the atmosphere. The ideal C:N ratio is ~25:1. The principal factors affecting composting are nutrient levels, aeration, moisture, temperature, pH, size of feedstock particles. Suitable temperature range for composting is 28-55^{o}C. Stages of composting are correlated with the pH of the pile. During the initial stages of decomposition, the pH is acidic (~5.0); but as the acids are decomposed, pH is as high as 8.5.

The optimal amount of water to be added to a compost pile is:

$$M_p = \frac{M_s X_s + 100 X_w}{X_w + X_s}$$

Where M_p is the moisture content when composting starts (%), M_s is the moisture content of the solids present (%), X_s is the mass of the solids on wet basis (tons), and X_w is the mass of water (tons).

Consider the decomposition of a glucose molecule in a compost pit:

Aerobic decomposition: $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$ + Energy

Anaerobic decomposition: $C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 6CO_2 + 6H_2O$

Degradability of organic waste is described by this stoichiometric equation:

$C_aH_bO_cN_d + 0.5(ny+2s+r-c)O_2 \rightarrow nC_wH_xO_yN_z + sCO_2 + rH_2O + (d-nz)NH_3$

Where $r = 0.5[b - nx - 3(d - nz)]$, $s = a - nw$ and $n = Ratio\ of\ moles\ of\ product\ to\ substrate$

There are three types of composting which are commonly practiced:

1. Aerated static pile composting – Compost is placed as piles and aerated with blowers or vacuum pumps.
2. Mechanically agitated in-vessel composting – Pile of waste is placed in a reactor where it is mixed and aerated.
3. Windrow composting – Compost is placed in long piles and mixed often.

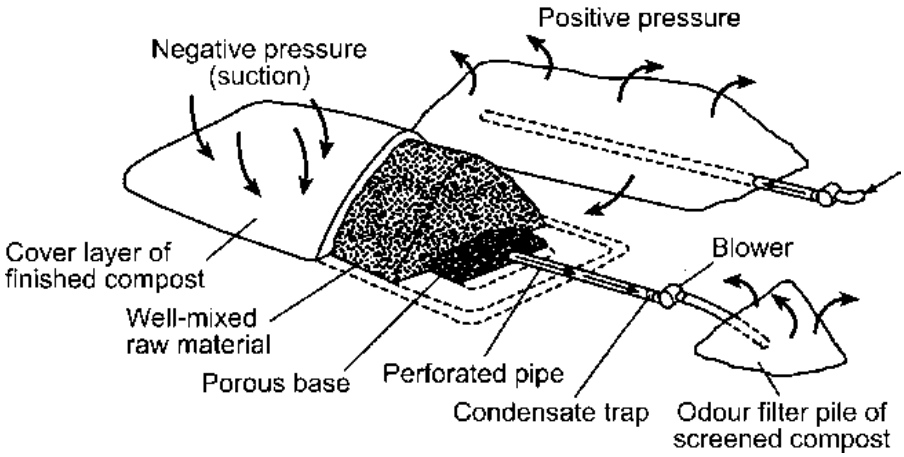

Fig. 3: Windrow composting

Source: On-farm composting methods www.fao.org

The limitations of composting are:

- Large amount of space required
- Excavation of contaminated soil and its subsequent transport may cause release of VOCs
- Large volumes of material are handled
- Heavy metals not treated by this method

Bioremediation

Bioremediation is the utilization of microorganisms to break down organic contaminants present in soil, groundwater, and sludge. To stimulate microbial activity, bioaugmentation or biostimulation is done. **Bioaugmentation** is the introduction of microorganisms to the contaminated site, if the existing concentration of microorganisms is too low to be effective. **Biostimulation** is the addition of nutrient media or electron donors/ acceptors so as to favour microbial growth. Bioremediation may be performed ex-situ or in-situ. In-situ processes treat the contaminants at the site where they are present, without removal to a different site. Ex-situ processes involve relocation of contaminated site to a designated treatment area.

Biological processes are usually implemented at a lower cost as compared to physicochemical treatment processes. Contaminants are destroyed completely in most cases. Sometimes, more toxic by-products are generated (TCE to vinyl chloride). These contaminants may become mobilized, especially in ground water. To remediate such a site, bioremediation will be performed above a low permeability soil layer, and groundwater monitoring wells will be placed downgradient of the remediation area. At times, it becomes necessary to extract groundwater and treat it ex-situ. Contamination occurs in different zones, as shown in the diagram below. The unsaturated zone is also referred to as the vadose zone. It is the portion of subsurface above the water table.

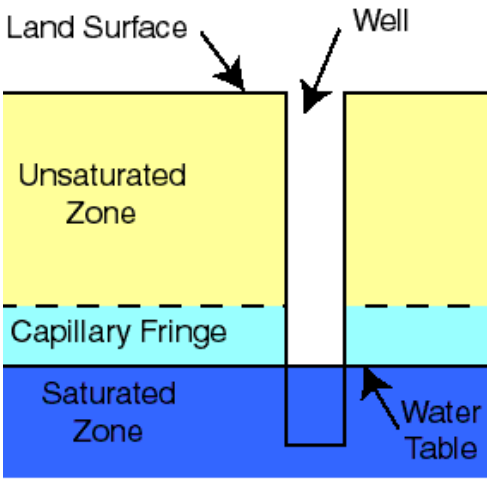

Fig. 4: Cross-section depicting different contamination zones in the subsurface
Source: http://toxics.usgs.gov/definitions/unsaturated_zone.html *USGS: Unsaturated Zone Definition Page*

Remediation with the help of microbes can be of two types: anabolic and catabolic. Catabolism is the generation of energy from the degradation of organic contaminants. Bonds which are easily broken contribute to more energy being released. Anabolism is the synthesis of new microbial cells. f_s and f_e are the fractions of substrate (electron donor) going to cell synthesis and energy generation respectively.

$$f_s + f_e = 1$$

f_s and f_e depend on the type of microbes present, as well as the nature of contaminant. If these fractions are known, it is possible to construct a complete balanced equation for the redox reaction which takes place. Thus, we need three components to write the overall reaction:

1. Electron donor half reaction (R_d)
2. Electron acceptor half reaction (R_a)
3. Cell synthesis half reaction (R_{cs})

Overall reaction: $R = f_e R_a + f_s R_{cs} - R_d$

Growth kinetics

A laboratory study of a microbial culture shows five unique phases:

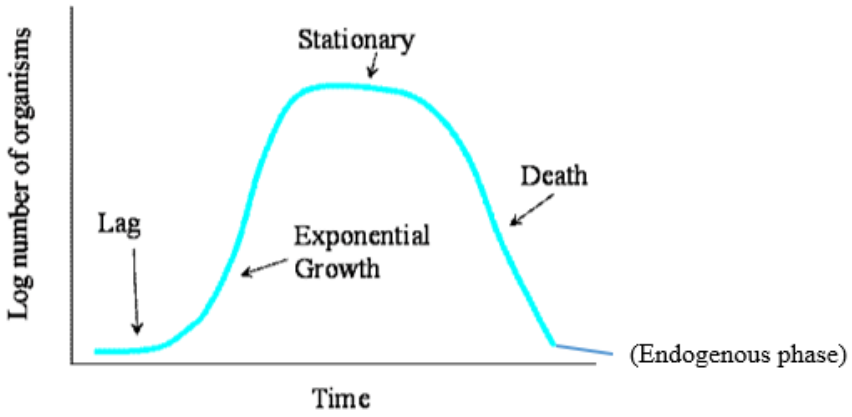

Fig. 5: Typical growth curve for a bacterial population
Source: Adapted from www.ecs.umass.edu

- **Lag phase**: Cells adapt to the new environment.
- **Exponential growth phase:** Cells divide at a constant rate that is greater than the rate at which cells are dying. The maximum growth rate is seen during this log phase.
- **Stationary phase:** As the substrate becomes the limiting nutrient, the death of cells balances the growth rate.
- **Death phase:** If nutrients are not added, the death of microbial cells is much higher than the rate at which new cells are formed.
- **Endogenous phase:** In some cases, rate of dying of cells slows down and imitates the stationary phase (as the number of dead cells become adequate enough to supply nutrients for the growth of new cells).

Inhibition:

Inhibitory growth occurs when the substrate becomes toxic to the microbial population, i.e., the concentration of one or more of the contaminants present is higher than the maximum concentration that can be tolerated by the microorganisms. Inhibition can also be caused by high concentration of inorganic compounds (metals), presence of antibiotics produced by other competing microbial populations, or presence of protozoa. Factors that affect growth rate are: population density, presence of toxins, availability of food, temperature, pH, light, disease.

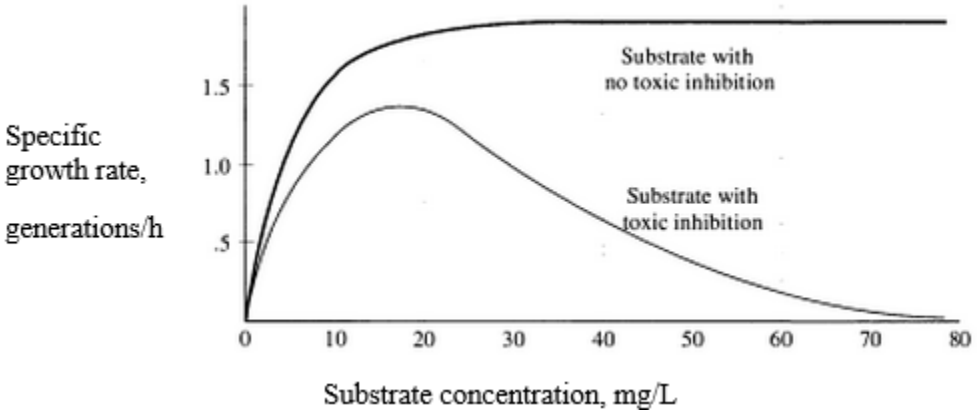

Fig. 6: Bacterial growth with and without inhibition
Source: Adapted from Hazardous Waste Management [LaGrega, Buckingham and Evans]

It is convenient to measure biomass, rather than individual numbers of bacteria. The growth of microorganisms is termed exponential.

$$\frac{dX}{dt} = \mu X$$

Where dX/dt is the growth of the biomass w.r.t time (mg/L min), μ is the growth rate constant (min^{-1}) and X is the biomass concentration (mg/L).

When integrated:

$X_t = X_o e^{\mu t}$, where X_o and X_t are biomass concentrations at the start of the reaction and at a time *t* respectively.

Due to the difficulty in measuring rate of equation, a model equation was developed. This is called Monod growth kinetics, which allows us to calculate the maximum growth rate.

$$\mu = \frac{\mu_m S}{K_s + S}$$

Where μ_m is the maximum growth rate constant (min^{-1}), S is the limiting nutrient concentration (mg/L), K_s is the half saturation constant or the nutrient concentration when $\mu=0.5\mu_m$ (mg/L).

The above equation does not take into account the natural death or decay of microorganism. The modified equation is as follows:

$$\frac{dX}{dt} = \frac{\mu_m S X}{K_s + S} - k_d X$$

Where k_d is the endogenous decay rate constant (min^{-1}).

If all of the food available to the microorganisms were converted to biomass, the rate of substrate utilization (dS/dt) would equal the rate of biomass production (dX/dt). Due to the inefficiency of the process, the rate of substrate utilization will be greater.

$$-\frac{dS}{dt} = \frac{1}{Y} . \frac{dX}{dt}$$

Where Y is the fraction of substrate converted to biomass. It is also known as the Yield Coefficient.

$$Y = \frac{\frac{mg}{L} of\ biomass}{\frac{mg}{L} substrate\ utilized}$$

Combining equations $\frac{dX}{dt} = \mu X$, $-\frac{dS}{dt} = \frac{1}{Y} . \frac{dX}{dt}$, $\mu = \frac{\mu_m S}{K_s + S}$

$$-\frac{dS}{dt} = \frac{1}{Y} . \frac{\mu_m S X}{K_s + S}$$

The objective of bioremediation is to ensure that the hazardous organic substance (carbon source) is the growth-limiting nutrient. Apart from target substrates, microorganisms require nitrogen, phosphorus, and micronutrients such as sulphur, potassium, calcium, magnesium, nickel, iron, copper, zinc, and various vitamins. The minimum amount of micronutrients present should be 1-100 μg/L.

Example: In a batch reactor, at t=0, you measure 0.45 mg/L of biomass. After six hours, the biomass concentration has increased to 0.70 mg/L. You also know that this substrate has a half-saturation constant of 7.5 mg/L. The starting substrate concentration was 6 mg/L and the reaction was observed for six hours again. Calculate growth rate assuming simple exponential growth and using Monod kinetics.

Solution:

Exponential growth kinetics: $X_t = X_o e^{\mu t}$

$0.7 = 0.45e^{\mu(6)}$

$$\mu = \frac{\ln\left(\frac{0.7}{0.45}\right)}{6} = 0.074\ hr^{-1}$$

Monod kinetics: $\mu = \frac{\mu_m S}{K_s + S}$

$$\mu_m = \mu.\frac{K_s + S}{S} = 0.074 * \frac{7.5 + 6}{6} = 0.167\ hr^{-1}$$

Example: Write a balanced reaction for the aerobic biological conversion of acetate to cells using NH_3 as the nutrient source.

Given:

$f_e = 0.41, f_s = 0.59$

Reaction for electron acceptor: $\frac{1}{4}O_2 + H^+ + e^- \rightarrow \frac{1}{2}H_2O$

Reaction for electron donor: $\frac{1}{8}CO_2 + \frac{1}{8}HCO_3^- + H^+ + e^- \rightarrow \frac{1}{8}CH_3COO^- + \frac{3}{8}H_2O$

Reaction for cell synthesis with ammonia as nitrogen source:

$\frac{1}{5}CO_2 + \frac{1}{20}HCO_3^- + \frac{1}{20}NH_4^+ + H^+ + e^- = \frac{1}{20}C_5H_7O_2N + \frac{9}{20}H_2O$

Solution:

$f_e R_a = 0.103O_2 + 0.41H^+ + 0.41e^- \rightarrow 0.205H_2O$

$f_s R_{cs} = 0.118CO_2 + 0.0295HCO_3^- + 0.0295NH_4^+ + 0.59H^+ + 0.59e^- \rightarrow 0.0295C_5H_7O_2N + 0.2655H_2O$

$-R_d = 0.125CH_3COO^- + 0.375H_2O \rightarrow 0.125CO_2 + 0.125HCO_3^- + H^+ + e^-$

$R = f_e R_a + f_s R_{cs} - R_d$
$= 0.125CH_3COO^- + 0.0295NH_4^+ + 0.103O_2 \rightarrow 0.0295C_5H_7O_2N + 0.0955H_2O + 0.095HCO_3^- + 0.007CO_2$

Example: What is the theoretical oxygen demand of this organic compound in an aerobic system?

$C_6H_6O + 7O_2 \rightarrow 6CO_2 + 3H_2O$

Solution:

1 mole of phenol (MW 94 g) requires 7 moles of O_2 (MW 32 g) → from the balanced equation.

Therefore, oxygen demand of phenol is $\frac{224}{94} = 2.38\frac{mg\ O_2}{mg\ phenol}$

In-situ bioremediation

In-situ bioremediation is the remediation of soils and/or groundwater utilizing naturally occurring microorganisms in order to biologically break down contaminants present. The media is not removed from its location. The development of microbial culture within the site can be brought about with oxygen (aerobic) or without oxygen (anaerobic or anoxic). The advantages of an in-situ treatment system are: ideal for small operational sites, minimal intrusion to above-ground structures. However, it is not suitable for sites with free phase contaminants.

In-situ bioremediation of soil involves supplying of oxygen and nutrients to the soil. Two such methods are bioventing and injection of hydrogen peroxide. Bioventing systems deliver air from the atmosphere to the soil above the water table through injection wells placed in the contaminated area. Injection of H_2O_2 on the other hand, delivers H_2O_2 which in turn stimulates microbial activity and helps speed up the biodegradation process. Injection of H_2O_2 is done only in instances when the groundwater is already contaminated. Generally, an in-situ groundwater bioremediation system will consist of an extraction well to remove groundwater, an above-ground treatment system, and an injection well in order to return the treated groundwater to the subsurface. If soil and groundwater are both contaminated, a single treatment system would be sufficient.

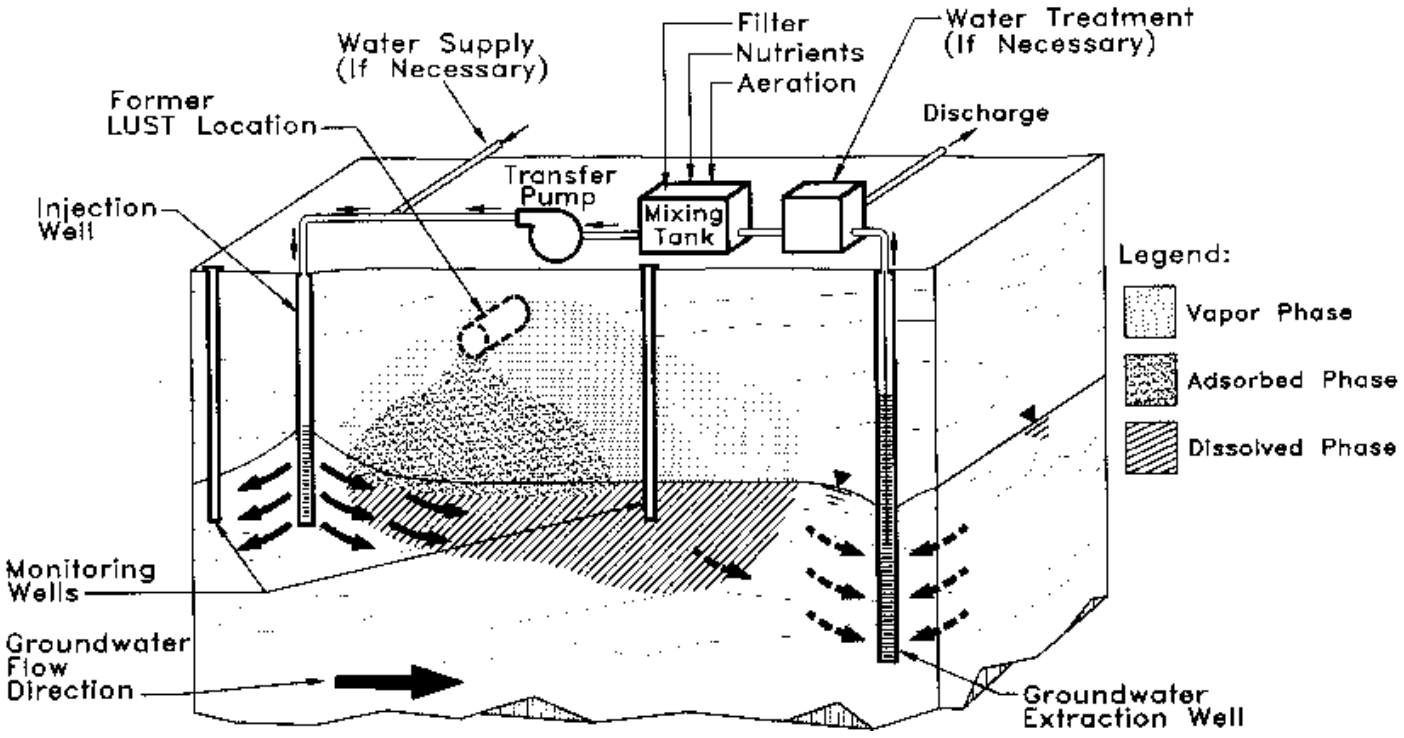

Fig. 7: Typical in-situ groundwater remediation system using injection wells

Source: http://www.nmenv.state.nm.us/ust/cleanup.html *New Mexico Environment Department: Cleanup Technologies.*

Aerobic bioremediation

Aerobic bioremediation is the oxidation of waste using O_2 as the electron acceptor.

For example: $HCHO + O_2 \rightarrow CO_2 + H_2O$

It is effective for hydrocarbons (such as mid-weight petroleum products like diesel and jet fuel). Lighter products like gasoline volatilize readily, and it is more effective to remove them using soil vapour extraction or air sparging. In a groundwater aquifer, different redox zones are present. Once an electron acceptor is used up by the contaminants, a redox reaction with a different electron acceptor occurs (in decreasing order of reduction potential). Oxygen is the most favoured electron acceptor, followed by nitrate, manganese, iron and so on. Most of the municipal waste components serve as electron donors.

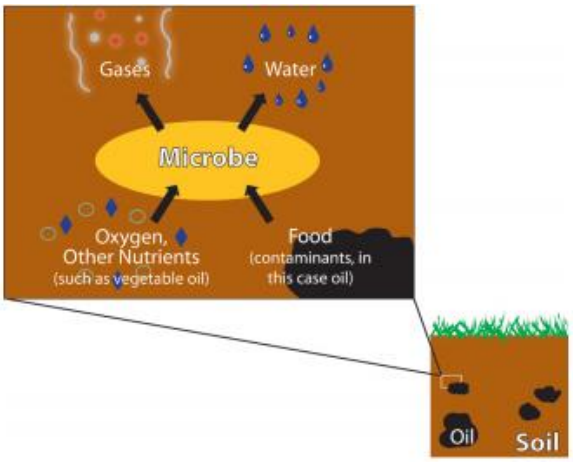

Fig. 8: Aerobic bioremediation of contaminants – microbes take in oil, oxygen, nutrients while releasing gases and water
Source: http://www.epa.gov/tio/download/citizens/a_citizens_guide_to_bioremediation.pdf *A Citizen's Guide to Bioremediation*[1].

Oxygen is usually a limiting factor in the progress of these reactions. At times, oxygen content in the media is enhanced by supplying oxygen externally. The process of supplying oxygen to the unsaturated zone is called bioventing. This method is used to treat contaminants such as benzene, toluene, acetone, phenol, chlorobenzene. It can take a long time (few years) for a contaminated site to be completely treated by bioventing. The process of supplying oxygen to the saturated zone is called biosparging. The success of biosparging depends on permeability of soil and the degree to which contaminants are biodegradable. This method is used to treat byproducts of petroleum refining which the soil layer has absorbed.

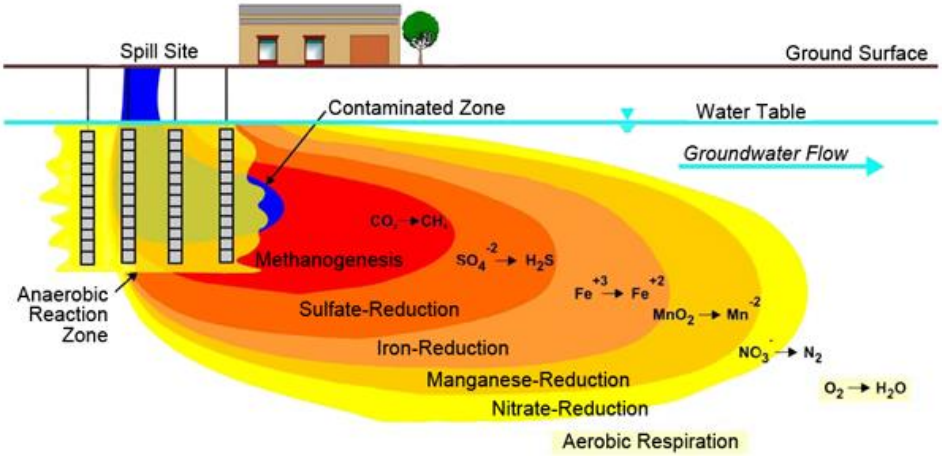

Fig. 9: Redox zones in a contaminant plume
Source: Adapted from www.clu-in.org *About Remediation Technologies: Bioremediation: Aerobic Bioremediation (Direct)*[3].

Anaerobic bioremediation

Under anaerobic conditions, microorganisms will degrade organic contaminants to methane, limited amounts of carbon dioxide, and trace amounts of hydrogen gas. Some anaerobic processes which occur are: fermentation, methanogenesis, sulphate and iron reducing reactions, denitrification, and reductive dechlorination. Due to the absence of oxygen, other electron acceptors are used: nitrate, iron, manganese, sulphate. Anaerobic reactions are used when there is a need to break down highly halogenated contaminants. Anaerobic bioremediation needs very little input compared to aerobic bioremediation.

For example: $HCHO \rightarrow CO_2$ (30%) + CH_4 (70%)

Reductive dehalogenation

This refers to the reduction of compounds such as PCE (perchloroethylene). It is a synthetic compound used in degreasers, spot removers and dry cleaning. In PCE, the oxidation state of carbon is +2. It is difficult to oxidize PCE. Hence, other compounds should be added, as an electron donor. A suitable electron donor must be found, which would supply electrons and act as a carbon source. Some electron donors used are acetate and ethanol. Care has to be taken if the contaminant is the electron acceptor: there must not be interferences posed by other compounds present in the system. It has been observed that chitin is the most successful electron donor for reductive dehalogenation. Since chitin is a complex compound, it does not get degraded easily. Hence, there is no competition from microbes feeding on chitin, as their population will grow slowly. Otherwise, clogging is seen. Thermodynamically, the reaction with chitin is not very favourable, even though it proceeds to degrade the halogenated compound. However, it is maintenance-free, which is why it is preferred. Chitin is a good source of carbon and nitrogen, and can be procured from shrimp shells.

Mechanism of dehalogenation of organic compounds:

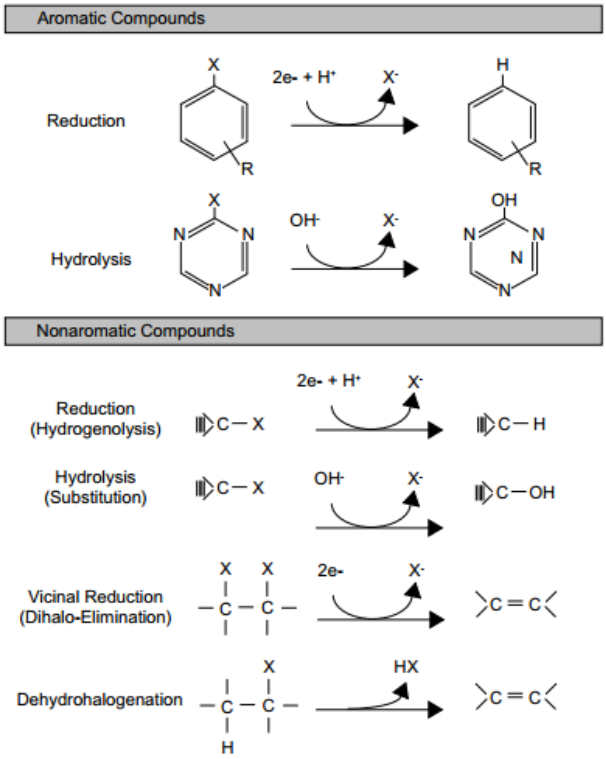

Fig. 10: Anaerobic dehalogenation mechanisms

Source: Reductive dehalogenation of organic contaminants in soil and groundwater (USEPA)[7].

Pathway for reductive dehalogenation:

$CCl_2=CCl_2$ → $CHCl=CCl_2$ → $CHCl=CHCl$ → CH_2CHCl → $CH_2=CH_2$

i.e., PCE (+2) → TCE (+1) → cis-1,2-DCE (0) → vinyl chloride (-1) → ethylene (-2)

The oxidation states of carbon are given within brackets.

In an in-situ remediation process, consider DCE to be the target contaminant. Acetate is supplied as electron donor. The electrons released by acetate will be accepted by DCE, thus reducing it to vinyl chloride and then ethylene. For this reaction to occur, the overall electron potential of the two half reactions must be negative. At times, in soil, oxygen may be present. In this case, oxygen becomes the favoured electron acceptor (owing to higher negative E^o value), and reduction of DCE does not occur. Therefore, it is important to ensure that anaerobic conditions are maintained.

Biomethanation plant at BARC – Nisarguna

The NISARGUNA biogas plant designed and operated by BARC is considered a successful application of aerobic and anaerobic processes for biodegradation of municipal solid waste. The waste processed by Nisarguna includes biodegradable waste such as paper, kitchen waste, food scraps, yard waste, green grass, animal litter and remains, cow dung, crop residue, sugarcane. Once waste is collected, the non-biodegradable matter is removed, and the biodegradable waste is made into a homogeneous slurry. It is then sent sequentially to an aerobic and anaerobic tank. The biogas generated in this process consists of methane, carbon dioxide and moisture. Around 70% of the water is recycled at the end of the process. Weed free manure is also obtained as a byproduct. It was observed that this manure has a C:N ratio of 12:1.

According to BARC, in order to set up a 1 ton/day biogas plant, the requirements are as follows:

Space	~100 m^2
Manpower	Two unskilled workers
Water supply	1.2 kL/ton/day
Cost	~INR 16,00,000 for 1 ton/day capacity plant
Power supply	3 phase AC

Cometabolic bioremediation

This is also known as incidental metabolism. Microorganisms while degrading one contaminant, produce an enzyme or cofactor that will in turn degrade another contaminant as well. Cometabolic bioremediation can be aerobic or anaerobic. In aerobic cometabolism, the contaminant is oxidized by an enzyme or cofactor produced during degradation of another contaminant with oxygen. In anaerobic cometabolism, the contaminant is reduced by an enzyme or cofactor produced during degradation of another contaminant. There is no energy or carbon benefit to the microorganisms in cometabolism. Chlorinated compounds like TCE, DCE, VC, trichloroethane, chloroform, dichloroethane are known to be oxidized cometabolically under aerobic conditions. The presence of a suitable substrate is necessary for cometabolic bioremediation. The electron donors in aerobic cometabolic oxidation include methane, ethane, propane, butane, toluene, phenol and ammonia. For e.g., methane is oxidized to methanol, and during this process methyl monooxygenase is produced. This enzyme is non-specific, and can degrade many more substrates, thus contributing to degradation of contaminants. At times, however, some intermediate products may inhibit microbial metabolic activity.

Ex-situ bioremediation

Ex-situ bioremediation is a biological treatment process in which contaminated soil is excavated and placed in a lined above-ground treatment area. Usually, this setup is aerated, to enhance biological degradation of contaminants. Nutrients and/or microbial cultures are added depending on the availability of each and rate of degradation.

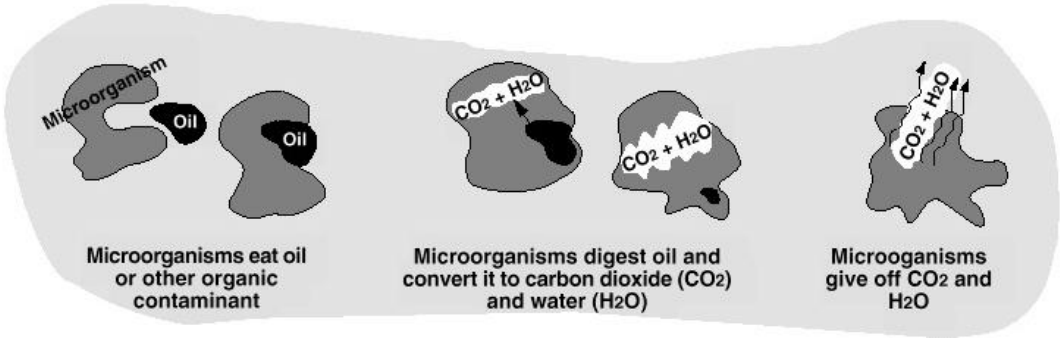

Fig. 11: Schematic representation of aerobic biodegradation of excavated soil
Source: http://staff.icar.cnr.it/spezzano/colombo/bioris/bioris.htm *Bioremediation. Accessed August 20, 2014.*

Bioreactors

Contaminants in extracted groundwater come into contact with microorganisms in attached or suspended growth biological reactors. In suspended systems (e.g., activated sludge treatment), contaminated groundwater is circulated in an aeration basin. In attached systems such as rotating biological contactors and trickling filters, microorganisms are populated on an inert support matrix. Bioreactors are a long term solution. The limitations of this technology are cost, and the proper disposal of hazardous sludge (in case of treating wastewater from crude oil refineries). The pollutants treated using bioreactors include VOCs, fuel hydrocarbons, any large organic compound which is biodegradable.

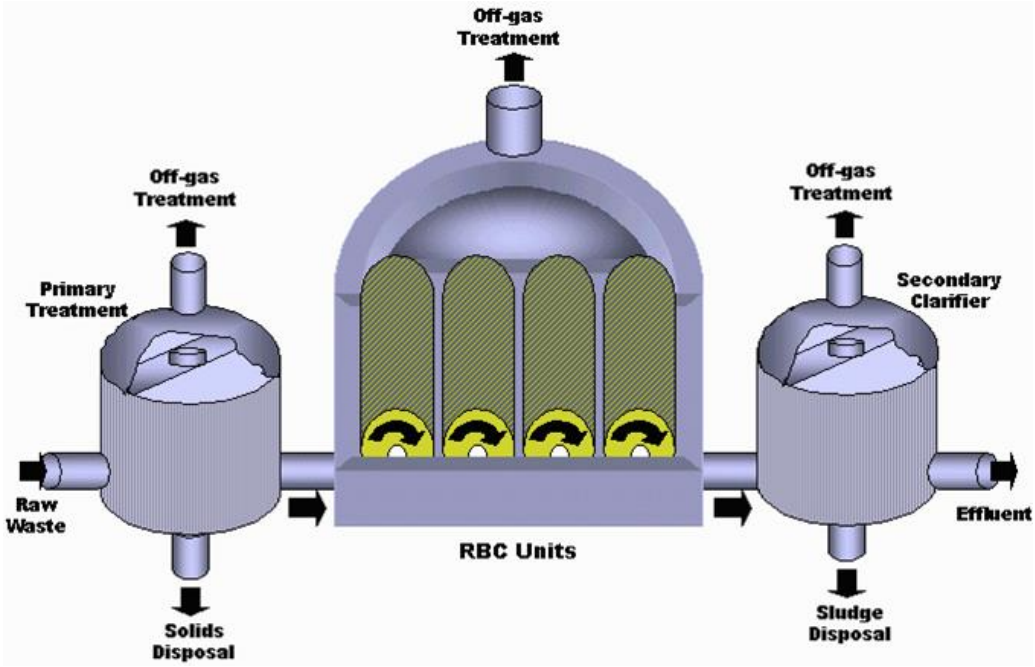

Fig. 12: Typical Rotating Biological Contactor (RBC)
Source: Bioremediation, Ex Situ www.responsiblebusiness.eu *Adapted from FRTR 2001.*

Slurry phase bioreactor

Slurry phase bioreactor is an ex-situ treatment technology for excavated soil. Stones and rubble are first separated from the soil. The soil is then mixed with water to a specific concentration (which depends upon concentration of contaminants, predicted rate of biodegradation, and physical properties of the soil). Typically, a slurry contains 10-30% solids by weight. The slurry is transferred to a reactor and mixed with oxygen and nutrients. pH is maintained by addition of acid or alkali if need be. Microorganisms are also added if a suitable population is not present naturally. When biodegradation is deemed complete, the slurry soil is dewatered (using clarifiers, pressure filters, vacuum filters, sand drying beds or centrifuges). Slurry phase bioreactors are usually used to treat VOCs, PCBs, halogenated compounds found in pesticides. Some of the limitations posed by this treatment method are: disposal of non-recycled wastewater is haphazard, dewatering of soil in the final stage may prove to be expensive.

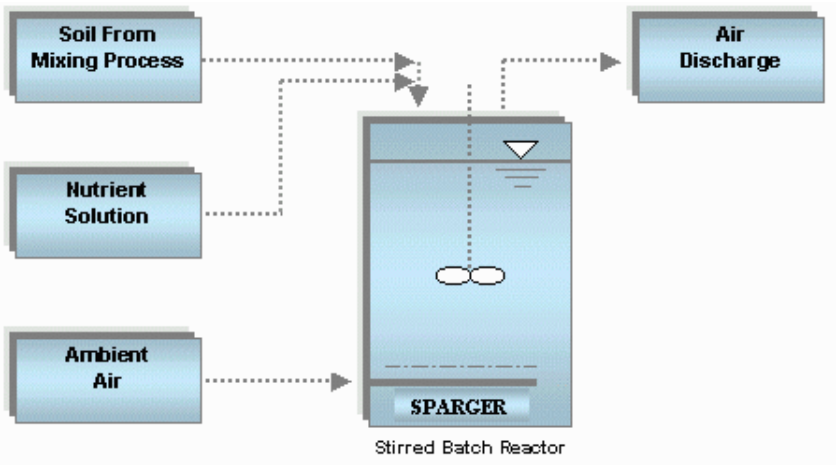

Fig. 13: Slurry phase bioreactor

Source: http://www.frtr.gov/matrix2/section4/4-14.html *FRTR[4].*

Design criteria:

Slurry phase bioreactors are operated as batch reactors. Hence, the time required for treatment of waste is an important design consideration.

$$\frac{C}{C_o} = e^{-kt}$$

$t = -\frac{\ln\left(\frac{C}{C_o}\right)}{k}$, where

C_o and C are the initial and design concentrations of the contaminant (in mg/kg), *k* is the first order decay constant (day^{-1}), and *t* is the time requirement (in days).

Example: A stockpile of 300 m^3 of soil contaminated with 3600 mg/kg xylene requires treatment to 100 mg/kg concentration. Pilot studies document first order kinetics with a reaction rate of 0.03 day^{-1}. What is the time required for degradation of xylene to desired level of concentration?

Solution:

Using the design equation given above:

$$t = -\frac{\ln\left(\frac{C}{C_o}\right)}{k} = -\frac{\ln\left(\frac{100}{3600}\right)}{0.03} = 119\ days$$

Constructed wetlands

Constructed wetlands are artificial wetlands that have been established with an aim to treat water that flows through it. They are modeled after natural wetlands, and within them we can find an ecosystem with vegetation, different kinds of soil, and assorted microbial populations to help improve water quality. Wetlands are constructed to mimic natural hydraulic flow patterns. If the site has highly impervious soils, a liner is installed first. Wetland vegetation is then planted and allowed to grow. The treated water from wetlands can be used to increase green cover, and also used by the public for sanitation purposes.

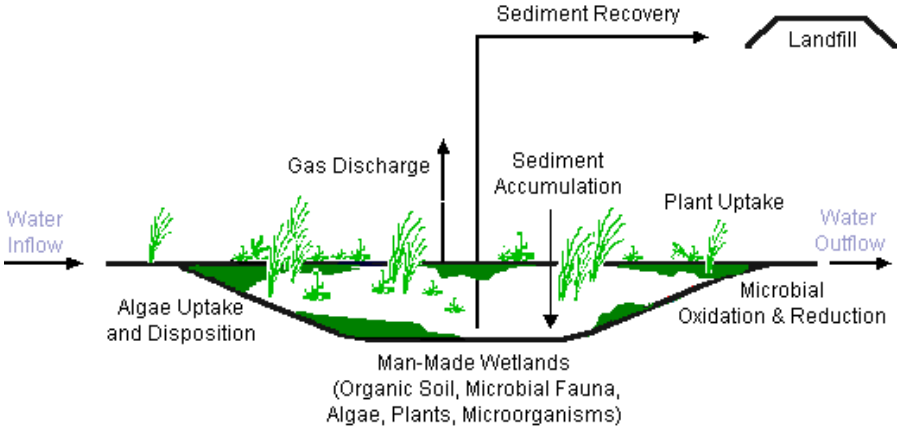

Fig. 14: A typical constructed wetland

Source: Bioremediation, Ex Situ www.responsiblebusiness.eu *Adapted from FRTR 2001.*

Force vented biopiles

This is another method to treat contaminated soil which has been excavated. The soil is placed in a pile 1.5-2 metres in height, and <6 metres wide in a lined area. It is aerated using a vacuum pump or air injection blower system. Microbial activity is this stimulated in the pile. The vapours released from the pile (VOCs) are collected and treated using granular activated carbon filters to control emissions into the atmosphere. It is imperative that any run-off or leachate is collected and treated, so as to prevent further contamination. As we already know, treatment time depends on concentration and nature of contaminant, soil properties, and even changes in weather.

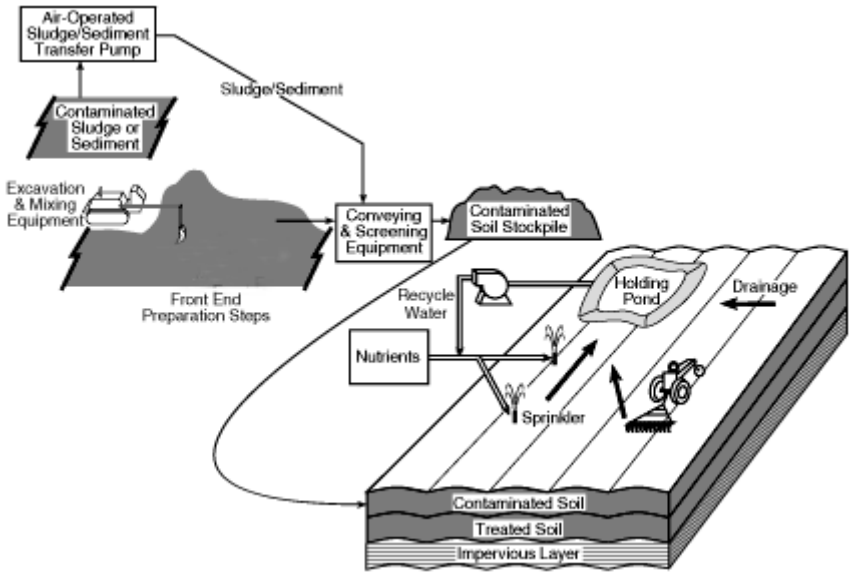

Fig. 15: Biopile for solid phase remediation

Source: http://www.frtr.gov/matrix2/section4/4_11.html *FRTR: Remediation Technologies Screening Matrix and Reference Guide Version 4.0*[4].

Appendix

Half reactions for biological systems

Source: *Thermodynamics and Stoichiometry.*
http://ocw.usu.edu/Biological_and_Irrigation_Engineering/Biochemical_Engineering/BIE_5810__thermodynamics.pdf
Accessed on August 19, 2014.

Reaction number	Half reaction	ΔG° (W),[b] kJ per electron equivalent
	Reactions for bacterial cell synthesis (R_{cs})	
	Ammonia as nitrogen source:	
1.	$\frac{1}{5}CO_2 + \frac{1}{20}HCO_3^- + \frac{1}{20}NH_4^+ + H^+ + e^- = \frac{1}{20}C_5H_7O_2N + \frac{9}{20}H_2O$	
	Nitrate as nitrogen source:	
2.	$\frac{1}{28}NO_3^- + \frac{5}{28}CO_2 + \frac{29}{28}H^+ + e^- = \frac{1}{28}C_5H_7O_2N + \frac{11}{28}H_2O$	
	Reactions for electron acceptors (R_a)	
	Nitrite:	
3.	$\frac{1}{3}NO_2^- + \frac{4}{3}H^+ + e^- = \frac{1}{6}N_2 + \frac{2}{3}H_2O$	−93.23
	Oxygen:	
4.	$\frac{1}{4}O_2 + H^+ + e^- = \frac{1}{2}H_2O$	−78.14
	Nitrate:	
5.	$\frac{1}{5}NO_3^- + \frac{6}{5}H^+ + e^- = \frac{1}{10}N_2 + \frac{3}{5}H_2O$	−71.67
	Sulfite:	
6.	$\frac{1}{6}SO_3^{2-} + \frac{5}{4}H^+ + e^- = \frac{1}{12}H_2S + \frac{1}{12}HS^- + \frac{1}{2}H_2O$	13.60
	Sulfate:	
7.	$\frac{1}{8}SO_4^{2-} + \frac{19}{16}H^+ + e^- = \frac{1}{16}H_2S + \frac{1}{16}HS^- + \frac{1}{2}H_2O$	21.27
	Carbon dioxide (methane fermentation):	
8.	$\frac{1}{8}CO_2 + H^+ + e^- = \frac{1}{8}CH_4 + \frac{1}{4}H_2O$	24.11
	Reactions for electron donors (R_d)	
	Organic donors (heterotrophic reactions)	
	Domestic wastewater:	
9.	$\frac{9}{50}CO_2 + \frac{1}{50}NH_4^+ + \frac{1}{50}HCO_3^- + H^+ + e^- = \frac{1}{50}C_{10}H_{19}O_3N + \frac{9}{25}H_2O$	31.80
	Protein (amino acids, proteins, nitrogenous organics):	
10.	$\frac{8}{33}CO_2 + \frac{2}{33}NH_4^+ + \frac{31}{33}H^+ + e^- = \frac{1}{66}C_{16}H_{24}O_5N_4 + \frac{27}{66}H_2O$	32.22
	Formate:	
11.	$\frac{1}{2}HCO_3^- + H^+ + e^- = \frac{1}{2}HCOO^- + \frac{1}{2}H_2O$	48.07

	Glucose:		
12.	$\frac{1}{4}CO_2 + H^+ + e^-$	$= \frac{1}{24}C_6H_{12}O_6 + \frac{1}{4}H_2O$	41.96
	Carbohydrate (cellulose, starch, sugars):		
13.	$\frac{1}{4}CO_2 + H^+ + e^-$	$= \frac{1}{4}CH_2O + \frac{1}{4}H_2O$	41.84
	Methanol:		
14.	$\frac{1}{6}CO_2 + H^+ + e^-$	$= \frac{1}{6}CH_3OH + \frac{1}{6}H_2O$	37.51
	Pyruvate:		
15.	$\frac{1}{5}CO_2 + \frac{1}{10}HCO_3^- + H^+ + e$	$= \frac{1}{10}CH_3COCOO^- + \frac{2}{5}H_2O$	35.78
	Ethanol:		
16.	$\frac{1}{6}CO_2 + H^+ + e^-$	$= \frac{1}{12}CH_3CH_2OH + \frac{1}{4}H_2O$	31.79
	Propionate:		
17.	$\frac{1}{7}CO_2 + \frac{1}{14}HCO_3^- + H^+ + e^-$	$= \frac{1}{14}CH_3CH_2COO^- + \frac{5}{14}H_2O$	27.91
	Acetate:		
18.	$\frac{1}{8}CO_2 + \frac{1}{8}HCO_3^- + H^+ + e^-$	$= \frac{1}{8}CH_3COO^- + \frac{3}{8}H_2O$	27.68
	Grease (fats and oils):		
19.	$\frac{4}{23}CO_2 + H^+ + e$	$= \frac{1}{46}C_8H_{16}O + \frac{15}{46}H_2O$	27.61
	Inorganic donors (autotrophic reactions):		
20.	$Fe^{3+} + e$	$= Fe^{2+}$	−74.40
21.	$\frac{1}{2}NO_3^- + H^+ + e^-$	$= \frac{1}{2}NO_2^- + \frac{1}{2}H_2O$	−40.15
22.	$\frac{1}{8}NO_3^- + \frac{5}{4}H^+ + e^-$	$= \frac{1}{8}NH_4^+ + \frac{3}{8}H_2O$	−34.50
23.	$\frac{1}{6}NO_2^- + \frac{4}{3}H^+ + e^-$	$= \frac{1}{6}NH_4^+ + \frac{1}{3}H_2O$	−32.62
24.	$\frac{1}{6}SO_4^{2-} + \frac{4}{3}H^+ + e$	$= \frac{1}{6}S + \frac{2}{3}H_2O$	19.48
25.	$\frac{1}{8}SO_4^{2-} + \frac{19}{16}H^+ + e$	$= \frac{1}{16}H_2S + \frac{1}{16}HS^- + \frac{1}{2}H_2O$	21.28
26.	$\frac{1}{4}SO_4^{2-} + \frac{5}{4}H^+ + e$	$= \frac{1}{8}S_2O_3^{2-} + \frac{5}{8}H_2O$	21.30
27.	$\frac{1}{6}N_2 + \frac{4}{3}H^+ + e^-$	$= \frac{1}{3}NH_4^+$	27.47
28.	$H^+ + e$	$= \frac{1}{2}H_2$	40.46
29.	$\frac{1}{2}SO_4^{2-} + H^+ + e^-$	$= SO_3^{2-} + H_2O$	44.33

[a]Adopted from McCarty (1975) and Sawyer et al. (1994).
[b]Reactants and products at unit activity except $[H^+] = 10^{-7}$.

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