A Review of Bioremediation & Gasoline Product Remediation

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Biological Remediation

Bioremediation is a method of remediation that encompanies the use of microorganisms. These microbes are relied on to clean up the contamination within the area of concern. Microbes used for bioremediation include various species of bacteria, yeast, and fungi that degrade the pollutants changing them into less toxic or harmless byproducts. This is done by stimulating the growth of the microbes that use the pollutant you are attempting to remediate as a food source. The biological remediation technique can be used for cleaning up sites polluted with metals, radionuclides, and organic compounds. It has been most successful when used to remediate petroleum products such as oil, various pesticides, and a wide range of solvents.

There are many different factors to consider when trying to decide which type of biological remediation to use. When trying to create an ideal environment for a specific microorganism conditions such as high temperatures, the appropriate ratio of phosphorus, potassium, and nitrogen, high moisture levels, and a sufficient supply of oxygen all need to be taken into account. If these conditions aren't met there is a chance that your microorganism will either work very slowly, or die and your pollutant will not be remediated.

If all of these conditions are met then the microbes grow and multiply at a much faster rate which in turn means that they are capable of consuming much more of the pollutants at a much higher rate than it would have been under any other condition. This method works in situ for soil, and in situ for groundwater if various additives called amendments are pumped into the groundwater through wells. These amendments can be things that you can find in your own kitchen like molasses or vegetable oil, or pumping air directly into the groundwater or oxygen producing chemical compounds. If these conditions can't be met in situ, usually because of the temperature of the soil/groundwater not being warm enough, then they are taken ex situ and treated above ground at the ideal conditions mentioned earlier mostly in tanks to prevent vaporized pollutants from being released into the air. These tanks can also be called bioreactors. The only difference between a bioreactor and a regular tank is that the amendments and microbes are added directly into the tank, as opposed to a regular tank where only the amendments are added.

There are four main techniques that are used in bioremediation. They are biostimulation, bioaugmentation, bioventing, and biosparging. Biostimulation is the process of providing everything that the present microbes need to ensure that they can digest the pollutants to their fullest capacity. Bioaugmentation is the act of adding more microbes into the soil to reinforce the already present bacteria. Both bioventing and biosparging involve injecting air and required nutrients into the contaminated zone. Bioventing is when you inject into the unsaturated zone of the soil, and biosparging is when you inject into the both the saturated and unsaturated zones in the soil.

Terminal Electron Acceptors and Electron Donors

The driving force behind bioremediation is energy. Just like in any chemical process, energy input and output is an absolute necessity. When considering bioremediation, it is important to understand the two components that are needed for microbes to perform any kind of remediation. These components are the terminal electron acceptors, and the electron donors which are the inputs for the microbial respiration process. What you get out of microbial respiration is waste products and energy.

Terminal electron acceptors are the chemicals that receive an electron in a reduction/oxidation reaction making it the reduced product in the reaction. There are six terminal electron acceptors with varying efficiency levels. From most efficient to the least efficient they are oxygen, nitrate, manganese (IV), iron (III), sulfate, and carbon dioxide. Once these chemical entities accept an electron from an electron donor, the electron donor's chemical nature changes into a much less volatile compound that is either a less harmful substance, or a harmless substance.

In bioremediation the goal is to encourage biological activity by providing ideal conditions through the introduction of electron donors as a food source for the microorganisms so that they will take in the pollutant as their terminal electron acceptor. If the ideal conditions are met biological activity will increase to a level that requires the microorganisms to consume all of the pollutants to continue their microbial respiration cycle. The byproducts are the energy used in the microbial respiration cycle and the waste products produced, which in this case are the less harmful chemicals that are the products of reduction and oxidation.

Conditions for Bioremediation

Bioremediation can be done under many different conditions. As long as the microbes that are present in the soil have access to an electron acceptor to keep the process of microbial remediation continuous, then bioremediation can be achieved in a wide range of site conditions. There are various microbes that operate under aerobic conditions, meaning the microbes live off of oxygen as their terminal electron acceptor. Oxygen is the most desirable terminal electron acceptor because it gives off the most Gibbs Free Energy, or the entropy change of a specified system under a specific temperature and pressure. This is the amount of energy that can be generated as work. When you generate Gibbs Free Energy from oxygen the process is called aerobic respiration. The rest of the terminal electron acceptors are all anaerobic and they all go through the reduction process where they gain an electron. As you descend in the amount of Gibbs Free Energy you will reach the least productive terminal electron acceptor, carbon dioxide, that goes through a process called methanogenesis, in which the carbon dioxide is changed into methane.

Bioremediation is generally done on volatile organic compounds or semi volatile organic compounds, but has also found some success in cleaning radionuclides and in rare cases metals. The most common and practical substance that is remediated in this way is petroleum and oil byproducts such as BTEX (benzene, toluene, ethylbenzene, xylene), TEL(tetraethyllead), MTBE(methyl tert-butyl ether), TCE(Trichloroethylene), and many more harmful pollutants. Bioremediation can be used in both the soil and the groundwater and pressure and temperature must be taken into account if the work is done in situ to maximize biological activities.

Bioremediation can be used alongside other remediation techniques, or as a stand alone process. Air sparging, airstripping and thermal resistance heating are all remediation methods that can benefit from the addition of bioremediation. Air sparging is injecting air into the soil, and because oxygen is the terminal electron acceptor that gives off the most energy, the microbes in the soil will increase their production levels and change the pollutants present into less harmful compounds. Airstripping, when used with bioremediation as the end goal, is injecting air to get the pollutants to the vadose zone where the microorganisms present will remediate the pollutants. Thermal resistance heating, when done in situ, can be used to warm the soil/groundwater to the ideal temperature for the native microorganisms to reach peak bioactivity and let them remediate the pollutants.

As standalone processes, biostimulation and bioaugmentation both involve interacting with the native microbe population directly. Biostimulation interacting with the abiotic factors and bioaugmentation interacting with the biotic factors. Biostimulation is used when the area of contamination is less than ideal for the native microorganisms to degrade the pollutant. Altering moisture content, nutrient levels, available oxygen, and temperature are all the factors that must be considered when using biostimulation while also keeping pressure, depth of pollutant, and soil content in mind. The advantage of using biostimulation is that the area doesn’t have to be contained when it is being used, and the only potential downside is nutrient runoff if there is an excess of additives. Bioaugmentation must be done in a contained environment because of the fact that you do not want your added microbes, that could possibly be genetically modified, leaving the test zone and possibly multiplying elsewhere causing an entirely new problem by itself. Microbes are introduced to reinforce the existing microbes in the area. Once the pollutant has been remediated some of the microorganisms are designed to terminate themselves, and others will die off because of their specific food source no longer being available.

Phytoremediation

Phytoremediation is a type of remediation that uses plants to deal with pollutants. These plants are utilized to either: extract, contain, volatilize, or destroy pollutants. These differing methods of utilization are what make plants useful tools in remediation. In reference to all the different methods of Phytoremediation as a whole, they provide the best results when overall contamination levels are low, and the plants are not limited by any other environmental factors. High pollution levels affect Phytoremediation through possibly stunting plant growth, as well as requiring an prolonged amount of time for proper remediation. Limiting Environmental factors also have the possibility to stunt plant growth, and in more extremely limited areas, plants may not be able to survive at all.

Extraction

Extraction is a method of Phytoremediation that removes pollutants from contaminated soil. A common application of this method is through Phytoremediation. This application uses hyperaccumulating plants to extract pollutants that are present within the soil they are rooted in. These extracted pollutants are then stored within the above ground tissue of the plants. Hyperaccumulator plants are not just a name given to plants being used for Phytoextraction, as it has a specific definition. The definition of a hyperaccumulator is a plant that can accumulate, at the bare minimum: 100 mg/g (0.01% dry wt.), Cd, As and some other trace metals, 1000 mg/g 1 (0.1 dry wt.) Co, Cu, Cr, Ni and Pb and 10,000 mg/g (1 % dry wt.) Mn and Ni (Reeves and Baker, 2000; Wantanabe, 1997). However, even though some plants do not meet the criteria set by the definition of a hyperaccumulator, the process of genetically modifying plants to become capable of extracting certain pollutants is a widely popular practice within this style of Phytoremediation.

The process of Phytoextraction begins by selecting a hyperaccumulator that will be able to grow at the site, based on the site characteristics. The hyperaccumulator chosen must not only be able to extract and accumulate the pollutant(s) present at the site, but also its roots must extend deep enough to reach the pollutant(s). If the hyperaccumulator does not meet either of these or else the process is a waste of time and no extraction will occur. There have been many studies done on which pollutants can be extracted by specific plants, so once all the information on the site and pollutant(s) is gathered, a decision can be made. Once a hyperaccumulator is chosen, it is either seeded at the contaminated site, or seeded at a greenhouse and transported into the soil at the contaminated site. Depending on site characteristics, maintenance measures such as, irrigation, fertilization, use of pesticides, weeding, etc… may need to be taken once the hyperaccumulator has taken to the soil. With the hyperaccumulator planted and taken to the soil, Phytoextraction should begin. However, in some cases, metal availability within the soil may not be sufficient for plant extraction, so sometimes acidifying agents are added to the soil. The acidification of metals usually results in them becoming more mobile and extractable for hyperaccumulators.

Phytoextraction is a long process that takes years to achieve full remediation. In order to know if the process is working, the site must be monitored to track the status of the contamination within the plants. Other important factors to monitor are soil pH, soil and plant nutrients, water flow, which are all important for pollutant extraction and overall plant health. If all goes right, and after years of waiting and monitoring, all the contamination that was once contained in the soil, will now be present within the plants. Certain hyperaccumulators, such as grasses, require continuous harvesting and collection of grown tissue, while poplar trees do not require constant harvesting, just removal at the end of remediation period. Proper disposal of these plants and harvested tissue could be incineration and then disposal at a hazardous waste dump. Another method of disposal is having the plants "mined", or extrated of any contaminants that may be of use or of value.

Another application of extraction is Rhizofiltration. This application follows the same process as Phytoextraction, but differs in the way pollutants are stored. The Rhizofiltration process has pollutants in solutions ahere to roots of hyperaccumulator, rather than traveling to above ground plant tissue. Another difference is that plants must be grown in a greenhouse to begin, rather than choosing between seeding on site or greenhouse seeding with Phytoextraction. Since rhizofiltration is used mainly to uptake metals, the pH of the solution must constantly be altered and monitored.

Containment

Containment is a method of Phytoremediation that immobilizes and stabilizes pollutants present in soil. A common application of this method is through Phytostabilization, or phyto-restoration. This method is unique, in that it is not aimed to remove pollutants from soil, it is aimed to stabilize pollutants and reduce human health risks and environmental impacts. Phytostabilization provides a few different processes of achieving the containment of pollutants. While these processes of Phytostabilization differ greatly, they each fall under one of two distinct definitions of Phytostabilization. Definition one: Immobilization of a contaminant in soil through absorption and accumulation by roots, adsorption onto roots, or precipitation within the root zone of plants. Definition 2: The use of plants and plant roots to prevent contaminant migration via wind and water erosion, leaching, and soil dispersion as discussed above.

One way this application achieves containment is through preventing contamination exposure as a result of wind and water erosion. This is accomplished through the root holding the soil together lessening soil erosion from water, and the plants above ground tissue acts as a wind barrier to prevent wind erosion. Phytostabilization also achieves containment by controlling the movement of water within the soil. This suppresses the vertical migration of contaminants into groundwater by allowing less overall movement of water within the soil. Lastly, Phytostabilization also achieves containment by both physically and chemically immobilizing pollutants through the use of root systems and chemically fixing soils by adding certain agents to amend the soil (lime, fertilizers, aluminum sulfate, etc…). Root sorption is the process in which roots of plants are used to immobilize contaminants. This process takes the pollutants out of the soil and either stores them in the plants within the roots themselves (absorption), or the contaminants adhere to the roots surface chemically (adsorption). The role that chemically fixing soils plays in immobilization is that certain pollutants can be immobilized through altering the pH of the soil they are present in. This is what is accomplished when soils are chemically fixed. For instance, aluminum sulfate can be applied to lower soil pH, while lime can be applied to raise soil pH. (Berti and Cunningham, 2000). .

The most important part of successfully applying the method of Phytostabilization is selecting plants that will be used. Plants that should be used for Phytostabilization are ones that do not translocate pollutants to above ground tissue. Plants that do this require harvesting of the tissue. If plants translocate pollutants to above ground tissue during the Phytostabilization process, then this creates an increase of risk and exposure to humans and the environment through the potential of the above ground tissue being consumed by an organism. Other important factors to consider when choosing plants to use are: large canopy presence, deep root system, site characteristics, and the presence of other contaminants on site.

Volatilization

Volatilization, or Phytovolatilization, is a method of Phytoremediation in which plants uptake pollutants present in soil, metabolize them into volatile forms, then transpire the pollutants, or modified forms of the pollutants, into the atmosphere. While the transpired pollutants tend to be harmless VOCs, some pollutants are quite harmful when volitized. It is for this reason that Phytovolatilization is a controversial, and highly discussed topic. However, the rationale behind this method is that pollutants being transpired into the atmosphere can be degraded much easier than pollutants within soils.

The method of Phytovolatilization begins with the plant's uptake of pollutants from the soil. These pollutants then travel to harversable, above ground tissue of the plant, where they can be metabolized. It is within the metabolization stage where pollutants can be transformed into modified forms. Once the pollutants are metabolized, they are released into the air through the plant's transpiration process. The pollutants that are transpired into the atmosphere now have the potential to be degraded through more effective or rapid natural processes.

What makes Phytovolatilization a unique method is the act of transpiring pollutants into the atmosphere. This is also what makes the pollutants it can treat unique too because in order for this method to work, the pollutant must be capable of being volitized. The pollutants that are subject to Phytovolatilization are mainly organic. While non-organic pollutants: Mercury, Selenium, and Arsenic have also shown potential to be Phytovolatilized, the pollutants that are subject to Phytovolatilization are mainly organic. Specifically, TCE (Trichloroethylene) is a dangerous pollutant that the Phytovolatilization method often is used to remediate. Through research, plants such as the Black Locust species, AlfAlfa, and Poplars have been found to potentially Phytovolatilize TCE.

Destruction

Destruction of pollutants via Phytoremediation is a method that is conducted through Rhizodegradation, or phytodegradation. The processes of Rhizodegradation consists of the breakdown of organic pollutants in soil through enhanced microbial activities in the root zone. Root exudates, which are compounds produced by plants that are then released by the roots, must be present within the soil in order to use microbial degradation. These root exudates are sources of nutrients for these microbes, and promote the increase of microbial populations and activity within the rhizosphere. These microbes then begin to use the pollutants as either an electron donor, or a terminal electron acceptor, which leads to the breakdown of the pollutants. Other ways plant roots promote microbial growth is through the aeration of the soil, as well as by moderating moisture content of the soil.

Destruction of pollutants can also be applied through Phytodegradation. The process of Phytodegradation's main difference from the process of Rhizodegradation is how the plant's roots are utilized. Phytodegradation degradeds pollutants with its tissue through metabolizing the pollutants, rather than promoting microbial growth through secreting root exudates. As discussed earlier, roots can promote microbial growth through aeration and moderating moisture content. The process of Phytodegradation relies on these root properties for microbial growth, since no root exudates are produced. It is because of the alternate methods of promoting microbial growth that the Phytodegradation process does not require root exudates.

Bioremediation of Gasoline Related Pollutants

Certain pollutants required specific bioremediations methods in order to remediate them from the medium that they are present in. One of the main applications of bioremediation is to remediate organic compounds, thus bioremediations methods can be used to target and remediate mediums that contain organic gasoline related pollutants. The method of bioremediating such pollutants consists of aerobic and anaerobic conditions, while the organic gasoline related pollutants are widely used as carbon sources for these methods of bioremediation. Differing methods of bioremediation could be used in order to remediate different gasoline related pollutants.

Natural Attenuation

The natural attenuation is a process that consists of physical, chemical, or biological processes that occur under favorable conditions that have the capability of reducing the mass, toxicity, mobility, volume, or concentration of contaminants in soil or groundwater. What makes this process natural is that the medium produces the physical, chemical, or biological processes without humans altering the medium. The only human interaction required for this method is monitoring the medium, in order to see whether or not the natural attenuation process is occuring. The contaminants subject to natural attenuation are specific, but this method has been studied to effectively remediate gasoline related pollutants. Specifically, natural attenuation has been shown to be extremely effective for benzene, toluene, ethylbenzene and xylene (BTEX) contaminated soils and groundwater, due to the pollutants high biodegradability rate (Mace 1997; Rice et al. 1995).

Remediation can occur from this process in two main ways: through microbial degradation of pollutants, and through reactions with naturally occurring chemicals, but the majority of remediation is down through microbial degradation. Through natural attenuation via microbial degradation, gasoline related pollutants are generally used by the microbes as a carbon source. Also, natural attenuation can occur under both aerobic and anaerobic conditions, depending on the conditions favorable to the microbe(s) that will be degrading the gasoline related pollutant. This method is not the fastest acting, nor is it a guarantee to remediate the pollutants present, but it is often the one that is chosen at gasoline related polluted sites due to costliness. This is due to the lack of human intervention with the medium, with nothing needed to be added to the soil, the process becomes far cheaper than other bioremediation methods.

Bioaugmentation

The process of bioaugmentation is the act of introducing microbes into a polluted medium in order to enhance the degradation of pollutants. Microbes can either be studied and be used for specific pollutants based on the results of the study, or genetically engineered to remediate the pollutant present within a medium. This method is often used when the process of natural attenuation is either found to not be a viable option for remediation, or fails to remediate the pollutant. This becomes a useful tool for the remediation of gasoline related pollutants because, while BTEX has shown great potential to be bioremediated through natural attenuation, methyl tert-butyl ether (MTBE) tends to be much less biodegradable than BTEX, so natural attenuation has little to no effect on MTBE.

One study conducted on the bioremediation of MTBE through bioaugmentation found that there is a strong relationship between the biodegradation of MTBE, propane, and a microorganism that grows on propane. This microbe, Rhodococcus ruber ENV425, is a propanotroph that has the ability to rapidly degrade MTBE. However, Rhodococcus ruber ENV425 only successfully degrades MTBE in the presence of a cometabolic substrate, propane (Steffan et al. 1997). This example uses MTBE as a carbon source, while propane is used as the electron donor within this anaerobic process. This study shows that bioaugmentation can be successfully applied to remediate MTBE from a medium. Also, since this method of bioaugmentation was a success, it can be replicated at other sites that contain a MTBE polluted medium through bioengineering microbes to contain the same MTBE degrading characteristics that are within Rhodococcus ruber ENV425.

Biostimulation

Biostimulation is the process of modifying the environment to stimulate existing microbes capable of bioremediation. This can be done through adding nutrients, which promotes the use of pollutants as a TEA, or supplying the medium with a TEA, which promotes the use of the pollutant as an electron donor. Oxygen would be applied as a TEA in aerobic conditions, while another TEA would be supplied in anaerobic conditions. Since gasoline related pollutants are carbon containing compounds, they are used as carbon sources for the method of biostimulation. This means that supplying the medium with either an aerobic or anaerobic TEA would be optimal in order to stimulate the existing microbes. Applying either one of these TEAs promotes the pollutants to be used as a carbon source, which is ideal for gasoline related pollutants.

Factors Affecting Bioremediation of Gasoline Related Pollutants Success Rates

Although gasoline related pollutants are the contaminants that bioremediation has had the highest success rate of remediating, the volatile and semi volatile organic compound groups bioactivity can be hindered in many different ways. Of the four bioremediation methods that are currently being used to remediate petroleum products, they each have their limitations that hinder the success of oil byproduct remediation. Natural attenuation can go wrong for a number of reasons, but the biggest problem with letting the problem fix itself with intensive monitoring is that natural attenuation as a technique has the potential to be ineffective. If petroleum products are left unchecked they could possibly mobilize and create larger problems spanning over a much larger area.

If bioaugmentation is the method being used there is a chance that the hydrocarbon degrading microbes will adapt very poorly to the contaminated site, and either have little production value, or die off and not complete the job they were designed to do. Bioaugmentation's success rate can also be inhibited if there are other pollutants present on the site. The microbes that are introduced to the system to degrade petroleum products will not interact with any other pollutants, and in turn will avoid areas that contain other pollutants even if there is petroleum present in the area. In certain cases the native microorganisms will inhibit the productivity of the introduced microbes and the pollutant can remain unremediated as a result.

Biostimulation has a very high success rate when all of the abiotic factors are specifically tailored to a site but the chances of every single factor being 100% perfect is very rare. Since no site is exactly the same, no two places can be treated exactly the same no matter how similar they are. The hindrance to the success rate of biostimulation is the fact that there are no exact calculations for new sites. Even in places where their conditions are ideal, the soil structure and the types of soil will all have different properties that require different levels of abiotic factors to maximize biological activity.

Phytoremediation can have varying success rates depending on how supportive the microbes are in the plant's roots. If the plume is too far down the roots of the plants will not be able to absorb all of the petroleum byproducts and could require further cleanup. When considering gasoline byproducts, all of them are toxic to the plants and can kill the plants if too much is taken up and if the present microbes don't have enough inputs to balance out the microbial respiration process.

An aspect of petroleum product remediation that is different from other pollutants is the amount of soil organic carbon directly affects the production rate and the adsorption rate which in turn affects the overall degradation rate of the system. Another large part of remediating petroleum pollutants is how soon the cleanup process begins after the pollutant has been introduced to the system. The sooner the petroleum byproduct is remediated, the easier it is to remove from the soil or the groundwater because of the increased bioavailability when the petroleum is first introduced. Once the bioavailability levels drop it becomes increasingly hard to remove from the soils.

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