Chapter 1

GENERAL INTRODUCTION

Abstract

Hazardous waste is generated in significant amount in refineries world wide. In India, oil refineries generate approximately 20,000 tonnes of oily sludge (a mixture of hazardous hydrocarbon waste) per annum. One of the major problems faced by oil refineries is the safe disposal of this oily sludge. Uncontrolled handling of these sludges often leads to environmental pollution and also affects the aesthetic quality. Recent legislation desires environment friendly sludge management system in the industries. Recycling of sludge in an environment friendly manner is one of the appropriate solutions of sludge management problem. When sludge cannot be recycled or incinerated, the only option left is secure landfilling. The treatment technologies developed can be grouped as physical remediation, chemical remediation and biological remediation.

The objective of this research is to study the feasibility of bioremediating the oily sludge from a refinery site. The strategy adopted is a multiple approach of phytoremediation, land farming and microbial enhanced oil separation in laboratory scale treatment systems.
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1.1 Definition and characteristics of hazardous waste

The generation of solid and hazardous waste is increasing day by day with the rapid development of industrial growth worldwide. Hazardous wastes have been variously defined in different countries.

The Hazardous Wastes (Management and Handling Act) 1989 of Government of India categorizes waste oil and emulsions including tank bottom from petroleum refinery industry, slop oil emulsion solid from refinery, and waste water ETP sludges within its purview of hazardous wastes.

According to US Environment Protection Agency (EPA), a waste is considered to be hazardous if it:

1. Exhibits characteristics of ignitability, corrosivity, reactivity and/or toxicity.
2. Is a non specific source waste (generic waste from industrial processes)
3. Is a specific commercial protector intermediate.
4. Is a mixture containing a listed hazardous waste
5. Is a substance that is not excluded from regulation under RCRA, Subtitle C-

Hazardous waste management (Wentz, 1989).

According to La Grega (1994) there are four main characteristics for hazardous wastes i.e. ignitability, corrosivity, reactivity, and extraction potential toxicity.

Ignitability

Ignitable wastes are liquids with a flashpoint below 600°C, or solids capable of causing fire under standard temperature and pressure.

Corrosivity

Corrosive wastes are aqueous wastes with a pH below 2 or above 12.5, or which corrode steel at a rate in excess of 0.25 inches per year.
Reactivity

Reactive wastes are normally unstable, react violently with air or water, or form potentially explosive mixture with water. This category also includes waste that emits toxic fumes when mixed with water and material capable of detonation.

Toxicity

The objective of this parameter is to determine whether toxic constituent in a solid waste sample will leach into ground water, if the waste is placed in a municipal solid waste landfill. If this is the case, then the waste will be declared hazardous.

According to the Hazardous Wastes (Management and Handling Act) 1989 of Government of India, hazardous wastes are characterised into eighteen categories (Trivedy, 2004) as given below

- Category One : Cyanide waste
- Category Two : Metal Finishing wastes
- Category Three : Bearing Heavy Metal Salts
- Category Four : Bearing Mercury, Arsenic, Cadmium
- Category Five : Non-Halogenated Hydrocarbons
- Category Six : Halogenated Hydrocarbons.
- Category Seven : Paint, Glue Industry
- Category eight : Waste from Dyes and Dye intermediates containing inorganic chemical compounds.
- Category nine : Waste from Dyes and Dye intermediates containing organic chemical compounds
- Category Ten : Waste Oil & Oil Emulsions
  - Tank bottom from petroleum refining industry
  - Slop oil emulsion solid from refinery
1.2 Management of hazardous waste

The potential damage for public health and to the environment from the mismanagement of hazardous waste justifies the need for implementation of effective hazardous waste management programme (Dawson et al., 1986, Freeman et al., 1988).

A hazardous waste management programme includes:-

- **Minimisation of waste**
  
The first step towards waste minimisation is inventory management and second step is equipment modification.

- **Waste recycling**
  
  Recycling is an important step in evolving cleaner approaches to chemical processing. Adopting recycling techniques would serve to increase productivity by proper utilization of feed components, avoidance of emission, unitisation of process heat for preheating, optimisation of operating parameters and re-utilisation of costlier catalysts and solvents.
Treatments of hazardous waste

Waste may be made less hazardous by physical, chemical, or biological treatment. Treatment of hazardous waste can serve to prepare the material for recycling or for ultimate disposal in a manner safer than disposal without treatment.

Disposal of hazardous waste

Landfilling: A landfill is defined as that system designed and constructed to contain discarded waste so as to minimize release of contaminants to the environment. Landfills are necessary because hazardous waste minimization technologies cannot totally eliminate the waste generated, and treatment technologies produce residue.

Incineration: It is used for complete destruction of the contaminants. Incineration is one of the most effective treatments available and usually adopted for those wastes that cannot be recycled, reused, or safely deposited in a landfill site. It destroys organic chemicals by converting them to carbon dioxide, water and other gases that are removed by scrubbers.

Deep well injection: It is a process by which waste fluids are injected deep below the surface of the earth. Only certain kind of geologic formation can be used for disposal by deep well injection. The formation must be deep, porous, enough to provide storage space and sandwiched between impermeable layers of rock.

Hazardous waste management in India is governed by the following two acts

Based on further suggestions received and considering the various new methodologies, Government of India has notified the new amendments as the HW (M&H) rules, 2000 and suggested modification in Schedule -1 with list of process generating hazardous wastes and Schedule-2 with list of waste substances with concentration limits.

1.3 Treatment of hazardous waste

Growing public awareness and concern about environmental degradation has resulted in evolving various treatment technologies which can serve to prepare the material for recycling, or for ultimate disposal in a manner safer than disposal without treatment. The treatment technologies developed can be grouped as physical remediation, chemical remediation and biological remediation

Physical remediation

Physical treatment methods are conducted in order to reduce the volume of the wastes and facilitate the solid-liquid separation. Several physical processes including sedimentation, clarification, centrifugation, flotation, filtration, evaporation, distillation, reverse osmosis etc. are used in hazardous waste management. The various physical treatment technologies available for different applications are carbon adsorption, air stripping, filtration, centrifuging, distillation, evaporation, solidification and encapsulation. (Riser-Roberts, 1998).

Chemical remediation.

Chemical treatment methods either destroy contaminants or convert them to different, less toxic form. Various chemical treatment technologies available are hydrolysis, neutralization, oxidation/reduction, precipitation, fixation, ion exchange and coal agglomeration.
**Biological remediation.**

Bioremediation, is the biological process transformation or mineralization of organic compounds introduced into the environment to less toxic or innocuous forms (Hazen, 1997, Brigmon et al., 2002). Bioremediation describes several technologies and practices that take advantage of natural systems and processes to clean up pollution.

Bioremediation technologies can be broadly classified as *ex-situ* or *in-situ* (Iwamoto, 2001). Ex-situ technologies are those treatment modalities which involve the physical removal of the contaminant material to another area for treatment. Bioreactors, landfarming, composting, and some forms of solid-phase treatment are all examples of *ex-situ* treatment techniques. In contrast, *in-situ* techniques involve treatment of the contaminated material in place. Bioventing for the treatment of contaminated soils, and biostimulation of indigenous aquifer microorganism are examples of these treatment techniques. If biological treatment of a hazardous waste is contemplated, care is required to ensure that the other components in the waste neither poisons the organism nor render the residue unfit for landfill disposal. The different types of bioremediation practices are biostimulation, bioaugmentation, intrinsic treatment and phytoremediation.

**Biostimulation**

Biostimulation aims at enhancing the activities of indigenous microorganisms that are capable of degrading the offending contaminant. It is applicable to oil contaminated sites, an extension of the natural remediation of soil. In many cases the additions of inorganic nutrient act as a fertilizer to stimulate biodegradation by autochthonous microorganism (Atlas and Philp, 2005).
Bioaugmentation

Bioaugmentation involves the inoculation of contaminated soil or water with specific strains or consortia of microorganism to improve the biodegradation capacity of the system for a specific pollutant organic compound. Bioaugmentation often is considered for bioremediation of compounds that appear to be recalcitrant i.e., contaminants that persist in the environment and appear to be resistant to microbial degradation. (Atlas and Philp, 2005).

Intrinsic treatment

The lack of intervention to the bioremediation is considered intrinsic bioremediation or natural attenuation. (Hart, 1996) Intrinsic remediation results from several natural processes, such as biodegradation, abiotic transformation, mechanical dispersion, sorption, and dilution that reduce contaminant concentrations in the environment. (Morin, 1997).

Phytoremediation

Phytoremediation may be defined as the use of plants to remove, destroy or sequester hazardous substances from the environment. The method may offer some solution for dealing with mixed wastes. Phytoremediation technologies exploit various biochemical processes in the rhizosphere including extraction, immobilization, and degradation of contaminants (Glick, 2003). The diverse processes in phytoremediation include phytodegradation, phytoextraction, phytostabilization, phytovolatilization and rhizofiltration. The area adjacent to a plant root, referred to as the rhizosphere, is a continuum extending from the root surface with maximum microbial activity as compared to the bulk soil, which has far less activity. The rhizosphere has nutrients and water exuded from the plant roots, resulting in enhanced microbial activity (Walton and Anderson, 1990; Hou et al., 2001; Hutchinson et al., 2001). The organic substrate produced from the decay of dead root hairs serves as an
important carbon source for rhizosphere microorganisms that have the potential to degrade organic pollutants (Heinonsalo et al., 2000).

1.4 Management of petroleum refinery wastes

The petroleum industry is a major contributor of hazardous materials releasing petroleum hydrocarbons to the environment in a number of ways. Severe subsurface pollution of oils and water can occur via the leakage of underground storage tanks and pipelines, spills at production wells and distribution terminals, and seepage from gasworks sites during coke production. Seepage of gasoline from underground storage tanks has caused widespread soil and aquifer contamination, threatening the safety of the various potable water supplies. The complex and diverse range of petroleum-derived organic compounds released from spillages is of major environmental concern. These consist of aliphatic, BTEX, and PAHs. BTEX and PAHs are of major concern because of their toxicity and carcinogenicity. (Atlas and Philp, 2005).

Oily sludge is generated in significant amount in the refineries during crude oil processing. Crude oil is usually stored in storage tanks. Impurities present in the oil are deposited at bottom of the tank. During cleaning of the tank, the sludge is recovered, and is treated as waste. Oily sludge is also generated from the treatment plant of oily waste water. The sources of oily sludge are API separator and TPI unit (Bhattacharya and Shekdar, 2003).

One of the major problems faced by oil refineries is the safe disposal of this oily sludge. Many of the constituents of the sludge are carcinogenic and potent immunotoxicants (Propst et al., 1999). Improper disposal of this leads to environmental pollution, particularly soil contamination, and poses serious threat to ground water (Chakradhar, 2002). Sludge characteristic differ from product to product depending upon raw material used and manufacturing process involved. Oily sludge which is generated in massive quantity from refineries, is highly viscous in
consistency. Sludge contains sufficient amount of grease and waxy material. The calorific value for the sludge is also high (4000-6000cal/g). It has been observed that heavy metals like chromium, cadmium, copper, nickel, lead, zinc etc. are commonly present in majority of the oil sludge. (Roberts, 1998).

Bioremediation of petroleum in contaminated soil using indigenous microorganism has proven effective (Fiorenza et al., 2000); however the biodegradation rate of more recalcitrant and potentially toxic petroleum contaminants, such as polycyclic aromatic hydrocarbons (PAHs), is rapid at first but declines quickly. Biodegradation of such compounds is limited by their strong adsorption potential and low solubility. Vegetation may play an important role in the biodegradation of complex organic chemicals in soil. For petroleum compounds, the presence of rhizosphere microflora may accelerate biodegradation of the contaminants (Fiorenza et al., 2000). Current research on land farming using oily sludge is expected to open a pathway for better management of oily sludge. Land farming involves the decomposition of oily sludge by microbial action in cultivated soil. The limitation of the method is the probable soil and groundwater contamination due to migration of leachates (Huddleston et al., 1986).

1.5 Scope and objectives of the present study

In India, oil refineries generate approximately 20,000 tonnes of oily sludge (a mixture of hazardous hydrocarbon waste) per annum (Bhattacharyya and Shekdar, 2002). This waste residue is dumped into specially constructed sludge pit, consisting of a leachate collection system and polymer lining system to prevent the percolation of contaminants into ground water (Bhattacharyya and Shekdar, 2003). However these pits face the draw backs of being rather expensive to construct and maintain, and increasingly more and more land is required for this purpose.
The objective of this research is to study the feasibility of bioremediating the oily sludge from a refinery site. The strategy adopted is a multiple approach of phytoremediation, land farming, and microbial enhanced oil separation in laboratory scale treatment systems.
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