

The Most Recent Researches in Oily Sludge Remediation Process

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Abstract:

This paper talks about the sludge characteristics and conventional methods for remediation of oil from sludge and also the main part of the study is focused on the previous literatures to describe the most recent researches in oily sludge remediation process. Conventional characterization parameters can be grouped in physical, chemical and biological parameters:

- Physical parameters give general information on sludge process ability and hand ability;
- Chemical parameters are relevant to the presence of nutrients and toxic/dangerous compounds, so they become necessary in the case of utilization in agriculture;
- Biological parameters give information on microbial activity and organic matter/ pathogens presence, thus allowing the safety of use to be evaluated.

Keywords: Remediation, sludge, treatment, degradation

1. Introduction

The sludge characteristics which are important to know strictly depend on the handling and disposal methods adopted. The measurement of stability can also involve the evaluation of the organic substrate concentration, such as volatile suspended solids, COD, BOD5 and organic carbon, ATP and enzymatic activity [1].

Oily sludge was produced during the drilling, transfer, and treatment of oil as well as manufacturing of production chemical substances. Biological sludge can be generated during the waste biological treatment of industrial chemical units.

Thus, while oily Sludges have traditionally been processed by landfarming bioremediation, these practices are banned in the United States and are being phased out in many other jurisdictions. Oil companies have therefore been forced to seek other disposal solutions. Treatment approaches other than biological involve capital-intensive physico-chemical methods including incineration, thermal desorption, refinery cooker use, burning in cement kilns and solvent extraction. Incineration and thermal desorption are regarded to be among the most expensive treatment methods and the high temperatures involved requires high energy input and results in significant greenhouse gas emissions. [2]

2.1. Thermal systems

Thermal systems are divided into two categories namely, thermal desorption and incineration. In thermal desorption, the oily wastes are normally heated in an inert atmosphere and the volatilized hydrocarbons and water are recovered and recycled into the main oil/water separation process. By comparison, the hydrocarbons are destroyed by heating to very high temperatures in the presence of air in thermal incineration processes. Thermal treatment processes are being coupled with current methods such as landfill, land farming, and land spreading for final residue disposal. Thermal treatment is the most efficient method for destruction of organics. It also significantly reduces the volume of inorganics such as metals and salts, and reduces their mobility so that the residue can be effectively

disposed of. Thermal processes can handle oily drill cuttings, contaminated soils (resulting from spills, reclamation of contaminated waste sites), tank bottoms and other process wastes. In other words, thermal technology is best suited to process oil (preferably brine free) contaminated solids [3].

2.2. Incineration

The purpose of incineration is not only sludge elimination but also recovery of energy. Incineration systems have been successfully used for the treatment of contaminated soils. Wastes can be burned which contain relatively high water contents, consists largely organic materials, and are in solid or semi-solid states. These types of waste provide little heat value and require significant supplemental fuel for complete combustion. The thermal processes applicable to detoxify organics in a solid/sludge matrix include rotary kiln, fluidized bed, anaerobic thermal processing, and infrared incinerators. [4] Rotary kiln incinerators are widely used for the incineration of hydrocarbon contaminated soils.

2.3. Thermal Desorption Systems

Thermal destruction consist of treatment methods which use high temperature oxidation to contaminated soils and sludges under controlled conditions to reduce a waste material to simple compounds including CO₂, H₂O, SO_x, NO_x, vapor, and ash. Thermal processes are typically used for highly toxic waste or highly concentrated organic waste. Thermal destruction processes operate at high temperatures (1,600 to 2,000 F°) provide at least a two second residence time for contaminants, and can achieve a destruction removal efficiency of greater than 99.99 percent for key organic contaminants. Thermal destruction has been used as a yardstick to compare other alternatives for remediation of hazardous waste sites since it provides complete destruction of organic contaminants Key issues for thermal destruction include: waste characterization, regulatory requirements, ash disposal, and costs[4]. Thermal desorbers are generally distinguished from incinerators by their ability to remove volatile components from contaminated soil without incinerating the soil. Since thermal desorption is completely dependent on volatilization, treatability is directly related to the volatility of the contaminant. Light hydrocarbons, aromatics (such as benzene, toluene, ethyl benzene, and xylenes), and other volatile organics are easily removed by this type of technology. However, heavier compounds such as polycyclic aromatic hydrocarbons are more difficult to treat. The non-volatile compounds (e.g. metals, salts, acids) are not affected by this technology [3].

3. Biological Treatment

Bioremediation is a technique for treating contaminants by microbial degradation. Biological treatment processes have an advantage over other common treatment technologies, because the organic contaminants are destroyed as they are used as food by bacteria or other organisms [4]. In this process, the hydrocarbons are oxidized to carbon dioxide and water and converted to new microorganisms[5]. basic concept of Bioremediation involves altering environmental conditions to enhance microbiological activity. The primary environmental factors are food sources, moisture content, pH, temperature, oxygen concentrations, and nutrients. Temperature is one of the more important factors in controlling microbiological activity and the rate of organic matter decomposition. Although biological treatment systems can function over a wide temperature range, most systems operate in the mesophilic region (20 to 45° C) [4].

3.1: Composting

Composting is a natural process whereby carbon and other nutrients are recycled from animal and plant detritus by soil microorganisms. Composting has also been used to treat organic wastes such as coal tar and explosives. This process can be used to treat E&P oily wastes/soil by changing them with bulking agents and placing the compost mixture in large piles. The pile retains the heat produced by microbial activity as biodegradation proceeds. The bulking agents (bark or other structuring) serve to increase water holding capacity, permeability and tilth. By improving these properties, biodegradation rates for E&P wastes can be accelerated. Therefore, composting is effective for wastes that are high in hydrocarbon content such as pit Sludges and tank bottoms. There are four composting methods: windrows, static pile, enclosed, and in-vessel. Windrows are elongated piles that are agitated mechanically. Static piles are placed on perforated piping for aeration as shown in Figure 1. Enclosed piles are sheltered to collect leachate and control volatile emissions. In-vessel composting requires reactors or rotating drums, and both aeration and emissions can be closely controlled in the vessels. Aerating the compost, whether by mechanical mixing or forced aeration, serves to optimize oxygen content, remove carbon dioxide, and to control temperature [6]. The process of composting is based on aerobic degradation of organic matter. The water content of a compostable mixture of organic wastes should be around 55% while the organic matter content should be greater than

70%, facilitating effective bio-degradation. High moisture content above 60% reduces the temperature, porosity and thus the oxygen concentration while low moisture content, below 50%, could limit the rate of composting. At values of 10-15% the bacterial metabolism generally stop to function. Bacterial activity is also influenced by pH, with the optimal with the optimal values being between 5.5 and 8[3].

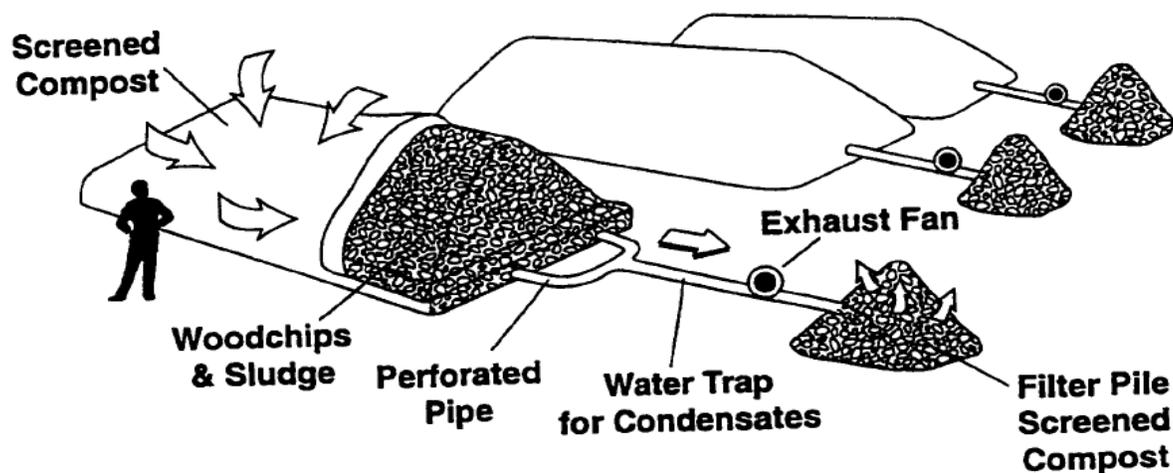


Figure 1. Schematic of Composting in Static Piles [6].

4. Landfarming

The term land farming refers to the process where hydrocarbon contaminated soils are spread out in a layer of 0.3–1.0 m thick, nutrients are added and the soils are mixed periodically. During the process of land farming, the total petroleum hydrocarbons, (TPH), may be lost through volatilization or biodegradation. Land farming refers to the combination of the two processes. Treatment regimens for land farms vary with climate, location, and temperature and soil type [7].

Maximum degradation rates are typically observed in the upper plough layer (10–15 cm) when hydrocarbon concentrations are maintained around 5%. The sludge–soil mix may be augmented with additives, including inoculate, organic and inorganic nutrients, surfactants and bulking agents, to enhance hydrocarbon degradation. Because landfarming conditions do not represent optimal and controlled conditions (temperature, pH, moisture, oxygen, mixing) for microbial activity, long treatment times are required. Land farming has proven consistently successful in warmer southern climates. For instance, in the 12-month operational period of an Australian land farm TPH levels were remediated from 4644 ppm to less than 100 ppm. Landfarming bioremediation practices for the treatment of oily wastes from the petroleum industry are not considered environmentally acceptable, since in the first instance large uncontaminated areas of land are first deliberately contaminated. Another major environmental disadvantage of landfarming relates to the large quantities of volatile organic carbons present in these wastes. Monitoring and containing these compounds are important because of their hazardous impact on health and their role in tropospheric ozone production [16].

5. Slurry Bioreactor

There are advantages for a biological reactor-based process over other solid-phase biodegradation approaches. The reactor-based process has the potential to be highly accelerated through proper process control/ optimization and can be fully contained. Since bioreactor systems can accommodate solids concentrations across 5–50% w/v, sludge-associated solids and insoluble oil substrates can be mixed in a manner approaching homogeneity. This mixing, combined with the control of key parameters, enhances rates and extents

of hydrocarbon degradation. Mass transfer limitations are minimized and contaminant desorption from solids is increased, resulting in much higher hydrocarbon removal rates than are observed in landfarm and other solid-phase systems [16].

Table 1. Biodegradation of petroleum hydrocarbons in oily sludges from different refineries. For shake-flask biodegradation tests, the initial total petroleum hydrocarbon (TPH) concentration in the sludge sample was adjusted to 5–7% and nutrient medium was added, as described by Ward and Singh. Flasks were inoculated with a 10% mixed culture inoculum and incubated at 30 °C for 14 days on a rotary shaker (200 rpm) [16].

Location of refinery	Sludge TPH (%)	Hydrocarbon fractions (% of total)				TPH degradation (%)
		Saturates	Aromatics	Resins	Asphaltenes	
Ontario (A)	18.8	49.6	32.7	10.3	7.4	93.5
Ontario (B)	15.8	42.0	42.0	6.9	9.1	95.6
Ontario (C)	13.2	44.9	40.4	7.1	7.6	94.2
Quebec	9.3	48.7	25.6	10.2	15.5	90.7
Western Canada	20.2	21.2	47.8	9.6	21.4	93.3
Eastern Canada	20.9	46.4	33.5	10.8	9.3	91.2
Western USA	17.1	45.4	37.8	3.9	12.9	95.0
Eastern USA	15.5	44.3	43.7	6.7	5.4	90.8
Latin America (A)	15.1	51.3	18.9	14.9	14.9	96.6
Latin America (B)	21.3	41.2	35.6	9.7	13.5	92.5
South-east Asia	33.7	44.7	40.8	6.5	8.0	90.3
Middle East	8.3	38.3	45.5	6.9	9.3	92.1

6. Applications of Biosurfactant in Hydrocarbon Remediation

In this section, we investigate about production of biosurfactant and effects of biosurfactant on hydrocarbon remediation.

6.1. Identification of Biosurfactant

Biosurfactants are amphiphilic compounds produced by microorganisms, which either adhere to cell surfaces or are excreted extracellularly in the growth medium [8]. They consist of two parts—a polar (hydrophilic) moiety and non-polar (hydrophobic) group [8]. Their hydrophobic moiety is either a long-chain fatty acid, a hydroxyl fatty acid, or a α -alkyl- β -hydroxy fatty acid while the hydrophilic moiety can be a carbohydrate, an amino acid, or a cyclic peptide phosphate. Many microorganisms are able to produce biosurfactants particularly when living on water immiscible substrates [15]. Many microorganisms produce biosurfactants during growth on a wide variety of substrates [8]. A characteristic feature of biosurfactants is a hydrophilic-lipophilic balance (HLB) which specifies the portion of hydrophilic and hydrophobic constituents in surface-active substances. Due to their amphiphilic structure, biosurfactants increase the surface area of hydrophobic water-insoluble substances, increase the water bioavailability of such substances and change the properties of the bacterial cell surface. Surface activity makes surfactants excellent emulsifiers, foaming and dispersing agents. In comparison to their chemically synthesized equivalents they have many advantages. They are environmentally friendly, biodegradable, less toxic and non-hazardous. They have better foaming properties and higher selectivity. They are active at extreme temperatures, pH and salinity and can be produced from industrial wastes and from by-products. This last feature makes cheap production of biosurfactants possible and allows utilizing waste substrates and reducing their polluting effect at the same time [9].

7. Classification and Properties of Biosurfactants

Unlike chemically synthesized surfactants, which are classified according to their dissociation pattern in water, biosurfactants are categorized by their chemical composition, molecular weight, physico-chemical properties and mode of action and microbial origin. Based on molecular weight they are divided into low-molecular-mass biosurfactants including glycolipids, phospholipids and lipopeptides and into high-molecular-mass biosurfactants/bioemulsifiers containing amphiphilic polysaccharides, proteins, lipopolysaccharides, lipoproteins or complex mixtures of these biopolymers. Low-molecular-mass biosurfactants are efficient in lowering surface and interfacial tensions, whereas high-molecular-mass biosurfactants are more effective at stabilizing oil-in-water emulsions [9].

Among the best studied biosurfactants are rhamnolipid that belong to the glycolipid class. Rhamnolipid have been identified predominant from *Pseudomonas aeruginosa* [10]. Examples of biosurfactants and their producers are depicted in Table 1. Biosurfactant

activities depend on the concentration of the surface-active compounds until the critical micelle concentration (CMC) is obtained [9]. The concentration at which micelles began to form was represented as the CMC [11].

At concentrations above the CMC, biosurfactant molecules associate to form micelles, bilayers and vesicles (Figure 2). Micelle formation enables biosurfactants to reduce the surface and interfacial tension and increase the solubility and bioavailability of hydrophobic organic compounds. The CMC is commonly used to measure the efficiency of surfactant. Efficient biosurfactants have a low CMC, which means that less biosurfactant is required to decrease the surface tension. Micelle formation has a significant role in microemulsion formation. Microemulsions are clear and stable liquid mixtures of water and oil domains separated by monolayer or aggregates of biosurfactants. Microemulsions are formed when one liquid phase is dispersed as droplets in another liquid phase, for example oil dispersed in water (direct microemulsion) or water dispersed in oil (reversed microemulsion)[9].

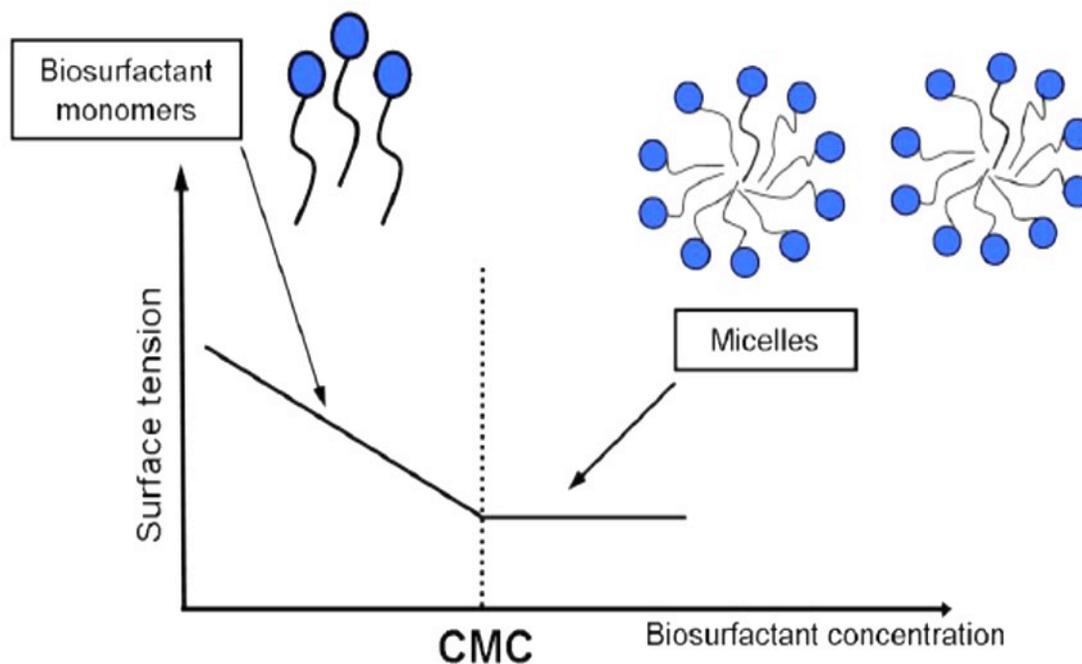


Figure 2. The relationship between biosurfactant concentration, surface tension and formation of micelles [9].

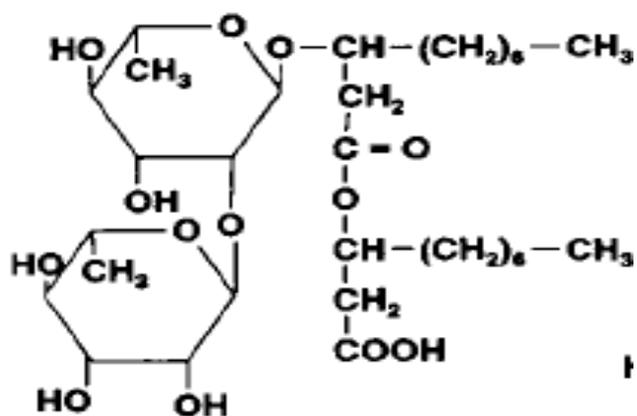


Figure 3. Chemical structures of Rhamnolipid biosurfactants [7].

Table 2: Classification of biosurfactants and their use in remediation of heavy metal and hydrocarbon contaminated sites[9, 10].

Biosurfactant		Microorganism	Applications in Environmental Biotechnology
Group	Class		
Glycolipids	Rhamnolipids	<i>Pseudomonas aeruginosa</i> , <i>Pseudomonas</i> sp.	Enhancement of the degradation and dispersion of different classes of hydrocarbons; removal of metals from soil
	Trehalolipids	<i>Mycobacterium tuberculosis</i> , <i>Rhodococcuserythropolis</i> , <i>Arthrobactersp.</i> , <i>Nocardiasp.</i> , <i>Corynebacteriumsp.</i>	Enhancement of the bioavailability of hydrocarbon
	Sophorolipis	<i>Torulopsisbombicola</i> , <i>Torulopsispetrophilum</i> , <i>Torulopsisapicola</i>	removal of heavy metals from sediments; enhancement of oil recovery
Fatty acids, phospholipids and neutral lipids	Corynomycolic acid	<i>Corynebacteriumlepus</i>	Enhancement of bitumen recover
	Spiculisporic acid	<i>Penicilliumspiculisporum</i>	Removal of metal ions from aqueous solution;
	Phosphati-dylethanolol	<i>Acinetobactersp.</i> , <i>Rhodococcuserythropolis</i>	Increasing the tolerance of bacteria to heavy metals
Lipopeptides	Surfactin	<i>Bacillus subtilis</i>	Enhancement of the biodegradation of hydrocarbons
	Lichenysin	<i>Bacillus licheniform</i>	enhancement of oil recovery
Polymeric biosurfactants	Emulsan	<i>Acinetobactercalcoaceticus</i> RAG	Enhancement biodegradation of the hydrocarbons ,removal of heavy metals from soil
	Alasan	<i>Acinetobacterradioresistens</i> KA-	enhancement of oil recovery
	Biodispersan	<i>Acinetobactercalcoaceticus</i> A2	Stabilization of the hydrocarbon-in- water emulsions
	Liposan	<i>Candida lipolytica</i>	Dispersion of limestone in water
	Mannoprotein	<i>Saccharomyces cerevisiae</i>	Stabilization of hydrocarbon-inwater emulsions

8. Discussion: Role of Biosurfactants in Biodegradation Processes

A promising method that can improve bioremediation effectiveness of hydrocarbon-contaminated environments is the use of biosurfactants. They can enhance hydrocarbon bioremediation by two mechanisms. The first includes the increase of substrate bioavailability for microorganisms, while the other involves interaction with the cell surface which increases the hydrophobicity of

the surface allowing hydrophobic substrates to associate more easily with bacterial cells .By reducing surface and interfacial tensions, biosurfactants increase the surface areas of insoluble compounds leading to increased mobility and bioavailability of hydrocarbons. In consequence, biosurfactants enhance biodegradation and removal of hydrocarbons. Addition of biosurfactants can be expected to enhance hydrocarbon biodegradation by mobilization, solubilization or emulsification (Figure 4) [14].

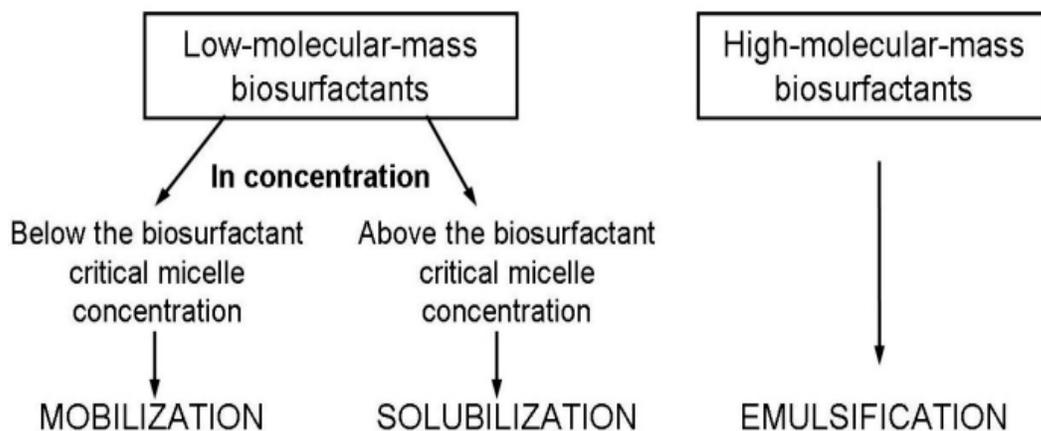


Figure 4. Mechanisms of hydrocarbon removal by biosurfactants depending on their molecular mass and concentration [9].

The mobilization mechanism occurs at concentrations below the biosurfactant CMC. At such concentrations, biosurfactants reduce the surface and interfacial tension between air/water and soil/water systems. Due to the reduction of the interfacial force, contact of biosurfactants with soil/oil system increases the contact angle and reduces the capillary force holding oil and soil together. In turn, above the biosurfactant CMC the solubilization process takes place. At these concentrations biosurfactant molecules associate to form micelles, which dramatically increase the solubility of oil. The hydrophobic ends of biosurfactant molecules connect together inside the micelle while the hydrophilic ends are exposed to the aqueous phase on the exterior. Consequently, the interior of a micelle creates an environment compatible for hydrophobic organic molecules. The process of incorporation of these molecules into a micelle is known as solubilization [14].

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