Bioremediation of Water Areas Due to Oil Spills

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ABSTRACT

There are various methods that can be used to cleanup an oil spill on a waterway. There are physical, chemical, and biological alternatives. The biological method is also known as bioremediation, which can be broken down into bioaugmentation and biostimulation. Bioaugmentation is the addition of microbe cultures to a contaminated area to increase the number of microbes that can degrade the oil and hydrocarbons. Biostimulation is the addition of nutrients to the contaminated area. These nutrients allow the resident microbial population to have enough nutrients to thrive and grow in numbers and size. This larger population then is able to degrade the toxins in the oil. Bioremediation is a new technology that is emerging. There are numerous tests going on to determine the effectiveness of bioremediation as well as the cost efficiency of this method. The Exxon Valdez hit a reef in 1989 and spilled millions of gallons of oil. This incident showed the lack of information that the US has regarding oil spills and how to clean them up (OTA, 1991). This led to increased research and the beginning of bioremediation. The Exxon Valdez oil spill was one of the first times that bioremediation was looked at as an alternative to cleaning up an oil spill. Extensive research was done to determine the feasibility of bioremediation as an alternative. Since this time, more research has been conducted and more will continue, to find the proper places to use bioremediation as an alternative to cleanup oil spills.

KEYWORDS

Bioremediation, bioaugmentation, biostimulation, oil spill, Exxon Valdez, Ashland oil spill

INTRODUCTION

Oil spills occur frequently throughout the world. There are both inland and oceanic spills. The different spills have different regulations and different people in charge of the clean up. Oil spills require quick action so that they cause as little damage as possible. According to the Environmental Protection Agency (EPA), "oil releases threaten public health and safety by contaminating drinking water, causing fire and explosion hazards, diminishing air and water quality, compromising agriculture, destroying recreational areas, wasting nonrenewable resources, and costing the economy millions of dollars" (2006).

REGULATIONS

"Between 1977 and 1990, the Coast Guard tracked approximately 105,000 oil spills in coastal and navigable waters, including the Great Lakes and inland regions. Ninety-five percent of these spills were less than 1,000 gallons and 74 percent were less than 50

gallons" (Michel, 1994). This is a large amount of oil to be spilled within one nation. Oil spills are cleaned up as fast as possible to reduce the damage done to the surrounding ecosystem. The cleanup of an oil spill within the U.S. has an On-Scene Coordinator (OSC) from either the EPA or Coast Guard. The EPA regulates the way spills are cleaned up, but most of the coastal oil spills are led by Coast Guard officials. The EPA leads more of the inland oil spills.

The regulations regarding the cleanup of oil spills come from the EPA's National Oil and Hazardous Substances Pollution Contingency Plan, specifically Subpart J. This is the part of the plan that determines which dispersants, surface washing agents, bioremediation agents, surface collecting agents, and other controls can be used to clean an oil spill (Nichols). There are many other acts and regulations regarding oil spills, but the EPA is the overall agency in charge.

Oil spills can cause an immense amount of damage if not contained and cleaned properly. In 1967, a ship wreck caused 95,000 tons (593,750 barrels) of oil to be spilled into the ocean. An attempt to clean the area was done using 10,000 tons (66,000 barrels) of chemicals. However, the chemicals used were highly toxic to marine life and were severely misused (Nichols). The following year, President Johnson and staff decided to have the EPA create a contingency plan and a list of chemicals and biological agents that can be used on oil spills (Nichols). This is the contingency plan that all oil spills are compared to when deciding on a course of action.

INLAND VS. OCEAN SPILLS

Oil spills can occur on inland freshwater or out on the open ocean. Inland spills, due to their close proximity to human populations, are more likely to have a negative affect on



Figure 1: Wildlife can become heavily oiled (EPA Ch 8)

drinking water, recreational water areas, and shoreline industry and facilities (EPA Ch 8). The main source for oil spills are from water vessels, but oil rigs for coastal areas and gas stations for inland areas are also large contributors to the amount of oil spilled every year (EPA Ch 8). Inland spills often receive less attention than ocean spills. This is bad practice because of the enormous affect inland spills have on the surrounding populations. This practice is done because inland spills are usually of smaller quantities. Unfortunately, there are approximately 2,000 inland oil spills every year (Zhu et al 2001, pg 8).

The EPA provides the OSC for inland spills and the United States Coast Guard provides the OSC for spills in the coastal regions. The EPA may act as a technical advisor during coastal spills, but it is not necessary.

The OSC must work closely with other agencies to find the best method to use, as well as receive as much information about the area as possible. The National Oceanic & Atmospheric Administration works with the Coast Guard to give current information about the ocean and atmospheric conditions. The Coast Guard then uses this data to determine the proper technology to use. The Department of the Interior is also contacted to determine if there are endangered habitats or species in the area (EPA Ch 8). If there are endangered areas nearby, proper action needs to be taken to try to contain the spill and not allow it to flow to that area.

METHODS

There are many different ways that oil spills can be cleaned. The methods chosen to clean up an oil spill are determined based upon the type of oil spilled, the location and its proximity to sensitive environments, and other environmental factors (EPA Ch 8). There are mechanical, chemical, and biological methods. Mechanical methods include booms (see Figure 2), skimmers, and truck vacuums. Chemical methods include dispersants, surface washing agents, and surface collecting agents. Biological methods are the use of microbiological cultures, enzyme additives, and nutrient additives to Figure 2: Oil Boom (Yahoo Pictures 1)



increase the rate of biodegradation of the contaminants. The natural method is another course of action. This simply allows the area to recover naturally and is cheaper than any other method.

BIOREMEDIATION

The use of microorganisms, fungi or bacteria, to decompose pollutants into simpler compounds is called bioremediation. The process of microbes breaking different substances down into water, carbon dioxide, and other compounds is called degradation. The prime goal of bioremediation is to create an optimal environment for the microbes to degrade pollutants. There are two types of bioremediation. The first type, bioaugmentation, is seeding the water which means adding the microbes to the area. The second is biostimulation, which is adding fertilizer and nutrients to water to increase the current microbes' degrading capabilities.

The use of bioremediation is often as a secondary treatment tool and is used once other methods have been used to cleanup part of the spill (Venosa). Bioremediation is a cost effective alternative but is a very slow process, sometimes taking weeks to months for results. An advantage of bioremediation is that the microbes are able to completely destroy the toxic hydrocarbon compounds and do not just transfer them to another area.

The effectiveness of bioremediation is difficult to determine. Recreating field conditions in a laboratory is almost impossible to do. That is why field studies, such as at the Exxon Valdez oil spill, are performed whenever possible. Well designed field studies can determine if oil is disappearing faster with bioremediation than without and if biodegradation is the main reason for the disappearance (Venosa).

Bioaugmentation

Bioaugmentation is the addition of microbes to supplement the current population to degrade oil and other hydrocarbons. This is usually not necessary, since these microbes are present in nearly every location. Microbes may need to be added if there are certain contaminants that the resident microbe population is unable to degrade (Venosa).

In order to utilize microbes, it is first essential to find which types of microbes are capable of degrading oil and determine their nutrient and environmental requirements.

There are 70 genera of microbes that are known to degrade hydrocarbons. Table 1 shows some of the more common bacteria and fungi that are capable of degrading hydrocarbons. Usually, only one percent of the natural microbe populations are oil degraders. In polluted environments, this amount can rise to more than ten percent of the microbe population (Gordon 1994). The degradation of oil will only occur if the other requirements are met, such as available nutrients and the proper environment temperature.

The highest concentration of microbes that can survive in most environments is affected by protozoans (who eat

| Table 1: Microbes Used in Bioremediation |
|--|
| (Gordon, 1994) |

| Bacteria | Fungi | | |
|----------------|-------------------|--|--|
| Achromobbacter | Allesheria | | |
| Acinetobacter | Aspergillus | | |
| Actinomyces | Aureobasidium | | |
| Aeromonas | Botrytis | | |
| Alcaligenes | Candida | | |
| Arthrobacter | Cephaiosporium | | |
| Bacillus | Cladosporium | | |
| Beneckea | Cunninghamella | | |
| Brevebacterium | Debaromyces | | |
| Coryneforms | Fusarium | | |
| Erwinia | Gonytrichum | | |
| Flavobacterium | Hansenula | | |
| Klebsiella | Helminthosporium | | |
| Lactobacillus | Mucor | | |
| Leucothrix | Oidiodendrum | | |
| Moraxella | Paecylomyces | | |
| Nocardia | Phialophora | | |
| Peptococcus | Penicillium | | |
| Psedomonas | Rhodosporidium | | |
| Sarcina | Rhodotorula | | |
| Spherotilus | Saccharomyces | | |
| Spirillum | Saccharomycopisis | | |
| Streptomyces | Scopulariopsis | | |
| Vibrio | Sporobolomyces | | |
| Xanthomyces | Torulopsis | | |
| | Trichoderma | | |
| | Trichosporon | | |

microbes), the surface area of the oil spill, and the effect of waves on the area. Added microbes also have a hard time competing with indigenous populations; therefore,

bioaugmentation is rarely the chosen method. Bioaugmentation has never shown long-term beneficial results (Venosa).

Bioaugmentation, when used, usually shows positive results for the destruction of different hydrocarbons. However, it is difficult to determine if the destruction is due to the additional microorganisms or some other entity. Some researchers have worked on developing a microbe that can destroy multiple types of hydrocarbons and other oil compounds. These genetically engineered organisms would be able to degrade all the necessary toxic compounds. Actual use of these organisms is questionable because of the public's negative response to letting a genetically engineered organism free into the environment without knowing the possible consequences (Zhu et al, 2001).

Biostimulation

Biostimulation is the addition of limiting nutrients to the indigenous population. The major nutrients necessary for most microbes include carbon, nitrogen, phosphorus, oxygen, and water. Other variables that need to be considered include pressure, temperature, salinity, pH, and concentration (Gordon, 1994). Of these, the most important elements are oxygen and temperature. Without oxygen, the microbes cannot perform the necessary degradation. Microbes can degrade oil at a variety of temperatures, however, a very low temperature or a very high temperature will reduce the effectiveness and speed of degradation (Gordon, 1994).





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Carbon is the basic structure of most matter, including oil, and is never the limiting nutrient. Nitrogen and phosphorus are the two other main chemical elements necessary for biodegradation to occur. These two elements are the most common limiting reagents in biostimulation. Oxygen is also a necessary element. Not only are all of these elements necessary, but they must be able to come in contact with the microbes. If there is a large amount of phosphorous, but it is in an unavailable form or below the microbial level in the water, then the phosphorous cannot be utilized and is ineffective.

Some areas have a problem with oxygen contact. Water areas can have an aerator added to get more oxygen into the water and help with the biodegradation. Another area where lack of oxygen is a concern is beaches and below surface rocks (Zhu et al, 2001). Bioremediation is difficult to use in these areas because oil and other hydrocarbons have been able to infiltrate into the ground. Microbes are unable to degrade below a few mm due to the anaerobic conditions.

When a fertilizer is added to a contaminated area, the rate of release of the nutrients must also be considered. For intertidal environments, the fertilizer needs to be slow release so as to overcome the washout effect. Oleophilic and other slow release formulas are used to prevail against the washout (Zhu et al, 2001). "Washout" refers to tide that carries water out to sea and takes some nutrients with it. Care needs to be taken to make sure the formulas are not too slow, otherwise they do not give the organisms enough of the necessary nutrients to allow for optimal growth.

Theoretically, the reduction of 1 g of hydrocarbon requires 150 mg Nitrogen and 30 mg Phosphorous. A common formula is then a stoichiometric ratio of C:N:P of 100:5:1 (Zhu et al, 2001). However, it has been found that different N:P ratios will yield different concentrations of various microbes. Because oils have different properties and every spill has different environmental factors, the correct ratios need to be determined for each oil spill.

The types of nutrients added can be in various forms. There are water soluble forms, granular forms, and oleophilic forms. Each form has different advantages and disadvantages. Water soluble nutrients are more readily available than granular and oleophilic forms. Water soluble forms can be easily washed away and may have to be applied more often. Granular nutrients are slow release and so do not wash away, but the release rate is often difficult to predict. Oleophilic nutrients are able to adhere to the oil and, thus, be very close to the microbes that need their nutrients. Table 2 summarizes the advantages and disadvantages of the different nutrient forms.

| Type of nutrients | Advantages | Disadvantages | Applications in the field or field trials |
|-------------------|--|---|---|
| Water soluble | Readily available Easy to manipulate for target nutrient concentrations No complicated effect of organic matter | Rapidly washed out by wave and tide Labor-intensive, and physical intrusive applications Potential toxic effect | Alaska (Pritchard <i>et al.</i> , 1992) Delaware (Venosa <i>et al.</i> , 1996) |
| Slow release | Provide continuous sources of nutrients and may be more cost effective than other types of nutrients | Maintaining optimal nutrient release rates could be a challenge | Alaska (Pritchard <i>et al.</i> , 1992) Nova Scotia (Lee <i>et al.</i> , 1993) |
| Oleophilic | Able to adhere to oil and provide nutrients at the oil-water interface | Expensive Effectiveness is variable Containing organic carbon, which may compete with oil degradation and result in undesirable anoxic conditions | Alaska (Pritchard <i>et al.</i> , 1992) Nova Scotia (Lee <i>et al.</i> , 1987, 1989,1995a &b) |

Table 2: Nutrient Forms and Respective Advantages and Disadvantages (Zhu et al, 2001)

Advantages/Disadvantages

There are many advantages and disadvantages to using bioremediation as an oil spill cleanup method. First of all, bioremediation is much cheaper than other methods. During the Exxon Valdez spill, the cost of cleaning 120 km of shoreline, when compared to physical washing, was less than a day's cost (Zhu et al, 2001). Bioremediation is also a more natural way to clean the environment compared to chemical additions. This helps with public relations. Most people do not want to add chemicals to our natural waterways and oceans. Bioremediation degrades toxins naturally, but it also is less disruptive to the contaminated site and surrounding ecosystems. Physical methods are not as good as biological because physical methods remove the oil from the site and are then transported to another place to clean the impure solution. Bioremediation does not necessitate moving any liquid from one place to another and reduces the potential to create a larger mess during transportation.

Biological methods also have disadvantages. For example, bioaugmentation is much less effective than biostimulation due to the microorganisms having to adjust to a new climate and compete against native populations. The success of bioremediation depends on having the appropriate nutrients available and the correct environmental conditions for those microbes to thrive. Bioremediation is also a slow process. Bioremediation requires that an analysis be performed to determine the best type of microbes and or nutrients to be added to the site. This process takes time perform and also can take weeks to months to show signs of improvement in the area. This may cause a different method to be chosen if immediate removal is necessary.

CASE STUDIES

The Exxon Valdez and the Ashland oil spill have been two of the biggest ocean and inland spills, respectfully, recorded. They happened a year apart from each other and helped contribute greatly to the research of bioremediation and other response tactics for oil spills.

The Exxon Valdez was an oil tanker that had just filled up at Valdez, Alaska. It had received 1.26 million barrels of oil (54 million gallons) before leaving the port. As it was traversing the Prince William Sound, it bottomed out on rocks of the Bligh Reef. This caused 8 of the 11 cargo holds on the ship to be broken. Within five hours, over 11 million gallons of oil spilled from the ship. The tanker still had 80 percent of its oil on the ship, but was resting on the rocks and was unstable. The removal of the remaining oil in the Valdez and the cleaning of the oil were the top priorities, but thought had to be given to the numerous habitats in the area. Trying to overcome many logistical problems, three different methods were tried to clean up the site. The methods include in-situ burning, chemical dispersants, and mechanical cleanup. None of these methods were extremely successful in cleaning up all of the oil. After three years, the Coast Guard decided that efforts to clean up the mess should cease. This incident attracted the attention of many different types of organizations, including the EPA who was trying to use bioremediation, then an experimental technology, to clean up the spill (EPA Ch 8).

The EPA was able to convince Exxon to try bioremediation on numerous test plots. The different areas were shown to have enough microbes, so oleophilic fertilizer was added to provide extra nutrients. This nutrient addition caused a 10,000 fold increase of oil-eating microbes (Gordon, 1994). Within two weeks, there was a noticeable change in the amount of oil covering the rocks and beaches. Testing showed that the reduction was from the added fertilizer and following degradation by microbes. This success in experimenting with bioremediation led to the EPA recommending a larger scale bioremediation project for the Exxon oil spill (Gordon, 1994). As the fertilization of the area continued, the cleanliness of the area increased and showed that bioremediation is a feasible alternative to remove oil contamination.



Figure 4: Exxon Valdez Oil Spill Contaminated Area (Gordon, 1994)

Figure 5: Merging of the Monongahela and Ohio Rivers (EPA Ch 8)



A year before the Exxon Valdez spill, the Ashland Oil Company had a four million-gallon storage tank collapse. The spill occurred near the Monongahela River in Pennsylvania. The oil flowed from the tank, across a parking lot, through a storm sewer to the Monongahela River and then into the Ohio River. Though the spill was less than half the size of the Exxon Valdez spill, it had a large impact due to its close proximity to populations. The oil spill caused the death of thousands of

waterfowl and fish. The spill also required that 15 municipal drinking water intakes be shut down and disrupted the water supply for 2.7 million people (Gordon, 1994). The

cleanup was done by using booms, vacuum trucks, and other equipment. Only 20 percent of the oil that reached the river was recovered (Gordon, 1994).

Though these incidents did not use bioremediation on a full scale, they show how other tools to cleanup oil spills can be ineffective. Embedding microorganisms into Prince William Sound is a way to keep the remediation going even if other methods cease. Biological remediation requires that organisms be placed in an area containing nutrients, then the organisms can deteriorate the oil without further assistance from agencies in the area.

These spills sparked public awareness and concern about the risks of oil spills. After the Exxon Valdez spill, congress passed more stringent regulations and enacted laws such as the Oil Pollution Act of 1990. There have been numerous spills have occurred since these, but they are not as large or have such an impact on enhancing the use of bioremediation as a clean up tool.

ADVANCEMENTS

Since the passage of the Oil Pollution Act of 1990, there has been considerable research done on oil spills. Information gained from this research include determining the effectiveness of marine oil spill bioremediation agents, statistical proof that bioremediation enhances the disappearance rate of crude oil hydrocarbons, the minimum nitrogen concentration needed on marine beaches, among other information (EPA, 2006). The difficulty with gaining more information is the difficulty with performing controlled experiments in the oceans or inland waters (OTA, 1991). The advancements that have been made are major achievements, but more research needs to be conducted.

Some of the questions still at hand about bioremediation include the following:

How do we determine the effectiveness of bioremediation? Is bioremediation a cost effective alternative for oil spill cleanup? What conditions make bioremediation the appropriate method for cleaning an oil spill?

If we can find the answer to these questions, we will be able to determine the full capability of bioremediation as a tool to cleanup oil spills.

CONCLUSION

Bioremediation has become an emerging technology that is feasible and cost effective. Bioaugmentation is not as effective as biostimulation, but it is an alternative when there is little or no resident microbial population. The difficulty with using bioremediation is that every spill has different characteristics. The type of oil spilled, its location to sensitive environments, availability of physical, chemical, and biological tools, and other environmental considerations need to be considered to determine the correct clean up method to use for the particular spill. Even within biological methods, the right microbe or fertilizer that needs to be added depends on these characteristics. That is why it is necessary to look at each case individually.

Cleaning up an oil spill needs to be a quick procedure. Precious time is lost if there is not an available contingency plan. The U.S. government realized this and had the EPA make a plan and a list of certified chemical and biological agents that may be used on oil spills. Quick action is necessary to prevent an increase in the contaminated area which would threaten more wildlife, human life, and clean drinking water.

The Exxon Valdez oil spill allowed a lot of research about bioremediation to be conducted. When it concluded, it was estimated that a spill that would normally take 5-10 years to get cleaned by natural conditions could be cleaned in 2-5 years when using bioremediation (Gordon, 1994). This shows the capabilities of bioremediation as a cleanup tool. Bioremediation, at first, is a slow process due to the lag time before the microbes reach their exponential growth phase. However, overall, bioremediation is a good technique to perfect. Bioremediation is cheaper, it takes less time overall to cleanup a spill, and will continue to clean up the area even after other methods are stopped.

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