BIODEGRADATION OF OILY WASTES AND SLUDGES

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Abstract

Improper disposal of petroleum hydrocarbons can cause hazardous effects to both the environment and life. Used and unused oils from several sources contribute to the problems of oil contamination in the environment. Physico-chemical treatment methods are not completely effective as the emission of secondary wastes such as waste gases and sludges are in the concern. Biodegradation which utilizing microorganisms is therefore an environmentally sound alternative. A case study on microbial isolation and screening of various oily contaminated samples showed that *Pseudomonas* sp. and *Vibrio* sp. were present in all oil samples. It was found that the degradation rates depend on incubation temperature.

Introduction

The utilization of crude petroleum all over the world as the sources for fuel and energy, lubrications, grinding, paper deinking, and other petrochemical products cause a lot of serious problems in oil contamination. These sources serve as the major contributor to the environmental pollution problems especially in the soil and water. Contamination of the environment by petroleum products is known to be toxic and hazardous to the environment. They effect the aquatic life and also hazardous to human health. These wastes come from several different sources. These wastes effect high organic loading, color, taste and odor of water, making unfit for domestic and industrial uses.

The activities of microorganisms are required for the total elimination of hydrocarbon contaminants in the environment. Safe disposal of hazardous sludge in soil requires a diverse and active microbial population, which can degrade and detoxify oily wastes and residue. Microbial growth will utilize these organic compounds as the source of carbon and decompose them into smaller molecules or their basic compounds which are carbon dioxide and water. The ability of microorganisms to 'use up' the organic compound is then manipulated to technologies that can resolve several pollution problems. The purpose of this paper is to review the current practices in oily wastes disposal and the biodegradation aspect of the wastes including a case study on microbial screening and isolation, and biodegradation kinetics.

Sources of Oily Wastes and Sludges

Oily wastes are typically found as three different types: free oils, industrial oil-water emulsions, and oily mousses which are usually a solid material such as that derived from marine oil spills (Mohamed and Abdullah, 1993). Oily wastes include process coolants and lubricants, wastes from cleaning operations directly following many other unit operations, wastes from painting process and machinery lubricants. Waste oil consists of both used oil and unused oil. Used oil is any oil that has been adulterated subsequent to use or that becomes contaminated as a result of such use. The oil can be either petroleum or synthetically-derived and may be used as a lubricant (engine, turbine or gear), hydraulic fluid, metal working fluid and insulating fluid or coolant. There are many sources of used oil. Besides by the do-it-yourself oil chargers, used oil is generated at automotive garages, service stations, truck and taxi fleet, military installation, and industrial and manufacturing facilities. Much of the used oil that is generated as a result of routine replacement of deteriorated lubricating oils or what can be classified as *viscosity breakdown*. Frequently, lubricants are replaced because they no longer meet their performance standards.

Unlike used oil, unused oil is any oil that becomes contaminated prior to its intended use. Examples of petroleum and synthetic compounds that are designated as oily waste include crude oil or virgin fuel oil that is spilled on land or water, oily sludge at the bottom of oil storage tanks and oily waste from refinery operations such as separator sludge. The sources of unused oil waste generation are widely dispersed.

Current Practice in Oily Wastes and Sludges Disposal

Used oils collected are normally being treated (recycled, reclaimed and re-refined) so that it can be reused for certain purposes. Shortages and high prices of oil plus environmental protection legislation help promote waste oil recycling. The energy requirements for recycling are considerably lower than those required for production of lubricating oils from crude oils. Also, waste lubricating oil contains more lubricating components, up to 85% than crude oil which normally contains 10-15% (Al-Ahmad and Al-Mutaz, 1991). According to Becker (1984), the term oil recycling, oil reclaiming and oil re-refining are defined in the following ways. Oil recycling is a term for processing used oil to regain useful material. Oil reclaiming is used for the application of cleaning methods to used oil for the removal of insoluble contaminates to make the oil suitable for further use. These methods include settling, dehydration, filtration and centrifugation. The application of petroleum refining processes to used lubricating oil is termed oil re-refining. Processes for re-refining of used oils fall into the following main categories (Al-Ahmad and Al-Mutaz, 1991):

- ***Chemical treatment***. Different chemicals are used too remove metals from used oil. These include sulphuric acid, diammonium phosphate, aluminium salts, and phosphoric acid.
- ***Physical treatment***. Physical separation processes, such as flash distillation, fractionation and thin film evaporation are often used. Other physical treatment processes are also possible. These include filtration, centrifugation, adsorption and heat treatment.

Solvent extraction. Many solvents are used for treatment of used oil, for example methyl ethyl ketone (MEK), butanol, propanol, isopropanol (ISP), tetrahydrofurfuryl alcohol and supercritical ethane.

Several methods have been proposed for oil spills cleanup but still provide certain drawbacks to the environment. Burning of oil has proven to be not successful due to difficulty in igniting the oil and yet the emissions of gases cause further environmental problem. On the other hand, improper use of detergent can cause significant ecological damage. Another popular method has been the absorption of the oil by straw, bark, clay, diatomaceous earth, silicon-treated sand and fly ash. The absorption materials are either picked up for burial or treatment or allowed to sink. Sunken oil may rise again and microbial degradation of oil is inhibited by some absorbents such as clay, Fuller's earth and straw (Brown, 1987). The application of biotechnology methods to confer a way of eliminating contamination often termed as bioremediation. Bioremediation refers to the use of microorganisms to remove or detoxify toxic or unwanted chemicals from an environment (Brock et al, 1994). The principle behind this technology is superficially simple: optimize environment conditions so that biodegradation occurs as rapidly and completely as possible (Morgan, 1992). Special fertilizers are developed to overcome the problem of carbon and inorganic deficiency in contaminated seawater. The fertilizers that contain nitrogen and phosphorus can be dissolved in oil or consist of inorganic compounds in an oleophilic base. There are five groups of fertilizers: slow-release briquettes; slow-release granules; oleophilic fertilizer; spray irrigation; a joint treatment with oleophilic fertilizer and granules (Morgan, 1992).

Several methods can be employed to treat contaminated soil or sludges such as using a slurry bioreactor. Applying fertilizers to soil, adjusting pH using liming, and irrigation and regular tilling of the soil is carried out during land farming. In soil banking, contaminated soil is piled into mounds and optimal conditions for biodegradation are provided. The soil bank is generally constructed on an impermeable base to prevent spreading of contamination. A drainage system may also be incorporated. Oxygenation can be achieved by natural diffusion or aeration.

In-situ cleaning of oil contamination is more often employed. Contaminated groundwater can be pumped to the surface, supplemented with nutrients and oxygen then reintroduced to the soil via an infiltration ditch, a spray irrigation field or an injection well. Potential stumbling blocks for in-situ cleanup fall into four broad areas: subsurface permeability, treatment processes, microbial activity, and treatment efficiency (Morgan, 1992). Provision of the amount of oxygen necessary for biodegradation of the pollutant is one of the major problems. Biodegradations of organic compounds are often enhanced by the utilization of chemical substances. This is to increase degradation abilities of microorganisms and to achieve a combination of chemical and biological degradations. Beside fertilizers, biological treatment methods for contaminated soils and groundwater including land farming, pump-and-treat bioreactors and in situ bioremediation, are using hydrogen peroxide (H_2O_2) as an oxidant to reduce cleanup time and save money.

In the case of refinery waste and sludges, the refinery is normally equipped with effluent treatment facilities to deal with such wastes and also accidental oil spills. Bio-oxidation ponds are built to deal with oily water discharges. Meanwhile, sludge farm or landfarming techniques are employed for dealing with oily solid wastes. In landfarming of such refinery wastes, the selection and preparation of the site should be carried out carefully. The site chosen should be cultivatable with ordinary farm equipment, unencumbered with surface or subsurface utilities and reasonably isolated from residental or public-use area. The general subsurface geology should be known and not include caverns, vertical faults, wells or other features that could provide access to groundwater. The time required to decompose the sludge is long, varies from three to nine months with some of the most important determining factors being moisture content and temperature of the soil and the types of hydrocarbons applied (Mohamed and Abdullah, 1993).

In Malaysia, there were trends of using incineration to treat oily wastes and sludges, even though it might cause air pollution due to waste gases produced. Oil sludge from refinery and spent oil from service stations, will be incinerated in rotary kilns. However, more recent technology was employing jet-burning systems where oily sludges and slop oil will be burned and liquefied to produce secondary oil which is free of dust and can be reused.

Biodegradation Aspect of Oily Wastes and Sludges

Biodegradation is the process of modification or decomposition of the wastes or products by microbes to produce ultimately microbial cells, carbon dioxide, and water. The entire process is not a simple one. In the case of oily wastes, in order for biodegradation to occur, the oil must first be solubilized before coming in contact with microorganisms. Therefore, the biodegradation process is controlled by many factors such as water solubility, the availability of oxygen, inorganic nutrients and water, the temperature and pH of the surrounding, and the concentration of microbial species and of the chemical to be degraded. The complexity of components in petroleum products causes difficulties in biodegradation processes. Mineral oils in lubricants being petroleum fraction having numbers of carbon atom ranging from C_{20} to C_{70} are compounds that cannot be easily biodegraded under normal conditions. Xenobiotic compounds in synthetic lubricants are also found to be recalcitrant to degradation by natural occurring microbial species.

Biodegradability of components in petroleum products is also of major concern in biodegradation processes. In summary, n-alkanes, n-alkylaromatic and aromatic compounds of C_{10}-C_{22} range are the least toxic and most readily biodegradable. n-alkanes, n-alkylaromatic and romatic C_5-C_9 range are biodegraded at low concentration but rather removed by volatilization in the environment. Gaseous n-alkanes, C_1-C_4 used only by a narrow range of specialized hydrocarbon degraders such as methanotrophs. Compounds above C_{22}, low water solubility, solid states, and their microbial transformations are low (Dragun, 1988). In a closed system, short-chain alkanes ($<C_{10}$) are the first components attacked by microflora, followed by alkanes intermediate chain length (C_{10}-C_{24}). Short-chain branched alkanes are next to degrade. The greater the chain length and the amount of branching, the more resistant the compound is to microbial attack. This is then followed by aromatic compounds (Brown, 1987). Branched alkanes and cycloalkanes of C_{10}-C_{22}, are less biodegradable than n-alkanes and aromatic analogs. Branching creates tertiary and quaternary carbon atoms that constitute a hindrance to β oxidation (Dragun, 1988). Cycloalkanes

of C_{10} and below have high membrane toxicity. Highly condensed aromatic and cycloparaffinic systems, with four or more condensed rings, and the partially oxygenated and condensed components of tar, bitumen and asphalt degrade slowly. Petroleum products contain a lot of additives added to enhance the performance. Most of the microbes posses the ability to transform a wide array of organic chemicals.

In order to use biodegradation process for treating oily wastes and sludges, it requires good microbial strains that capable to degrade the oil at wide range operating conditions. To design an appropriate bioreactor, a good understanding on the strains, affecting parameters (temperature, pH, and aeration), and bioreactor design is necessary. Many workers had determined microbial species responsible for the degradation of petroleum hydrocarbons. Bossert and Bartha (1984), had isolated microbial species from soil samples contaminated with waste oils. Two groups of microbe, bacteria and fungi were found resulted from the isolation (Table 1). A similar finding was also reported by Dragun (1988).

Previous studies on biodegradation processes were more concern on the optimum conditions for in-situ elimination of oily wastes. Furthermore, conventional treatment methods for wastewater normally employ large aeration ponds for the activities of microbial organisms. This however, will be a problem when there is inadequate space. Future study, therefore, should aim for improving the existing system while trying to look at a possibility of designing a smaller and simple bioreactor which can handle a wide range of oily wastes such as wastes in the form of oil-in-water emulsion.

Table 1: List of bacteria and fungi isolated form oily waste contaminated soil (Bossert and Bartha, 1984)

Bacteria		**Fungi**	
Achromobacter	*Acinetobacter*	*Acremonium*	*Aspergillus*
Alcaligenes	*Bacillus*	*Beauveria*	*Botrytis*
Brevibacterium	*Chromobacterium*	*Candida*	*Chrysosporium*
Corynebacterium	*Cytophaga*	*Cladosporium*	*Cochliobolus*
Erminia	*Flavobacterium*	*Debaryomyces*	*Cylindrocarpon*
Micrococcus	*Mycobacterium*	*Fusarium*	*Geotrichum*
Nocardia	*Proteus*	*Gliocladium*	*Graphium*
Pseudomonas	*Sarcina*	*Humicola*	*Monilia*
Serratia	*Spirillum*	*Mortierella*	*Paecilomyces*
Streptomyces	*Vibro*	*Penicillium*	*Phoma*
Xanthomonas		*Rhodotorula*	*Saccharomyces*
		Scolecobasidium	*Sporobolomyces*
		Sprotrichum	*Spicaria*
		Tolypocladium	*Torulopsis*
		Trichoderma	*Verticillium*

Case Study – Microbial Isolation, Screening and Biodegradation Kinetic Studies

A case study has been carried out to study the biodegradation process of oily wastes. Three oily contaminated samples form workshops, shipyards and oleochemical industry were examined in terms of the types of microbes present. 4 genera of microorganisms were isolated from the samples as shown in Table 2. It was found that *Pseudomonas* sp. and *Vibrio* sp. were present in all samples. *Pseudomonas* sp. and *Vibrio* sp. seemed to be the potential microbes that might be involved in degradation of the hydrocarbons.

The degradation capability of different types of oily wastes by isolated and screened *Pseudomonas* sp. was studied. To assess the capability, chemical oxygen demand (COD) test was carried out. The objective of test is to evaluate the performance of biodegradation process in terms of quantity of oxygen consumed by the microbes. The biodegradation rate of the samples can then be expressed in terms of:

$$-dS/dt = K(S_O-S)^n$$

where the S_O and S are COD initial and at time t respectively. K is the COD reduction rate constant and n is the order of the reaction.

It was found that the optimum degradation temperature lies between 25 to 30°C. At this optimum temperature, the microbes will grow faster. However, any deviation from this optimum temperature will result in an adverse effect on their growth rate. The result also shows that the microbial species have a very narrow temperature range for growth. The summary of K and n values for different types of wastes at different temperatures is shown in Table 3.

Table 2: Microbes present in different types of wastes

Types of wastes	Microorganisms
1. Oleochemical	- *Pseudomonas sp.* - *Aeromonas sp.* - *Vibrio sp.* - *Bacillus sp.*
2. Workshop	- *Aeromonas sp.* - *Pseudomonas sp.* - *Vibrio sp.* - *Bacillus sp.*
3. Shipyard	- *Pseudomonas sp.* - *Vibrio sp.*

Table 3: Values of K and n at different incubation temperature for different types of wastes

Types of Waste	K			n		
	25°C	30°C	35°C	25°C	30°C	35°C
Oleochemical	1.78	4.71	4.41	0.14	0.34	0.23
Workshop	1.80	5.35	5.21	0.04	0.63	0.57
Shipyard	1.85	6.46	4.05	0.14	0.34	0.19

The values of K and n are the highest at 30°C. This indicates that the degradation rate by bacterium is occurring at the maximum rate. At 30°C, the complex hydrocarbon molecules are degraded to small molecules of different sizes and structures more quickly compared to other temperatures.

Conclusion

Physical and chemical treatment methods for oily wastes and sludges often face many limitations in terms of total elimination of such wastes from the environment. The ability of microbial organisms to utilize petroleum hydrocarbons as their carbon sources should be viewed as a great potential in providing an alternative to treat such wastes and sludges. However, this biodegradation process depends on several environmental and biological factors such as pH, temperature and aeration. These factors as well as its kinetic parameters must be studied since it is important for the purpose of designing the suitable and optimum bioreactor.

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