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Bioremediation of Crude Oil Spills and its Effect on Aquifer Geochemistry

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Summary

Crude oil is basically formed by anaerobic conversion of biomass under high pressure and temperature. It consists of many hydrocarbons consisting both light and heavy components. It can be divided basically into four fractions:

- *Saturates (or alkanes).*
- *Aromatics, including benzene, toluene, ethylbenzene and xylene (BTEX) and polyaromatic hydrocarbons.*
- *Resins, consisting of compound containing nitrogen, sulphur and oxygen that are dissolved in oil.*
- *Asphaltenes, which are large and complex molecules that are colloids dispersed in oil.*

The proportions of these fractions vary from site to site. Of these, lighter aromatics (Eg. BTEX) and the short chain alkanes are readily biodegradable.

Currently, petroleum hydrocarbons are the most abundantly used chemicals in the world. Manufactured from crude oil, petroleum hydrocarbons are found in gasoline, kerosene, fuel oil, asphalt, and even some chemicals used in home or at work. Almost every person on this planet has once or more used a petroleum product or byproduct. Due to their wide demand, they are transported all over the world by ship, rail, trucks and pipelines. Unfortunately, because of the large volumes of petroleum hydrocarbons produced and their subsequent releases during transport, use and transport, petroleum hydrocarbons have become one of the most prevalent contaminants in the surface and subsurface environment. There are a number of incidents in which significant quantities of oil were accidently released into the environment causing environmental disasters of epic proportions. Exxon Valdez (1989) and Gulf War (1990) oil spills are possibly the most publicized and studied environmental tragedies in history.

When petroleum hydrocarbons are released or spill into the environment, they migrate down through the soils, becoming adsorbed to the soil particles until they reach groundwater, where they dissolve in groundwater, float on the water surface or sink to the bottom of the aquifer. Any petroleum hydrocarbons that dissolve in the water will then travel with the flowing groundwater to some extent. Lighter products like gasoline, are more volatile, tend to float on the surface of the aquifer, whereas the heavier ones will tend to sink to the bottom.

A variety of techniques have been successfully used to cleanup soil and groundwater contaminated with petroleum hydrocarbons, including pump and treat of groundwater, excavation of shallow contaminated soils, and vapour extraction. Many of these methods, are however very costly or not fully efficient and are unable to completely remove the contaminants. Biological treatment however has emerged as one of the most promising methods of removal of petroleum hydrocarbon contaminants. It was first used to counter the Exxon Valdez oil spills (1989) and showed remarkable results and has since been developed as a major tool to remove the contaminants ever since.

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Introduction

Bioremediation is a treatment process whereby contaminants are metabolized into less toxic or non-toxic compounds by naturally occurring microorganisms. The microorganisms use the petroleum hydrocarbons as a source of carbon and energy. Usually, the products are carbon dioxide and water. Though formation of other products is also there. Once the microorganisms consume the contaminants, the microbial population becomes dormant or dies out. Bioremediation can take place under aerobic or anaerobic conditions in the presence of other suitable electron acceptors such as nitrate, sulphate or carbonate. Bioremediation has shown to be effective in treating a broad range of chemicals including petroleum hydrocarbons like BTEX and gasoline.

Method

Bioremediation of petroleum hydrocarbon contaminated sites can be done in two ways:

1) In situ: In this method of bioremediation, the contaminants are treated at the site of contamination. The microbial activity is increased at the site.

2) Ex situ: This type of bioremediation involves excavation of the contaminated and being treated somewhere else.

Both the above mentioned methods have their pros and cons and have to be applied according to the conditions of the contamination sites.

There are several techniques that can be applied to enhance the biological degradation of petroleum hydrocarbon contaminants and speed up the restoration of soil and groundwater:

1) Supplementation with suitable sources of nitrogen and phosphorus to enhance biodegradation of site contaminants by indigenous microbial population.

2) Enhancing the oxygen concentration by injecting air or oxygen to optimize aerobic bioremediation of contaminants.

3) Application of surfactants to increase bio-availability of hydrocarbon contaminants.

4) Bio-augmentation.

5) Infusion of external microbes. This has to be done only after checking the compatibility of the microbes with the local conditions.

The last two techniques are less used as compared to others.

Oxygen is typically the limiting factor in the bioremediation process. If the oxygen availability is optimized, then bioremediation can be at its optimum rate.

In this study, we are using a combination of microbes and studying its effects. The reason for the use of a combination of microbes is that a particular set of microbes will reduce the contaminants to certain products. These products will then be further reduced by another set of microbes and so on. In this way, the whole system will not be redundant at any time. An optimum concentration of each microbe is derived from the study.

As expected, bioremediation is a slow process. The various factors affecting it will also be studied. As the bioremediation proceeds, the aquifer that is contaminated with the hydrocarbons witnesses a change in its geochemistry. There are a number of reasons for it:

1) As mentioned above, there are some byproducts also. These significantly changethe geochemistry of the aquifer.

2) The various techniques that are employed to increase the microbial activity are also a reason for the same. Eg: The methods by which oxygen concentration is increased has significant effects.

3) As bioremediation is a slow process, the intermediate products that are formed in the process also significantly affect the aquifer geochemistry.

It has been seen that even small changes like the above mentioned produce noticeable effects in the aquifer geochemistry. Aquifer geochemistry is important because it determines the environmental stability of the area. This study will try to determine the causes, effects and the preventive measures (if any) against the alteration in the aquifer geochemistry and also see if any change is required in the bioremediation approach.

Bioremediation and its principle

Enormous quantities of organic and inorganic compounds are released into the environment each year as a result of human activities. In some cases, these releases are deliberate and well regulated (e.g., industrial emissions) while in other cases they are accidental (e.g., chemical or oil spills). Many of these compounds are both toxic and persistent in terrestrial and aquatic environments. The contamination of soil, surface and groundwater is simply the result of the accumulation of these toxic compounds in excess of permissible levels.

Whether due to regulatory or legislative requirements, due to public pressure, due to insidious side effects on humans or due to enlightened corporate behavior, there is growing realization and movement to clean up such environmental messes. However, the cost of restoring the burgeoning global inventory of contaminated ecosystems to healthy and acceptable levels is virtually incalculable. As a result, the government, industry and the public have acutely felt the need for more cost-effective alternatives to traditional physical and chemical methods of remediation of these contaminated sites.

Factors Affecting Bioremediation

The parameters of bioremediation processes

The factors that must be optimized for successful bioremediation are: oxygen and inorganic nutrients, pH, temperature, water availability, and adsorption effects.

- **Adequate supply of oxygen and inorganic nutrients**
  Most fungi and bacteria that degrade petroleum hydrocarbons require free or dissolved oxygen. In the presence of adequate oxygen, oil degradation also requires mineral elements such as C, Ca, Mg, K, S, Fe, N, P and various trace elements.

- **pH**
  The optimum pH for biodegradation of hydrocarbons is around pH 6 – 8 .Biodegradation of crude petroleum in an acid soil (pH 4.5) could be doubled by liming to pH 7.4.

- **Temperature**
  Temperature as a limiting factor does not seem to be a problem in tropical and temperate zones. Disappearance of hydrocarbon contaminant from agricultural land can be correlated with monthly temperature averages; generally, hydrocarbon biodegradation increases with temperature and peaks around 30– 40^{0}C .

- **Water availability**
  Soil that is hydrated with 50% to 80% of the maximum water-holding capacity has the greatest microbial activity below that level, osmotic and matrix forces limit the availability of water to microbes; above that level, the reduction of air space and oxygen decrease microbial activity.

- **Adsorption Effects**
  Hydrocarbons that are adsorbed onto organic matter are less susceptible to microbial attack. Indeed, the rate- limiting process in biodegradation may be the desorption of contaminants.

Examples

Two case studies were conducted. Both of them were performed upon two sets of the same apparatus. The apparatus consisted of a set of microbes, a laboratory scale of the soil strata with a firm aquifer and a sample of crude oil. The BOD (Biological oxygen demand) and COD (Chemical Oxygen Demand) were measured using standard apparatus. The reason for this action will be seen in the subsequent sections. Some of the microbes are:

- Pseudomonas (majority concentration)
- Penicillium
- Bacillus
- Cyanobacterium
- Vibrio
- Flavobacterium
- Arthrobacter
- Trichoderma

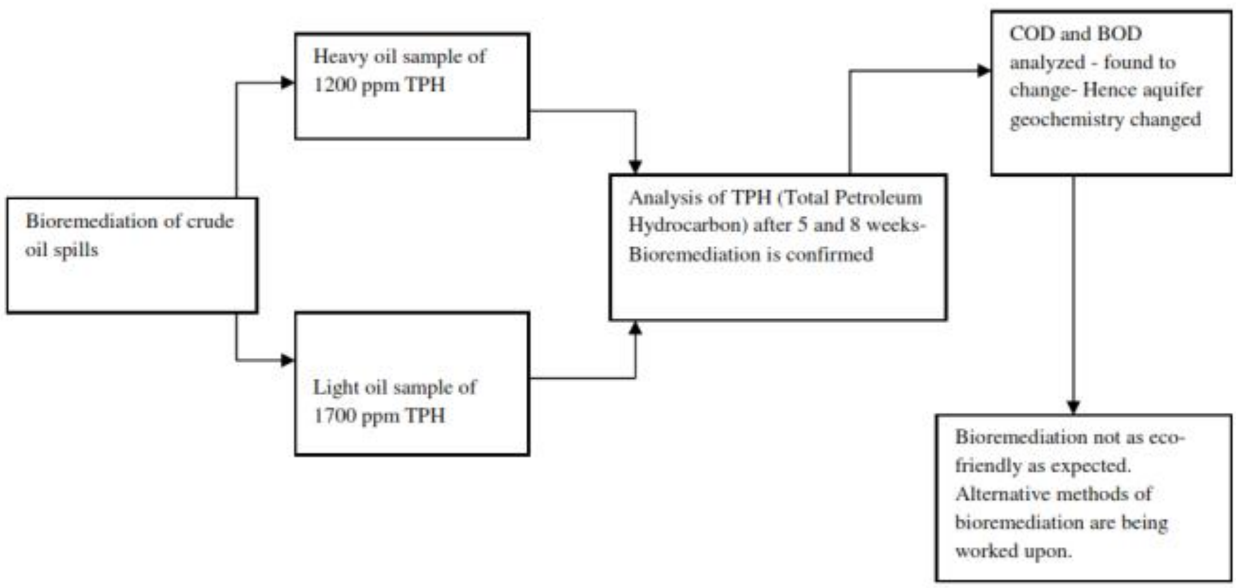
Some other microbes were also used but they have been withheld until the completion of the experiment.

Both of these case studies differed only in one aspect:-the quality of crude oil used. In the first case, heavy crude oil was used and in the second one, light crude oil was used.

Heavy crude consists more of long chained C22 plus alkanes, which are harder to biodegrade at extremely high concentrations whereas light crude oil consists more of smaller and volatile compounds and they are easy to degrade them too. For this reason, the concentration of light crude was taken more than that of heavy crude oil. The concentration of the heavy crude oil taken was 1700 ppm of TPH (total petroleum hydrocarbons) and that of light crude oil sample was 1200 ppm of TPH. A gas chromatography apparatus was also used for the determination of TPH by standard set programs. The crude samples were spilled on par with the soil samples. After a stipulated time of 24 hours, the set of microbe emulsion was also spilled on the contaminated sample. The TPH was analyzed two times- once after 5 weeks and the other after a total of 8 weeks.

The TPH was analyzed in a cumulative manner. The TPH was analysed with the help of Infrared Spectroscopy using standard EPA programs. It was seen to be decreasing as expected.

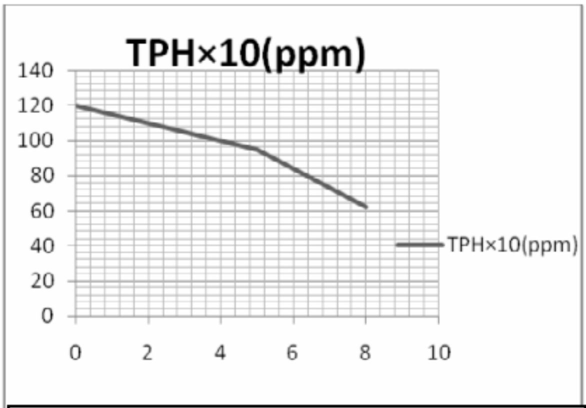
The following flowchart shows how the experiment was conducted in due course of time



EXPERIMENTAL FLOW DIAGRAM

#1. Bioremediation of heavy oil in soil

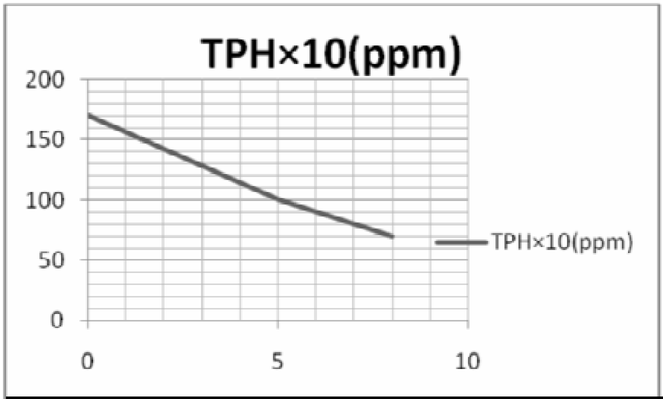
Time (in weeks)	Concentration of TPH (ppm)
0	1200
5	950
8	620



The graph of TPH vs time (in weeks)

#2. Bioremediation of light oil in soil

Time (in weeks)	Concentration of TPH (ppm)
0	1700
5	1000
8	700



The graph of TPH vs time (in weeks)

The TPH also decreases in this case but the rate of decrease is more than that of heavy oil which is according to expected results as light crude oil consists of lighter and volatile components and hence is easier to degrade.

Effect on the Geochemistry

To measure the effect on the geochemistry, the COD (Chemical Oxygen Demand) and the BOD (Biological Oxygen Demand) were measured. This was done because if the oxygen demands change, many corresponding properties would also change and as a result the geochemistry will change.

Biological Oxygen Demand (BOD): It is the amount of dissolved oxygen needed by aerobic biological organisms in a body of water to break down organic material present in a given water sample at certain temperature over a specific time period. It is not a precise quantitative test, although it is widely used as an indication of the organic quality of water. The BOD value is most commonly expressed in parts per million (ppm).

The following two tables show the BOD values for heavy and light crude oil samples that we have used in our experiment.

Heavy Oil

Time (in weeks)	BOD (ppm)
5	200
8	350

Light Oil

Time (in weeks)	BOD (ppm)
5	150
8	250

Chemical Oxygen Demand (COD): It is commonly used to indirectly measure the amount of organic compounds in water. Most applications of COD determine the amount of organic pollutants found in water, making COD a useful measure of water quality. It is also usually expressed in parts per million (ppm) which indicates the mass of oxygen consumed.

Heavy Oil

Time (in weeks)	COD (ppm)
5	400
8	850

Light Oil

Time (in weeks)	COD (ppm)
5	300
8	600

Inferences

Inferences from the case study were:-

1) There was presence of certain emulsion like substances in the aquifer. It was probably due to the fact that the microbe population increased considerably and formed emulsion like substances in the presence of a aquifer.
2) There was also the presence of compounds like fatty acids and other broken compounds which were able to flow in the aquifer. Their formation probably stems from the fact that the compounds in the crude oil sample were broken down into end products like fatty acids.

Conclusions

Conclusions from the case study were:-

1) The oxygen content in the water was more. This was probably due to the fact that for growth, microbes needed oxygen and hence the concentration of dissolved oxygen increased.
2) The increase in COD and BOD shows that the geochemistry has changed as this does not occur in natural biodegradation.
3) A set of different micro organisms gives more optimum results compared to a single set.

In natural biodegradation, the change in COD and BOD is very minimal because of the fact that the degradation of the crude oil is always at equilibrium with respect to the surroundings. But in bioremediation, the COD and BOD increase because of the increase in concentration of micro-organisms, oxygen. The change in COD and BOD shows that the geochemistry has changed and this contributes to the fragility of the ecological stability of the local area as it depends on the aquifer stability. Therefore, bioremediation may not be as eco- friendly as expected.

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