CHAPTER 2

REVIEW OF LITERATURE

2.1 Overview

Since early nineties phytoremediation has emerged as a promising clean up technology adopted all over the world. Some of the pioneering works done by some eminent workers in the world are reviewed in the following.

Microbial degradation of petroleum hydrocarbon in hydrocarbon contaminated soil was done by Atlas (1981). Polyaromatic hydrocarbon in crops from long-term field experiments amended with sewage sludge was done by Wild et al. (1992). Accumulation of nickel (Ni) and zinc (Zn) in plants was done by Baker et al. (1994a). Cunningham et al. (1995c) studied phytoremediation of contaminated soils. Chaîneau et al. (1997a) worked on phyto-toxicity and plant uptake of fuel oil hydrocarbons. Kastner (2000) worked on degradation of aromatic and polyaromatic compounds. Liste and Alexender (2000a) worked on plant promoted pyrene degradation in soil. Phytoremediation of aged petroleum sludge was done by Hutchinson et al. (2001).


In India important work related to remediation of hydrocarbon contaminated sites are done by Hanson et al. (1993) who published a rapid and simple screening technique.

The literature so far available can be categorised into experiments with different plants and microorganisms and different mechanisms of phytoremediation.

2.2 Experiments with different plants and microorganisms

This can be categorized into following general categories:

2.2.1 The ability of certain plants to uptake and tolerate specific contaminants

Briggs et al. (1982) studied the relationships between lipophilicity and root uptake and translocation of non-ionized chemicals by barley. They found significant degradation and uptake of contaminants in tissues. Burken and Schnoor (1996a) studied and published on plant uptake of atrazine and role of root exudates. A predictive relationship for uptake of organic contaminants by hybrid poplar trees was evaluated by Burken and Schnoor (1998b). Orchard et al. (2000) studied the uptake of trichloroethylene by hybrid poplar trees grown hydroponically in flow through plant growth chambers. Benzene toxicity and removal in laboratory phytoremediation studies is done by Burken et al. (2001c). Ramaswami and Rubin (2001) worked and published on measuring phytoremediation parameters for volatile organic compounds and found significant degradation and uptake of the hydrocarbons. Phytoremediation of MTBE with hybrid poplar trees was studied by Ma et al. (2004). Phytoextraction potential of the nickel hyperaccumulators *Leptoplax emarginata* and *Bornmuellera tymphaea* was studied by
Chardot et al. (2005). Nichols and Musella (2009) studied and published on the differences in PAH desorption and sediment organic matter composition between non-vegetated and recently vegetated fuel-oiled sediments. A field lysimeter study of heavy metal movement down the profile of soils with multi metal pollution during chelate-enhanced phytoremediation was carried out by Hu et al. (2007). Phytoremediation of cadmium-contaminated soils using *Amaranthus tricolor* was studied by Watanabe et al. (2009). Soongsombat et al. (2009) worked on lead tolerance and accumulation in *Pteris vittata* and *Pityrogramma calomelanos*, and their potential for phytoremediation of lead contaminated soil. Screening of poplar clones for cadmium phytoremediation using photosynthesis, biomass and cadmium content analyses was carried out by Pietrini et al. (2010). Rai (2010a) studied and published on microcosm investigation on phytoremediation of Cr using *Azolla pinnata*. Lunney et al. (2010) worked on the effect of organic matter additions on uptake of weathered DDT by *Cucurbita pepo* ssp. pepo cv. Howden. Bioremediation of co-contamination of crude oil and heavy metals in soil by phytoremediation using *Chromolaena odorata* (L) King & H.E. Robinson was studied by Atagana (2010a). Barbaferi et al. (2011) studied and published on uptake of heavy metals by native species growing in a mining area in Sardinia, Italy: discovering native flora for phytoremediation. Atagana (2011b) studied the potential of *Chromolaena Odorata* (L) to decontaminate used engine oil impacted soil under greenhouse conditions. Chaturvedi et al. (2012) studied on phytostabilization of Iron ore tailings through *Calophyllum inophyllum* L. Effects of organic amendments on Cd, Zn and Cu bioavailability in soil with repeated phytoremediation by *Sedum plumbizincicola* was studied by Wu et al. (2012). Gomes et al. (2013) worked on phosphorus improves arsenic
phytoremediation by *Anadenanthera peregrina* by alleviating induced oxidative stress. Lewińska and Karczewska (2013) studied and published on influence of soil properties and phosphate addition on arsenic uptake from polluted soils by velvet grass (*Holcus lanatus*). Metal uptake and allocation in trees grown on contaminated land: An implication for biomass production was studied by Evangelou et al. (2013). Wei et al. (2013) studied on Cd Hyperaccumulative characteristics of Australia ecotype *Solanum nigrum* L. and its implication in screening hyperaccumulator. Study on evaluation of plant growth regulators to increase nickel phytoextraction by *Allysum species* was done by Cabello-Conejo et al. (2013). Effects of Cd, Pb, Zn, Cu-resistant endophytic *Enterobacter* sp. CBSB1 and *Rhodotorula* Sp. CBSB79 on the growth and phytoextraction of *Brassica* plants in multimetal contaminated soils was studied by Wang et al. (2013). They found significant degradation and uptake of heavy metals in plants. Mok et al. (2013) worked and published on native Australian species are effective in extracting multiple heavy metals from biosolids.

### 2.2.2 Monitoring contaminant degradation in pot experiments

Shahandeh and Hossner (2000) studied plant screening for chromium phytoremediation. Campbell et al. (2002) studied and published on remediation of benzo[a]pyrene and chrysene-contaminated soil with industrial hemp (*Cannabis sativa*) and found significant degradation. Degradation of crude oil in the rhizosphere of *Sorghum bicolor* was studied by Banks et al. (2003a). Effectiveness of phytoremediation as a secondary treatment for polycyclic aromatic hydrocarbons (PAHs) in composted soil was studied by Parrish et al. (2004). Influence of fertilizer levels on phytoremediation of crude oil with the tropical pasture grass *Brachiaria brizantha* (Hochst. ex A. Rich. Stapf).
was studied by Merkl et al. (2005a). Brandt et al. (2006) worked and published on potential of Vetiver (Vetiveria zizanioides L. Nash) for phytoremediation of Hydrocarbon-contaminated soils in Venezuela. Influence of catclaw Mimosa monancistra on the dissipation of soil PAHs was studied by Alvarez-Bernal et al. (2007). Batty and Anslow (2008) studied on effect of a polycyclic aromatic hydrocarbon on the phytoremediation of zinc by two plant species (Brassica juncea and Festuca arundinaceae) and found significant degradation of zinc and PAHs. Muratova et al. (2008) studied on phytoremediation of oil-sludge contaminated soil. Contaminated soil phytoremediation by Cyperus laxus Lam. Cytochrome P450 erod-activity induced by hydrocarbons in roots was studied by Lopez-Martinez et al. (2008). Choi and Chang (2009) studied on nitrogen fertilization effects on the degradation of aged diesel oil in composted drilling wastes. Degradation of PAH in a creosote-contaminated soil a comparison between the effects of willows (Salix viminalis), wheat straw and a nonionic surfactant was studied and published by Hultgren et al. (2010). Effect of growing Esamum indicum L. on enhanced dissipation of lindane (1, 2, 3, 4, 5, 6-hexachlorocyclohexane) from soil was studied by Abhilash and Singh (2010). Endophytes and their potential to deal with co-contamination of organic contaminants (toluene) and toxic metals (nickel) during phytoremediation was studied by Weyens et al. (2011). Nwaichi et al. (2011) worked on evaluation and decontamination of crude oil-polluted soils using Centrosema pubescen Benth and amendment-support options. The Inoculation method affects colonization and performance of bacterial inoculant strains in the phytoremediation of soil contaminated with diesel oil was studied by Afzal et al. (2012). Chouychai et al. (2012) studied on the effect of corn plant on survival and
phenanthrene degradation capacity of *Pseudomonas Sp. UG14Lr* in two soils. Phytoremediation of trichloroethylene and dichlorodiphenyltrichloroethane—polluted water using transgenic *Sesbania grandiflora* and *Arabidopsis thaliana* plants harboring rabbit cytochrome P450 2E1 was studied by Mouhamad et al. (2012). Betancur-Galvis et al. (2012) worked and published on enhanced dissipation of polycyclic aromatic hydrocarbons in the rhizosphere of the athel tamarisk (*Tamarix Aphylla* L. Karst.) grown in saline-alkaline soils of the former lake texcoco. Enhancing degradation of total petroleum hydrocarbons and uptake of heavy metals in a wetland microcosm planted with phragmites communis by humic acids addition was studied by Sung et al. (2013). Wang et al. (2012) worked on oxalic acid enhances Cr tolerance in the accumulating plant *Leersia hexandra* Swartz and found significant tolerance and degradation capability. Mandal et al. (2012) studied phytoremediation of arsenic contaminated soil by *Pteris vittata* L.I. influence of phosphatic fertilizer and repeated harvest. Effect of metal tolerant plant growth promoting bacteria on growth and metal accumulation in *Zea mays* plants grown in fly ash amended soil was studied by Kumar and Patra (2013). Study on phytoextraction of metals and rhizoremediation of PAHs in co-contaminated soil by co-planting of *Sedum alfredii* with ryegrass (*Lolium perenne*) or castor (*Ricinus communis*) was done by Wang et al. (2013).

### 2.2.3 Monitoring degradation in the field

Zynter et al. (2001) studied and published on bioremediation of diesel contaminated soil and found significant degradation of diesel oil. Nehnevajova et al. (2005) worked on screening of sunflower cultivars for metal phytoextraction in a contaminated field prior to mutagenesis. Zalesny Jr. et al. (2005) studied on clonal
variation in survival and growth of hybrid poplar and willow in an in-situ trial on soils heavily contaminated with petroleum hydrocarbons and found significant degradation of the hydrocarbons. Multispecies and monoculture rhizoremediation of polycyclic aromatic hydrocarbons (PAHs) from the soil was studied and published by Maila et al. (2005). Differences in sediment organic matter composition and PAH weathering between non-vegetated and recently vegetated fuel oiled sediments was studied by Gregory III and Nichols (2008). In-situ selection of suitable plants for the phytoremediation of multi-metals-contaminated sites in Central Taiwan was studied by Yu Lai and Chen (2009). Mohsenzade et al. (2009) worked on phytoremediation of petroleum-contaminated soils: Pre-screening for suitable plants and rhizospheral fungi. Ebbs et al. (2010) studied and published on a comparison of the dietary arsenic exposures from ingestion of contaminated soil and hyperaccumulating Pteris ferns used in a residential phytoremediation project. Karimi et al. (2010) worked on analysis of arsenic in soil and vegetation of contaminated area in Zarshuran, Iran and found significant degradation. Heavy metal pollution in lentic ecosystem of sub-tropical industrial region and its phytoremediation was studied by Rai (2010b). Lin et al. (2010) worked and published on vegetation changes and partitioning of selenium in 4-year-old constructed wetlands treating agricultural drainage. Liu et al. (2010) studied on phytoremediation of oilfield sludge after prepared bed bioremediation treatment. Field Note: successful establishment of a phytoremediation system at a petroleum hydrocarbon contaminated shallow aquifer: Trends, trials, and tribulations were studied by Cook et al. (2010). Yu-Hong et al. (2010) worked on distribution and mobility of copper, zinc, and lead in plant-sediment systems of Quanzhou bay estuary, China. Ji et al. (2011) studied on in-Situ
cadmium phytoremediation using *Solanum Nigrum* L.: the bio-accumulation characteristics trail. Niazi et al. (2011) worked on phytoremediation potential of *Pityrogramma calomelanos* Var. Austroamericana and *Pteris vittata* L. grown at highly variable arsenic contaminated site. Removal of nitrogen and phosphorus by *Eucalyptus* and *Populus* at a tertiary treated municipal wastewater sprayfield was studied by Minogue et al. (2012). Rathod et al. (2013) studied field Evaluation of willow under short rotation coppice for phytomanagement of metal-polluted agricultural soils was done by Slycken et al. (2013). Wilson et al. (2013) studied plants as bio-indicators of subsurface conditions: impact of groundwater level on benzene, toluene, ethylbenzene, and xylenes (BTEX) concentrations in trees. Performance of deep-rooted phreatophytic trees at a site containing total petroleum hydrocarbons was studied by Ferro et al. (2013). Thomas et al. (2013) worked on native Michigan plants stimulate soil microbial species changes and PAH remediation at a legacy steel mill. Enhancing degradation of total petroleum hydrocarbons and uptake of heavy metals in a wetland microcosm planted with *Phragmites communis* by humic acids addition was studied by Sung et al. (2013). Madejón et al. (2013) studied on long-term biomonitoring of soil contamination using poplar trees: accumulation of trace elements in leaves and fruits.

### 2.2.4 Modeling transport and degradation pathways

Assessing plant phytoextraction potential through mathematical modeling was studied by Gonnelli et al. (2000). Chiou et al. (2001) worked on a partition-limited model for the plant uptake of organic contaminants from soil and water. Quinn et al. (2001) studied and published on predicting the effect of deep-rooted hybrid poplars on the groundwater flow system at a large-scale phytoremediation site. Kinetic modeling of
bioavailability for sorbed-phase 2,4-dichlorophenoxyacetic acid was studied by Park et al. (2001). Tischer and Hübner (2002) worked and published on model trials for phytoremediation of hydrocarbon-contaminated sites by the use of different plant species. A mathematical model of phytoremediation for petroleum-contaminated soil: model development was studied by Thoma et al. (2003). Karthikeyan et al. (2003) worked and published on Modeling jet fuel (jp-8) fate and transport in soils with plants. Solute transport and extraction by a single root in unsaturated soils: model development and experiment was studied by Kim et al. (2004). Mezzari et al. (2004) studied mathematical modeling of RDX and HMX metabolism in poplar (Populus deltoides × Populus nigra, DN34) tissue culture. Phytoextraction: simulating uptake and translocation of arsenic in a soil-plant system was studied by Ouyang et al. (2005). Collins (2008) worked on a semi-quantitative approach to deriving a model structure for the uptake of organic chemicals by vegetation. Modeling of heavy metals removal from municipal landfill leachate using living biomass of water hyacinth was studied by El-Gendy (2008). Study on chromium induced modulation in the antioxidant defence system during phonological growth stages of Indian mustard were done by Diwan et al. (2010). Couselo et al. (2010) worked on expression of the phytochelatin synthase TaPCS1 in transgenic aspen, insight into the problems and qualities in phytoremediation of Pb. The use of chloro-complexation to enhance cadmium uptake by Zea mays and Brassica juncea: testing a “free ion activity model” and implications for phytoremediation was studied by López-Chuken et al. (2010). Effects of soil amendments and EDTA on lead uptake by Chromolaena odorata: Greenhouse and field trial experiments were studied by Tanhan et al. (2011). Smesrud et al. (2012) worked and published on using pilot test data to refine an alternative cover
design in Northern California. Investigating polycyclic aromatic hydrocarbons profiles in higher plants using statistical models was studied by Sojinu et al. (2013). Khataee et al. (2003) worked on potential of the aquatic fern *Azolla filiculoides* in biodegradation of an azo dye: modeling of experimental results by artificial neural networks.

### 2.2.5 Investigation of bioavailability and aging of the contaminants

five garden flower species grown in artificially cadmium-contaminated soils. Assessment of bioaccumulation of heavy metal by *Pteris vittata* L. growing in the vicinity of fly ash was studied by Kumari et al. (2011). Rofkar and Dwyer (2011) studied effects of light regime, temperature, and plant age on uptake of arsenic by *Spartina pectinata* and *Carex stricta*. Gonzaga et al. (2012) worked on predicting arsenic bioavailability to hyperaccumulator *Pteris vittata* in arsenic-contaminated soils. Effect of plants on the bioavailability of metals and other chemical properties of biosolids in a column study was done by Huynh et al. (2012). Wu et al. (2012) studied and published on the effects of organic amendment on Cd, Zn and Cu bioavailability in soil with repeated phytoremediation by *Sedum plumbizincicola*. Fungal inoculation and elevated CO₂ mediate growth of *Lolium mutiforum* and *Phytolacca americana*, metal uptake, and metal bioavailability in metal-contaminated soil: Evidence from DGT measurement was studied by Song et al. (2013).

2.2.6 Investigation related to plant-microbe-contaminant-soil interactions that contribute to soil remediation

Enhancing the growth of *Vicia faba* plants by microbial inoculation to improve their phytoremediation potential for oily desert areas was studied by Radwan et al. (2005). Liste and Prutz (2006b) worked and published on plant performance, dioxygenase-expressing rhizosphere bacteria, and biodegradation of weathered hydrocarbons in contaminated soil. Impact of microbial/plant interactions on the transformation of polycyclic aromatic hydrocarbons in rhizosphere of *Festuca arundinacea* was studied by Ho et al. (2007). Gaskin et al. (2008) worked on screening of Australian native grasses for rhizoremediation of aliphatic hydrocarbon-contaminated
soil. Petroleum-degrading microbial numbers in rhizosphere and non-rhizosphere crude oil-contaminated soil was studied by Kirkpatrick et al. (2008). Yateem et al. (2008) worked and published on investigation of microbes in the rhizosphere of selected trees for the rhizoremediation of hydrocarbon-contaminated soils. Alarcon et al. (2008) studied on arbuscular mycorrhiza and petroleum-degrading microorganisms enhanced phytoremediation of petroleum-contaminated soil. Al-Awadhi et al. (2009) studied and published on plant associated bacteria as tools for the phytoremediation of oily nitrogen-poor soils. Isolation and characterization of hexavalent chromium-reducing rhizospheric bacteria from a wetland was studied by Gutiérrez et al. (2010). Yang et al. (2011) studied on application of rhizosphere interaction of hyperaccumulator Noccaea caerulescens to remediate cadmium-contaminated agricultural soil. Wei et al. (2012) worked on arsenic in the rhizosphere soil solution of ferns and found significant degradation of arsenic. Song et al. (2013) studied on fungal inoculation and elevated CO$_2$ mediate growth of Lolium mutiforum and Phytolacca americana, metal uptake, and metal bioavailability in metal-contaminated soil: Evidence from DGT measurement. Yang et al. (2013) worked on the effect of metal tolerant plant growth promoting bacteria on growth and metal accumulation in Zea mays plants grown in fly ash amended soil was studied by Kumar and Patra (2013). Copper-resistant bacteria enhance plant growth and copper phytoextraction was studied by Yang et al. (2013). Effects of bacteria on cadmium bioaccumulation in the cadmium hyperaccumulator plant Beta vulgaris Var. Cicla L. was studied by Chen et al. (2013).
2.3 Different mechanisms of phytoremediation

The process of phytoremediation involves various mechanisms. Some of the mechanisms on which experimental work has been done are described below.

Survey of literature reveals that there are different mechanisms involved in phytoremediation. These mechanisms are phytoextraction, phytovolatilization, phytodegradation, rhizodegradation, rhizofiltration, phytostabilization, and hydraulic control. The soil itself, both chemically and physically, has a large effect on phytoremediation due to its influence on the composition of the microbial population, the type of vegetation that can grow, and the transport and availability of the contaminant. Factors such as: pH, nutrient concentration, cation exchange capacity, soil texture, permeability, and bulk density, temperature, moisture content and organic matter influence phytoremediation (Donahue et al. 1983; Rending and Taylor 1989). Many of these factors are interrelated, so amendments to the soil must be carefully planned.

Biodegradation is the microbially mediated chemical transformation of organic compounds (Lyman et al. 1992) while microbial uptake is the direct removal of the contaminant by adsorbing compounds to the membrane surface or absorbing compounds through the membrane. These two processes are interrelated in that the contaminant take up may be the original contaminant or a biotransformation product. Enhanced microbial activity in the rhizosphere also may, in some situations, benefit the health of the plant which affects the health of the rhizosphere and the entire phytoremediation system. The mechanisms will have an effect on the volume, mobility, or toxicity of contaminants, as the application of phytoremediation is intended to do (USEPA 1994a).
Removal of metals and other compounds from the subsurface and translocation of these compounds to the leaves or other plant tissues comes under the phytoextraction. The plants may then need to be harvested and removed from the site. In phytovolatilization contaminants are being taken up into the body of the plant, but then the contaminant, a volatile form thereof, or a volatile degradation product is transpired with water vapour from leaves (USEPA 2000c). Phytodegradation has been observed to remediate some organic contaminants, such as chlorinated solvents, herbicides, and munitions, and it can address contaminants in soil, sediments, or groundwater (USEPA 2000c). Phytodegradation can be divided into two components: first, absorption, translocation and metabolism of contaminants by the plants; and, second, degradation of the contaminants by root exudates. Root exudates may also aid remediation in a number of other ways such as by: increasing the bioavailability of the contaminant, lubricating the soil, and acting as cometabolites with contaminants. Phytovolatilization can occur with contaminants present in soil, sediments, or water and has been found to occur with volatile organic compounds, including trichloroethene, as well as inorganic chemicals that have volatile forms, such as selenium, mercury, and arsenic (USEPA 2000c).

Other ways root exudates may aid remediation is by increasing contaminant bioavailability, “the extent to which a contaminant is available to living things” (Farrell et al. 2000), lubricating the soil, and acting as cometabolites. Organic acids in root exudates may increase the bioavailability of contaminants by competing with the contaminant for sorption sites in the soil. Lipids and sterols are released by roots, have been found to increase the bioavailability of contaminants by causing organic matter to swell and
expose previously non-exposed sorbed contaminants, making them available for microbial degradation. Lipids and sterols also lubricate the soil to facilitate root passage.

The localized nature of rhizodegradation means that it is primarily useful in contaminated soil, and it has been investigated and found to have at least some success in treating a wide variety of mostly organic chemicals, including petroleum hydrocarbons, polycyclic aromatic hydrocarbons (PAHs), chlorinated solvents, pesticides, polychlorinated biphenyls (PCBs), and BTEX (USEPA 2000c). The microbial breakdown and removal of contaminants in the soil occurs through two distinct interrelated processes, biodegradation and microbial uptake. The potential of a particular PHC to be degraded, independent of soil properties, depends on its chemical structure. The main considerations for biodegradation are the size of the contaminant and the types and geometry of its bonds. Some PHC have bonds that microbes have difficulty in breaking or are not able to break. Microbes may also find different molecular configurations more difficult to degrade than others.

Studies have documented up to 100 times as many microorganisms in rhizosphere soil as in soil outside the rhizosphere (McCutcheon and Schnoor 2003). Microorganisms may be so prevalent in the rhizosphere because the plant exudes sugars, amino acids, enzymes, and other compounds that can stimulate bacterial growth. The roots also provide additional surface area for microbes to grow on and a pathway for oxygen transfer from the environment. McCutcheon and Schnoor (2003) did extensive work on phytovolatilization.
When the phytodegradation mechanism is at work, contaminants are broken down after they have been taken up by the plant. As with phytoextraction and phytovolatilization, plant uptake generally occurs only when the contaminant’s solubility and hydrophobicity fall into a certain acceptable range (USEPA 2006d). Rhizodegradation is believed to be carried out by bacteria or other microorganisms whose numbers typically flourish in the rhizosphere (USEPA 2006d). Although microbes are able to completely degrade certain contaminants on their own, the health of the rhizosphere and the associated microbial community is dependent on the growth and survival of the vegetation. Microbes have been found to aid plant health by reducing the phytotoxicity of certain contaminants and by providing nutrients. Phytotoxicity of contaminants and limited nutrient availability may retard soil remediation by slowing or preventing plant growth.

Although the microbial community in the rhizosphere is enhanced by the plant, the health of the plant is not necessarily enhanced by the microbial community (McPherson 2007). Decreased phytotoxicity and increased nutrient availability are not always necessary. For example, many contaminants are not phytotoxic and, for those that are, root exudates may degrade these compounds, to non-phytotoxic forms; the plant itself may not be available for plant uptake due to interactions within the soil. Also, in soils with sufficient amounts of nitrogen, nitrogen-fixing bacteria may not be needed.

Sufficient concentrations of macro-nutrients (nitrogen, phosphorous, organic carbon and potassium) and micro-nutrients (zinc, calcium, manganese, magnesium, iron, sodium and sulphur) must be available to maintain the health of the microbial population and vegetation. In PHC contaminated soils the large amounts of organic carbon available
tend to result in rapid depletion of other nutrients, with the limiting nutrients generally being nitrogen and phosphorus (McPherson 2007).

The contaminant has a large influence on phytoremediation. Although plant-contaminant and microbe-contaminant interactions are extremely important, they can not occur if the contaminant is not available for uptake and degradation. Bioavailability governs contaminant uptake and degradation by plants and microbes. Contaminant bioavailability is dependent on the amount of organic matter in the soil, the type and concentration of the contaminant and the amount of time the contaminant has been in the soil.