Chapter

Soil Contamination: A Menace to Life

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Abstract

The dire concern for soil contamination includes the safety of food, ecological environment, public's health and capacity of social sustainable development. Soil is polluted by heavy metals and pesticides which are far beyond pollution standards. The soil biodiversity and agricultural sustainability are adversely affected in long-term harmful effects by the prolonged intensive and indiscriminate use of agro-chemicals. It needs immediate attention for the whole world to curb continual deterioration of soil pollution and remediate contaminated soil as soon as possible to decrease harm on people's health and ecological environment. In fact, acceleration of related legislation, increased capital investment and technical development to remediate soil contamination and must achieve some progress. However, due to all sorts of the constraints, whether soil management system or technical capacity for decontamination is relatively outdated, so there remains a lot of work need to be done. Developing countries, including Brazil, India and so on, are also facing similar problems. Approaches to solve soil problems could benefit developing countries in process of industrialization and urbanization, so it's a very meaningful job to deep analyze and study the current situation and countermeasures soil pollution. In this Chapter, the overall situation of soil pollution is introduced, the concrete causes and hazards of soil contamination are discussed, and technologies and processes of soil remediation are suggested for improvement of the status of soil contamination and social sustainable capacity.

Keywords: soil quality, xenobiotics, soil microbiota, remediation, environment sustainability

1. Introduction

The fundamental to human life on Earth is Soil. In Natural environment soil forms the vital part and is as important as plants, animals, rocks, landforms, loch and rivers. The distribution of plant species are influenced by the soil and also it provides a habitat for a wide range of organisms. The flow of water and chemical substances between the earth and atmosphere is controlled by the soil and it acts as a source of all types of gases in the atmosphere. Natural processes are not only reflected by the soil but the human activities both at present and in past are also recorded [1].

The reduction in the productivity of soil is due to the presence of soil pollutants. The presence of any chemical substance or toxic chemicals (pollutants) in soil at a higher concentration than normal that adversely affects any non-targeted organism or pose a risk to human health and/or the ecosystem. Contaminants occurring naturally in soil even at low concentrations pose a risk. Direct assessment of contamination in soil cannot be achieved, which makes it a hidden danger [2]. According to the report of FAO, soil contamination concerns are growing in every region, they are not restricted to degradation but also, poisoning our food, air and water too.

Soil pollution is caused by fertilizers, pesticides, chemicals, organic manure, radioactive wastes, discarded food, plastics, clothes, carcasses, leather goods, paper, bottles, tins-cans etc. Industrial wastes contain chemicals like copper, iron, zinc, lead, mercury, cyanides, cadmium, aluminum, acids and alkalies etc. which reach the soil indirectly through air or directly with water. The basic composition of soils are getting altered and becoming toxic for plant growth due to continuous and improper use of herbicides, pesticides and fungicides to protect the crops from pests, fungi etc. [3].

Due to global warming, agricultural fertilizers and pesticides arable lands are turning to desert and becoming non-arable at ever-increasing rates, lessening the hope that we can feed our booming population. Food production should be increased by 40% and that to on the fertile soils that cover around 11% of whole surface of Land. But the problem is that there is very little new land that can be used for production because existing land id lost and degraded. Due to erosion, water logging and salination, annually 75 billion tons of soil (nearly 10 million hectares/25 million acres) of arable land is lost, as stated by UNFAO leading to degradation of soil [4].

Contamination of soil survives for many years with "memory". Analysis of the load by elements and substances of anthropogenic origin from the period of "industrial revolution" in the soils or sediments can still be done [5]. Inorganic contaminants form the natural part of soil and can be redistributed due to anthropogenic activities predominantly in the environment [6]. Soil contamination can result in many negative effects like reduction in the decrease of microbial activity leading to the humification process reduction, decrease in water retention in soil and increase of soil erosion vulnerability [7].

Exposure to these agents attributes towards epidemiological evidence which shows the increased incidence of a variety of human cancers, such as lymphoma, leukemia, and liver and breast cancers [8]. These effects are dependent upon the properties of soil which is responsible for the mobility of contaminants in food chains or transfer from root to shoot, bioavailability of toxic chemicals, and carcinogenicity and residence time of contaminants [9].

Around the world, intensification in agriculture, industrialization, mining and wars have left a bequest of contaminated soils [10]. Soil has been used as a sink for dumping solid and liquid wastes since urban expansion. It was reviewed that once concealed and out of sight, the contaminants would not cause any risk to health of human being or the environment and that they would disappear [11]. Assessing the adverse effects caused due to contamination and taking measures to meet the expectations of environmental standards according to current legal requirements comes under management.

Soil contamination is mainly caused due to industrial/commercial activities diffusing heavy metals, nuclear power plants, oil industry and military camps. Various industrial points are the anthropogenic sources of heavy metals, for example, present and former mining activities, foundries, smelters, and diffuse sources such as piping, constituents of products, combustion of by products, and traffic related to industrial and human activities [12].

On the basis of toxicity, bioaccumulation, mobility and environmental persistence, priority should be given to the pollutants, according to WHO [13]. Heavy metals are considered to be carcinogenic such as arsenic, cadmium, nickel, chromium, PAHs and dioxins, based on human and animal studies exposed to high levels [14]. Depending upon the exposure level and duration some of these substances produce toxic effects on animal organs like CNS, liver, heart, kidney, skin etc.

2. Key concepts in understanding soil contamination

2.1 Soil properties

Soil organic matter (SOM), Inorganic minerals, water and air comprise soil. Soil physical properties including texture, structure, and porosity, the fraction of pore space in a soil, are influenced by the composition and proportion of these components. The physical properties of soil in turn affect air and water movement in the soil, and thus the soil's ability to function.

2.2 Soil health

Physical, chemical and biological properties constitute a healthy soil which allows the soil to carry out important functions. Human health is linked to agricultural soil health, as poor soils with decreased nutritional value yield fewer crops. Erosion is limited by healthy soils, and helps improve air and water quality too [15]. Soil contamination affects the functions of soil in ecosystem. It is considered to be "functionally dead" once contamination exceeds threshold value. Pollution is sometimes irreversible which is caused by heavy metals and many organic contaminants.

2.3 Causes of soil pollution

Soil contamination is caused by two main causes (a) natural and (b) anthropogenic Natural causes include earthquakes, volcanic eruptions, tsunamis etc. while; anthropogenic causes include radioactive wastes, metals (trace and heavy metals) and chemicals. These hazardous substances persist for long duration in the environment during which they are absorbed by the atmosphere, stockpiled to higher concentration potentially toxic to organisms in the food chain.

2.3.1 Natural sources

Accumulation of chemicals and toxic compounds (e.g. Perchlorate) naturally in soil surface leads to soil contamination.

a. Volcanic Eruptions. Volcano produces hazardous substances in huge amount that can destroy the areas nearby and even living beings. The fertile top layer of the soil gets destroyed by the lava and ash particles released from the volcano which is called as Soil erosion.

b. Earthquakes. Due to the movement of tectonic plates below the surface of soil there is sudden release of energy in the surface of earth which is termed as Earthquakes. It results in the damage of the agricultural soil which becomes non-fertile.

c. Alterations in Rainfall Patterns. The composition of organic matter in the soil is sensitive to alterations in rainfall pattern which forms the soil structure framework; balance the nutrients, oxygen and water of soil. Alterations in rainfall results in acidification or alkalization of the soil [16].

d. Geographical Changes. Soil quality is affected by Changes in the geographical factors. The two recently developed techniques i.e. geographic information system (GIS) and remote sensing techniques (RS) are helpful in knowing the connection between soil erosion and geographical factors and also to obtain the information on soil quality and heterogeneity of soil surface as well as to investigate the extent of land degradation.

e. Tsunamis. Tsunami results in salting of agricultural land and drinking water. Different pollutants in large amount are carried away with the flooded water and get deposited resulting in water and land pollution [17].

2.3.2 Anthropogenic sources

Industrial, municipal, domestic and agricultural wastes are considered as major anthropogenic source of soil pollution [18]. Some of these wastes can be recycled into useful materials so all of them are not considered as contaminant. Solid wastes are the discarded materials which are of no use [19]. Depending on their source these wastes can be further classified as municipal waste, industrial wastes and hospital wastes.

a. Municipal Solid Wastes (MSW). Waste like kitchen wastes, livestock, poultry wastes, domestic waste, market wastes, slaughterhouse wastes, ceramic wastes, glass and metals waste comprises municipal wastes. Municipal wastes cause major environmental threat in developing countries due to improper waste disposal. Soil as well as ground water contamination results due to open disposal of municipal wastes.

b. Hospital Wastes. Wastes produced as a result of diagnosis, treatment and immunization of animals and human beings are considered as Hospital wastes. Improper disposal of these wastes and release of pollutants during incineration cause several health hazards on public health as well as the environment [20].

c. Industrial Wastes. Industrial wastes are high toxic in nature and they affect the chemical and physical nature of soils and fertility of soil. These chemicals get accumulated by the crops and pose serious health issues and environment related problems.

d. Agricultural Practices. In order to deal with the challenge of food and to enhance crop yield agrochemicals are used to protect the crops (from pathogens and insects). Agrochemicals can be classified as pesticides (herbicides, insecticides and fungicides), fertilizers, hormones and animal manure. These chemicals possess environmental and health risks at the value more than threshold value and they can persist for longer duration in environment and are non-biodegradable [21].

e. Radioactive Wastes. Byproducts of nuclear power plants and research stations contribute radioactive wastes. Unstable elements having atomic number > Bi-83 (Bismuth) are radioactive. Ionizing radiations are releases from these radioactive wastes which lead to several health issues [22]. Accumulation of radioactive material in soil not only affect the characteristics (Physical, chemical and biological), but also leads to magnification through food chain and affects living beings.

f. Chemical Wastes. Chemical wastes are classified as organic and inorganic which includes polynuclear aromatic hydrocarbons, petroleum hydrocarbons, various solvents and other heavy metals. These chemical wastes possess several health risks such as, allergies, cancers related to immune, reproductive and nervous system. Transformation of organic contaminants in soil occurs through different methods which include leaching, volatilization and biological transformation [23]. Furthermore, bioaccumulation in living organisms can result in various adverse effects at each trophic level of food chain.

g. Heavy metals. Heavy metals includes metalloids, lanthanides and actinides and are characterized by atomic number < 2 and atomic weight 22.98 to <40 [24]. Soil productivity, fertility and quality have been considerably affected by the heavy metal contamination in soil in the past decade. Heavy metals at high concentration are toxic for human beings.

3. Effects of soil pollution

3.1 Agricultural

- Reduction in soil fertility
- Reduction in ability of nitrogen fixation
- Increase in erosion of soil
- Nutrients loss
- Silt Deposition
- Crop yield Reduction
- Imbalance in soil fauna and flora

3.2 Industrial

- Underground water contamination
- Ecological imbalance
- Gas release causing health problems
- Release of radioactive rays
- Reduced vegetation

3.3 Environmental

- Unavailability of soil for food
- Low crop yield

- Soil Erosion due to lack of crops
- Change in makeup and microorganisms that live in soil

4. Techniques for controlling soil pollution

Soils are considered to have purification property which is due to their properties like physical, chemical and biological [25]. In order to prevent soil erosion, construction in sensitive area can be limited. In general we would also use less fertilizer and pesticides to adopt all the three R's: Reduce, Reuse, and Recycle for generation of less solid waste.

Measures to control soil pollution

- Minimal use of pesticides and chemical fertilizers
- Cropping techniques should be improved
- Wastes should be dumped properly
- Forest management
- Prevention of soil erosion
- Public awareness
- Recycling and Reuse of wastes
- Ban on Toxic chemicals

5. Interaction of pollutants with soil constituents

Pollutants interaction and behavior with soil depends upon different processes (physical, chemical, and biological) that occur in components of soil. Processes include

1. Detainment of pollutants on or within the soil medium
2. Transport, percolation and diffusion in soil medium
3. Chemical changes processes occurring within the soil medium

As soon as the pollutants enter into the soil, they undergo physical, physico-chemical, microbiological, and biochemical processes that help them to retain, reduce or get degraded [26].

5.1 Sorption of contaminants

A process by which a substance is accumulated within the phase of the boundary of phases physically or chemically is called sorption. It is of two types- chemical (as with ionic and hydrogen binding) and physical (as with van der Waals forces). Positively charged molecules participate in cation exchange while negatively charged molecules in anion exchange. The transition in cationic or anionic states of some ions or molecules in the soil is pH dependent which can control the mobility of contaminants [27].

5.2 Bioavailability, mobility and degradation of contaminants

Interactions between chemicals and organisms that determine the exposure is referred to as bioavailability. Major hurdle for applying bioremediation techniques for segregation of pollutants are sorption by strong bonding and slow release. Moreover, concepts related to soil screening and understanding risk level should also be reconsidered. According to Semple *et al.* (2004) [28] material is considered to be bioavailable which is "freely available" and is able to cross organism's cellular membrane from the medium where it inhabits.

6. Impacts of soil pollution on the food chain and ecosystem services

Quality and yields of crops are reducing due to the presence of soil contaminants which are affecting our food security. During the formation of research policies for use of poor natural resources in agriculture healthy crops should be the main motto. Key points that should be kept in mind during crops production are include monitoring of agricultural fields, tracking of wastewater units of sewage and industrial and inputs added on crops [29].

The top level predators have highest concentration of contaminants in bodies and experience the bad health effects in the food chain and also lost of apex predators occurs [30]. As a result, effect of pollution in food web scale increases. Response to contaminants may be sequential or remains inert may be serious with drastic change. The uptake and translocation of contaminants into above ground tissues are conditioned by genetic and physiological differences of plants as well as by the concentration of contaminants in the soil and the exposure time [31]. These changes results in abrupt degradation of ecosystem services which may not recover.

The exposure to environmental contaminants depends upon the routes, concentration, bioavailability, frequency and duration. It also depends upon the feeding behavior and habitat [32]. Difference in the fate of a contaminant within an organism and its toxicological effect is also seen among and within species [33]. This complexity leads to an impact on particular species and indirectly on the diversity. Indirect effects in food web is known as "Tropic cascade" in which disturbances in food chain is due to change in highest tropic level or change in resources [30]. Another well-known effect is "paradox of enrichment" where the increase of prey resources results in predators shift but the exposure to contaminants may inhibit the paradox of enrichment and drive them back to a fixed equilibrium [34].

Health implications ranging from minor to major fatalities including long term effects are observed due to contaminants in food chain [35]. Contaminants in food chain can adversely affect humans various systems [36].

7. Methods to assess soil contamination

Due to rapid development particularly urbanization and industrialization over the last century's contamination of the environment considerably has increased [37]. Due to this, assessment and control of soil contamination is an object of interest of researchers, scientists and authorities dealing with environmental protection. Data related with the spatial distribution of soil pollution are of great importance for the environmental protection, regional development, and spatial planning [38].

Soil assessment can be done through various approaches because of different types of soil contamination. This can be done both from a functional and structural perspective. The relationship between them is ecology which is receiving a lot of attention but assessments related to ecotoxoicology have not arisen. Part IIA of the Environmental Protection ACT (1990) [39] was put forward for assessing contamination related to land/soil which is causing significant harm to human health, water, livestock and ecological systems [40].

Data usage, accuracy and precision play an important role in the choice of monitoring methods of soil contamination. Biological, chemical and geophysical approaches are included in assessing methods. To measure specific contaminants using special instruments like MS, AAS or GC are included in chemical methods. In biological methods organisms or byproducts of biodegradation are used as indicators of soil contamination. And in Geophysical methods changes in physical properties of soil and contaminants are assessed.

Development in the methods of assessing soil contamination includes better extraction process for improved recovery and enhanced detection limits and also alternative methods development for soil contamination monitoring such as isotopic signatures or immunoassays. On site analysis, research based techniques and innovative methods that are cost effective, sensitive and easy to use should be developed for assessing organic, inorganic and radioactive contaminants in soil.

The overall success of analysis of soil contaminants depends upon the nature of soil matrix, association/interaction of pollutants with soil, forces including chemical and physical with which they bind to the soil particles Therefore, efficiency of assessment depends upon the procedure of extraction of contaminants from soil for analysis because soil contaminants migrate down with time and become less approachable [41].

Tool for evaluation of risk at contaminated sites are thought of as more appropriate and cost-effective and has the potential of focusing assessment and evaluating the contaminant. The risk assessment methods are the source to know the risk of undesired effects on ecosystems caused by various factors which are associated with human activities. Tools of assessing ecological effects includes: experiments related to ecotoxicity under controlled conditions, ex situ bioassays (simple laboratory assays) and mapping of community in field [42].

ERA allows the assessments of toxicants and their effects through changes in predation and competition. This could be achieved through the use of standardized terrestrial test procedures. Experiments related to ecotoxicity under controlled conditions have their own benefits of measuring direct toxicity of chemicals and their interpretation. In this context, Bioassays are one of the frequently used higher tier alternatives because of its advantage of assessing the toxicity in the soil. Contaminants in soil can be assessed using multispecies mesocosms or lysometers by evaluating intrinsic populations of the soil or by introducing species to system.

8. Soil remediation approaches

Selection of soil/sediment remediation approaches depend on various factors viz. type of soil, composition of soil, properties of soil, nature of contaminant etc. The properties of soil can be influenced by the addition of nutrients and chemicals for the growth of microbes [43]. These additions and approaches cause contamination and destruction of soil components yielding harmful products [44].

Economic solutions to cover the areas used for horticulture and agriculture are with low- or uncontaminated topsoil or with sandy and rocky soils [45].

Types of remediation methods

- In-situ: Contaminated soil is treated at the site where it is occurring [46]
- Ex-situ: These methods require the excavation of contaminated soil [47]

8.1 Containment technologies

Conventional civil engineering techniques are most frequently used approach for isolating contaminated media from surrounding environment. These approaches are typically convenient when the excavation process or the soil removal could lead to potential hazards. The advantages involved in using these technologies lie in, a) non requirement of soil excavation, b) low to moderate cost of treatment in spite of the requirement for long-term monitoring and maintenance of equipment.

To prevent migration of contaminants due to flow of groundwater, use of physical barriers are preferred which includes surface capping and subsurface barriers (vertical and horizontal). This result in limiting infiltration of surface water and reduce the migration of contaminated groundwater laterally or vertically [48].

8.2 Immobilization technologies

To prevent the migration of contaminants, addition of chemicals/reagents to soil to form insoluble low toxic matter is preferred. This technology covers a broad spectrum of inorganic contaminants however; it is a temporary solution because contaminants are still in soil. Therefore the immobilization technique should be applied only to surface soil [49]. Immobilization is achieved by working directly on the contaminants present in the soil and can be classified as solidification and vitrification.

8.3 Solidification and stabilization

Process that encapsulates or captures the contaminants within stabilized integrity and not involves any chemical interaction is called solidification. It involves reduction of contaminants hazard potential by their conversion in order to reduce their solubility, mobility, or toxicity. Use of cement, asphalt or phosphate, or alkalies that increase the pH helps in precipitation and immobilization of contaminants [50].

8.4 Vitrification

Vitrification involves the process of pyrolysis (1600–2000°C) and oxidation for melting and immobilization of contaminants. It can be applied for in and ex situ methods of remediation of inorganic substances, such as metals and radionuclides and organic compounds. Other process of vitrification involves heating by plasma, direct power, combustion, induction or microwave at a temperature of 1100–1400°C [51].

9. Technologies for treatment of contaminated soil

Treatment technologies can be classified into three main categories: (1) biological technologies (2) thermal technologies and (3) physicochemical technologies.

9.1 Biological technologies

Also called as Bioremediation, the use of microorganisms (mainly, bacteria and fungi) to clean up contaminated soils [52]. Microorganisms act on contaminants by following mechanism which includes biosorption, bioleaching, biomineralization, intracellular accumulation, and enzyme-catalyzed transformation [53]. Three main approaches are there for the bioremediation of contaminated areas [54] which includes

a. Natural attenuation

b. Biostimulation

c. Bioaugmentation and

d. Phytoremediation

Bioremediation is widely used to remediate organic contaminants which include:

- hydrocarbons
- halogenated organic solvents
- halogenated organic compounds
- non-chlorinated pesticides and herbicides
- nitrogen compounds
- metals (lead, mercury, chromium)
- radionuclides

Natural attenuation means remediation carried out by native population of microbes occurring in contaminated area. In natural attenuation process some factors affect the degradation process which includes: Native population of microbes and their metabolic capacity; soil physicochemical properties and chemical nature of contaminants. Some contaminants are efficiently degraded by natural attenuation process and some show null or low degradation especially aged contaminants [55].

In **Bioaugmentation,** inoculation of specific microbial strains which is having the ability to degrade the target contaminants is focused to stimulate the biodegradation. Consortium inoculation is more frequent as compared to individual strain inoculation as microorganisms in consortium show combined metabolic activities for remediation process. Also, selection of different strains for consortium should be based on their compatibility and ecological fitness in soil. To improve biodegradation efficiency of microorganisms, genetic modification for optimization of enzyme production and metabolic pathways relevant for degradation, has also been studied [56].

Various authors have been reported successful bioremediation of soil contaminated with hydrocarbon sources through bioaugmentation process. The efficiency of pollutant removal by selected microorganisms including five cultures of microbes and 3 bacterial strains- *Pseudomonas sp., Arthrobacter species and Mycobacterium* species was evaluated using hydrocarbon as sole carbon sources [57]. Bacterial consortium of *Bacillus cereus*, *Bacillus sphaericus, Bacillus fusiformis, Bacillus pumilus, Acinetobacter junii* and *Pseudomons* sp. results in degradation of diesel contaminated soil [58]. Ying et al., 2010 [59] studied PAH degradation using *Paracoccus s*p strain HPD-2 and observed 23.2% decrease in total PAH concentrations in soil after 28 days.

This process of bioaugmentation is not always an effective solution for soil contamination remediation as microbes from lab scale rarely grow and biodegrade contaminants as compared to indigenous microbes. Also, process of bioaugmentation is still not popular yet; mostly the use of microbes which are genetically engineered when added to soil may affect the ecology of the environment and also cause risk to environmental health if they persist for long time even after remediation.

And in case of **Biostimulation,** modification of the environmental conditions for the stimulation of biodegradation of target contaminants is focused. The efficiency of process can be enhanced by stimulation of degrading capacity of the indigenous microbial populations by providing them essential nutrients (organic and inorganic), available oxygen, moisture and temperature. Enrichment of soil by nutrients also called fertilization is a remediation approach in which fertilizers are added to contaminated environment for stimulation of indigenous microbial growth. Microorganism requires some key elements such as Carbon, Nitrogen, Oxygen and Phosphorous for their growth and activity, addition of fertilizers to soil fulfills their need and in turn enhance the process of biodegradation.

Studies have suggested that the carbon addition in form of pyruvate in soil stimulates the growth of microbes and increase the rate of PAH degradation [60]. Also, use of compost, organic wastes like banana skin or melon shell can enhance the rate of degradation process by mixing the compost with the contaminated soil [61]. In the treatment of organo pollutant contaminated sites mushroom compost and spent mushroom compost can be applied [62]. Efficiency of degradation by the addition of SMC was enhanced up to 82%, also it reduced the toxicity of PAH [63].

For cleaning hydrocarbons bioremediation is currently used commercially because of the capacity of microorganisms to biodegrade organic and inorganic contaminants (National Research Council 1993). Some microorganism can utilize molecular oxygen as electron acceptor and this process is called as Aerobic respiration. By utilizing oxygen, carbon is oxidized to carbon dioxide for energy generation and water molecule is formed.

Reaction: organic substrate (electron donor) + O_2 (electron acceptor) → biomass + CO_2 + H_2O + metabolites + energy.

While some microorganism cannot utilize molecular oxygen by process called anaerobic respiration in which metals such as Fe^{3+} and manganese Mn^{4+}, sulfate $SO_4{}^{2-}$, or even CO_2 can be used to accept electrons from contaminants being degraded [64]. Microorganisms involved in this remediation process include iron and manganese reducing bacteria, sulfur reducing bacteria and methanogenic bacteria. These microorganisms complete geochemical reactions such as bacterial corrosion, sulfur cycling, organic decomposition and methane production.

Reactions are as follows:

Iron reduction: organic substrate (electron donor) + Fe $(OH)_3$ (electron acceptor) + H^+ → biomass + CO_2 + Fe^{2+} + H_2O + energy.

Manganese reduction: organic substrate (electron donor) + MnO_2 (electron acceptor) + H^+ → biomass + CO_2 + Mn^{2+} + H_2O + energy.

Sulfanogenesis: organic substrate (electron donor) + SO_4^{2-} (electron acceptor) + H^+ → biomass + CO_2+ H_2O + H_2S + metabolites + energy.

Methanogenesis: organic substrate (electron donor) + CO_2 (electron acceptor) + H^+ → biomass + CO_2 + H_2O + CH_4 + metabolites + energy.

There are three ways by which contaminants can be demobilized by microorganisms:

1. Sorption of organic hydrocarbon molecules by biomass of microbes

2. Precipitation of metals (Oxidized/reduced) produced by microorganisms

3. Degradation of organic compounds bound to metals for its solubilization

Phytoremedation

Phytoremediation is a technique in which the plants are used to remediate environmental media. It is followed as a new approach for cleaning of contaminated soils and waters. It involves the interaction between plant roots and microorganisms associated with them for soil remediation. This technique is cost effective for the remediation of soil and groundwater contaminated with various types of wastes and also has less impact on environment as compared to other traditional remediation methods. All necessary nutrients are extracted from soil and water by the plants. Some plants have ability to store large amounts of contaminants, called hyperaccumulators, even though not required for plant functioning, while some can utilize these organic contaminants as a source for various physiological processes.

Plants act as filters or traps and break down the contaminants in soil or water. Process involves growing plants in contaminated area for a period required for the growth of plant to remove contaminants or facilitate immobilization or detoxification of the contaminants. Further plants can be harvested, processed and disposed off if required. This system focus on the symbiotic (Synergistic) relationships among microorganisms, plants, soil and water. Aerobic and anaerobic microorganisms both are present in the vicinity of plant roots supplied with both physical habitat and building blocks. Plant root and shoots provides colonisable surface area, organic exudates, leachates and oxygen to microbes for degradation of contaminants.

Mechanism of phytoremediation:

Contaminants are taken up by the roots of the plants which prevents the plants from toxicity. Root system provides large surface area that helps in absorption and accumulation of water and nutrients essential for growth [65]. Due to release of organic and inorganic root exudates at root-soil interface affects the number and activity of microorganisms, and in turn the availability of the contaminants through changes in chemical composition of soil. Process of phytoremediation is different for different environments and types of contaminants. Each of these processes has an effect on toxicity of contaminants and its mobility.

i. **Phytovoltalization:** In this process plants are used to transform the contaminants into volatile forms and transpire them in atmosphere with water vapor through leaves [66]. Diffusion of contaminant takes place from stem and travel through various parts before it reaches to leaves [67].

ii. **Phytoexraction:** Also called as phytoaccumulation and it refers to absorption, concentration, translocation and precipitation of contaminants from soil by the roots of plants. For this purpose hyperaccumulators are best for the removal of contaminants like Nickel, Zinc and copper. Phytoextraction process is cost effective and it removes the contaminant from soil permanently and up to 95% [68].

iii. **Rhizofilteration:** This process is used for the low concentration contaminant from groundwater, surface water and wastewater. It takes place by absorption of contaminants onto plant roots of in surrounding of root zone. Rhizofiltration is used for Chromium, Lead, Cadmium, Nickel and Zinc. Plants like sunflower, rye, tobacco, spinach, mustard and tobacco have been used for removal of contaminants significantly.

iv. **Phytostabilization:** Also called as in place activation and used for remediation of sludge, sediment and soil. This process immobilizes contaminants through adsorption, absorption and accumulation and reduces the mobility and bioavailability of the contaminant and prevents migration into the food chain. It can be used for treatment of lead, cadmium, chromium, copper, zinc and arsenic & also used to restore vegetation thereby decreasing migration and transport of contaminants.

v. **Phytodegradation:** Process involves degradation of complex to simple molecules and further incorporation into tissues of plant, also called as phytotransformation. During this process contaminants are absorbed and broken down.

vi. **Rhizodegradation:** It involves the breakdown of contaminants within the rhizosphere due to the secretion of plant exudates like sugars, amino acids, enzymes, and other compounds that can stimulate bacterial growth which carry out the degradation of contaminants. It has been investigated and found that variety of different chemicals like PAHs, Pesticides, PCBs, benzene and xylenes can be degraded by this process.

9.2 Physicochemical technologies

9.2.1 Stabilization and solidification

A process in which chemicals or reagents are mixed with contaminated soil in order to reduce toxicity and mobility of the contaminants is called stabilization. Stabilization involves trapping or binding the contaminants in soil and is permanent remedial solution. In stabilization process two types of chemicals can be used: Binder and Sorbent. Binder increases the strength of product and sorbent retains the contaminant. Examples include cement, pozzolans, pumice, ground blast furnace slag, lime, silicates etc. [69]. In solidification sufficient quantities of solidifying agents are added to contaminants for solidification. Mechanisms involved in stabilization/solidification are microencapsulation, absorption, adsorption, precipitation and detoxification. The process can be applied for PCBs, Oils, organic compounds and metals [70].

9.2.2 Soil flushing

Soil flushing is a type of in situ treatment technology in which an aqueous solution, that increases the mobility or solubility of contaminants adsorbed onto the soil matrix, is injected or infiltrated into the contaminated soil. The flushing solution consists of surfactants, cosolvents, acids, bases, oxidants, chelants, water or other solvents. Flushing is generally accompanied by other remediation technologies, namely activated carbon, biodegradation, and pump-and-treat [71].

9.2.3 Chemical reduction/oxidation

Hazardous contaminants are converted to less toxic compounds by reduction/oxidation (Redox) reactions. In this reaction, there is transfer of electrons from one to another i.e. reactant is oxidized another is reduced which results in the breaking of bonds. This process is a well established technology called as chemical redox which is used for drinking water and waste water disinfection.

9.2.4 Soil washing

Soil washing is an ex situ technique for removal of contaminants from the soil using a) physical separation and b) chemical leaching by aqueous solutions. In the initial steps of this process, the coarse particles are separated by homogenization based on the differences in their density. Since most organic and inorganic contaminants tend to bind to clay, silt, and inorganic particles, the washing processes separate the fine (small) clay and silt particles from the coarser. In the second step, the contaminants are selectively dissolved and then chemically converted or recovered. Based on the contaminant being treated, the additives and reagents that are added to water are decided [72].

9.2.5 Soil vapor extraction

Soil vapor extraction (SVE) is used to remediate unsaturated zone soil that uses application of vacuum on the soil to induce a controlled flow of air and helps in the removal of volatile and semi volatile organic contaminants. SVE is an in situ technology, although, in some cases, it can be used as an ex situ technology. In situ SVE, otherwise known as soil venting or vacuum extraction, vacuum is applied to the soil through the wells constructed near the source of contamination. Vacuum creates a negative pressure gradient, which in turn induces the controlled flow of air and remove the contaminants from the soil through an extraction well. Extracted vapor is treated before it is released into the atmosphere. The augmented airflow through the subsurface also stimulates the biodegradation of some of the contaminants, especially the less volatile substances. Advantageously, in situ SVE have greater depth of reach than other methods requiring removal of soil, the wells and the equipment are simple to install and maintain. On the other hand, ex situ SVE is a full-scale technology in which soil undergoes extraction and is placed over a grid of aboveground piping where it is subjected to vacuum in order to volatilize organic contaminants [73].

10. Thermal treatment

Treatments which involve destruction and remediation of the contaminants in soil by the use of heat including thermal destruction, thermal desorption, vitrification, and incineration [74]. Thermal treatment of contaminants results in volatilization of contaminants and removes them from the soil.

Thermal desorbers (100–300°C) are used for volatile and semi-volatile organic contaminants. The vapors formed are collected and treated in a gas treatment system. Technique is used for the removal of PCBs, pesticides, paint wastes, hydrocarbons, chlorinated solvents etc.

Vitrification is a process which involves melting and fusion of materials at temperature above 1200°C followed by rapid cooling. During this process, immobilization of nonvolatile metals within glass occurs and volatile materials are converted into vapors. Vitrification process is used to treat small quantities of contaminants and for radioactive wastes, asbestos containing waste and those that can not be treated by other technologies.

Thermal destruction involves destruction of contaminants by reduction, oxidation, hydrogenation and pyrolysis [75]. Catalytic oxidation involves the remediation of contaminants from industries by the use of electric heater, catalytic reaction, tube heat exchanger and scrubber. Pyrolysis is chemical process in which the wastes are heated in the absence of oxygen at temperatures 400 to 1200°C.

11. Advanced remediation technologies- zero valent iron nanoparticles and nanoremediation

Zero-valent iron is a reducing agent which dissolved in water in presence of oxygen is capable to oxidize organic pollutants. In the reaction, ZVI reacts with O_2 to produce H_2O_2which is reduced to water or can react with Fe^{2+}, also called as Fenton reaction, producing (hydroxyl radicals (·OH). This is able to degrade contaminants due to its oxidizing capability. Zero-valent iron nanoparticles (NZVI) are more effective remediators as compared to others [76] and also have great diversity in reacting towards different contaminants. Ability to oxidize to ferrous or ferric iron zero-valent iron provides electron for reducing other compounds making them less harmful [77]. NZVI helps in preserving characteristics of soil, enhance the process of remediation and improves the mobility and lowers the toxicity of the contaminants due to its nanometric size.

There are some studies which aims to develop new techniques in which the mixture or combination of techniques are applied for the remediation of contaminated soil like zero valent iron nanoparticles (nZVI) and compost. The application of nZVI for remediation of As and Cr showed a decrease in the concentration at contaminated industrial site and the addition of nanoparticles and compost results in decrease in aliphatic hydrocarbons upto 60% [78].

Nanotechnology use for the remediation of environment has received significant attention from community of scientists. Nanoparticles are effective against degradation of contaminants such as heavy metals [79], insecticides, dyes, organic halogenated hydrocarbons [80] and nitrates. Also, for the bioremediation of PAHs, SiO2 nanoparticles coated with a lipid derivative of choline have been used. Other nanomaterials like iron sulfide stabilized with carboxymethylcellulose is tested for immobilizing Hg in soils [81].

Nanoproducts can be applied in six main areas for remediation purpose which includes a) Photocatalytic degradation of organic pollutants [82], b) Propulsion area [83] c) biosensor technology [84] d) Water contaminant [85] e) Quick sensing of environmental stimuli [86].

Nanomaterials like nanocrystals and carbon nanotubes have provided a wide range of application to environment such as antimicrobial agents, sensors, pollution preventers etc. [87]. For example, hybrid carbon nanotubes (HCNTs), NM_s like single-walled carbon nanotubes (SWCNTs) and multiwalled carbon nanotubes (MWCNTs) have been used for the remediation of ethylbenzene.

Enzymes function as biocatalysts and are specific and effective, in bioremediation. However, enzymes have short catalytic lifetimes and less stability due to oxidation, which limit their use as an alternative to synthetic catalysts. Therefore, to increase the longevity, stability and reusability, attach them to magnetic iron NPs. This results in easy separation of the enzymes from reactants or products by applying a magnetic field. Two enzymes, peroxides and trypsin were attached to magnetic nanoparticles that increased the activity and longevity of enzymes making them more stable and efficient [88].

Hydrophobic organic contaminants get adsorb strongly to soils and are difficult to remove like polynuclear aromatic hydrocarbons (PAHs). A nanoparticle made of amphiphilic polyurethane (APU) has been synthesized for use in remediation of soil contaminated with PAHs. The particles are made of polyurethane acrylate anionomer (UAA) or poly(ethylene glycol), modified urethane acrylate (PMUA) precursor chains that can be cross-linked in water. The resulting particles have the ability to enhance PAH desorption and transport to the soil surface [89].

Uraninite can be used for bioremediation strategies of subsurface U (VI) contamination due to its small particle size, high dissolution rates and its molecular scale structure. Nanoparticles can be prepared from vegetation namely, *Gundelia tournefortii, Centaurea virgata, Reseda lutea, Scariola orientalis, Eleagnum angustifolia*, and *Noaea Mucronata*, have the ability to accumulate heavy metals. Based on the results, nanoparticles were prepared from the plants e.g. *N. mucronata* and were evaluated for the accumulation of heavy metals and found that the amount of heavy metals decreases during bioremediation process [90].

12. Sustainable remediation

Remediation of contaminated environment lays on the fact that application of any remediation technology should maximize the environmental benefit and minimize the impact through continous practices. With the focus on sustainable development as a key factor, Green remediation was introduced because it considers all effects and aspects of applying technology. Sustainable remediation reflects the perception that activities related to remediation can have wider, holistic approach with both positive and negative impacts on social, economic and environmental [91]. So this approach helps to contribute the solutions to short and long term problems generating through human health and ecosystem and facilitates risks assessment, benefits and future use for long term.

Therefore, some initiatives, efforts or progress have been observed towards disseminating sustainable approaches in the remediation and management of contaminated areas [92]. For this the Forum for sustainable remediation (SURF) was established in 2006, in collaboration between US remediation industry professionals, researchers and industries and focused on sustainable remediation. Now, other countries like UK, Brazil, China, Netherlands, New Zealand, Australia, Cananda etc. have joined and form an international forum. In addition to this SURF, the US environmental Protection Agency (USEPA), American Society for Testing and Materials (ASTM), Interstate Technology and Regulatory Council (ITRC) and Network for Industrially Contaminated Land in Europe (NICOLE), have developed focus on the application and evaluation of sustainable remediation.

Common issues like social equity, sustainability tripod, long term efficiency, democratic process and ecological integrity are generally addressed in the application of sustainability remediation. For this, analytical methods with the identification of indicators, metrics and tools are used for evaluation of the sustainable remediation. These methods help in decision making about the aspects of social, economic and environment for assessment and application of sustainable remediation project [93].

Although advances have occurred in area of sustainable remediation, problems and challenges related to adoption and acceptability of the sustainable remediation have been observed. There is no such method that can be used for standardization and assessment of degree of sustainability and the existing methods does not fulfill

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the criteria of sustainability assessment in remediation of contaminated areas [93]. In order to implement the sustainable remediation approach, a new way of thinking including social, economic and environmental variables should be considered as fundamental factor. Industries, government and academicians all should play key role in ensuring sustainable remediation approach for the incorporation of sustainability projects in developed and developing countries.

13. Conclusions

In this chapter, the main perspectives related to the development of technologies for soil remediation have been discussed. One of the approaches that are widely discussed is the use of green technologies as phytoremediation, biostimulation and biodegradation. Nanotechnology in the degradation of contaminants and the importance of sustainable remediation approaches are also currently under discussion.

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