Chapter 5
Bioremediation of Waste Gases and Polluted Soils

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Abstract The recent expansion of human industrial activity, including mining, smelting, and synthetic compounds, has increased the amount of toxic harmful gases released in the atmosphere, water, and soil which contaminated the environment directly and indirectly. There has been a significant rise in the levels of heavy metals (Pb, As, Hg, and Cd) and toxic gases due to their increased industrial usage, causing a severe concern to public health as well as enviornment. Accumulation of these heavy metals generates oxidative stress in the body, causing fatal effects to important biological processes leading to cell death. The ability to prevent and manage this problem is still a subject of much debate, with many technologies ineffective and others too expensive for practical large-scale use, especially for developed and developing nations where major pollution arising. Currently, green technologies require pressure to develop the management of contaminated sites which benefit the society directly and indirectly. Bioremediation, is another biological mechanism of waste recycling in another form which can be used and reused by other organisms. Therefore, to reduce the potential toxicity of any pollutant in the environment, by degradation, change, bioremediation is the form of bio-systems through microbes and plants, by stabilizing these undesirable substances into less harmful forms.

Keywords Bioremediation · Waste gases · Microbes · Plants · Pollution · Nanotechnology

5.1 Introduction

Bioremediation or natural remediation is a cost-effective eco-friendly biotechnological process. It includes the utilization of living beings such as plants and microscopic bacteria to remediate and stabilize polluted areas (Anyasi and Atagana 2011; Perelo 2010; Sharma 2012). In bioremediation, few advances have been acknowledged with the assistance of the different field of molecular biology, microbiology, environmental engineering, biochemistry, chemical and analytical chemistry, etc. The process of bioremediation is an alternative to incineration process and use of catalytic barrier and absorbents. It involves only biological agents such as plants and microorganisms to change and degrade contaminants into less hazardous or almost non-hazardous substances (Dua et al. 2002; Park et al. 2011). Different living

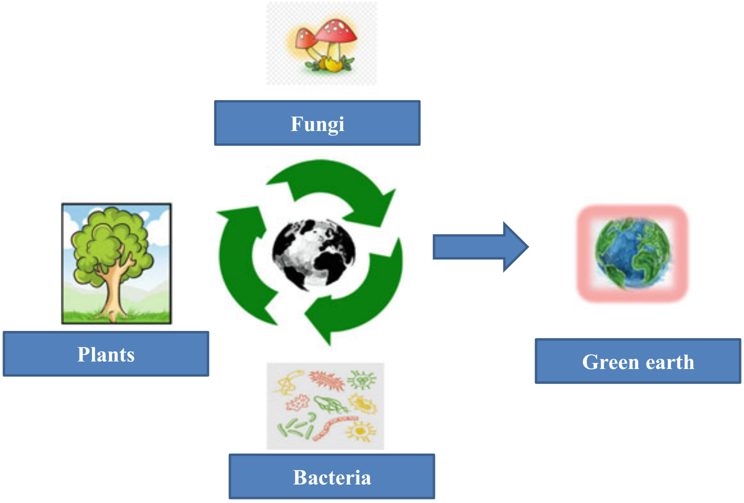

Fig. 5.1 Bioremediation through microbes and plants

organisms such as bacteria, fungi, yeast, algae, and plants have been used as natural operators to proficiently bioremediate hazardous pollutants and clean up the environment (Vidali 2001; Strong and Burgess 2008). With the increment in the population, the demand for food supply has likewise increased. This created pressure on natural resources. Thereby, farmers are forced for intensive agriculture by utilizing more and more pesticides to get more yields. But utilization of these pesticides degrades the texture nature and quality of the soil. Also, excess input of these wastes had prompted deficiency of clean soil and water and thus diminishing crop yield (Kamaludeen et al. 2003). So, bioremediation is being used as an effective method to clean up the environment from these hazardous substances such as hydrocarbons, organic compounds and solvents, nitrogenous compounds, herbicides, pesticides, nitrogenous waste gases, and heavy metals (Fig. 5.1) (Park et al. 2011). The contaminants and the hazardous substances present in the environment act as energy sources for the microbes and provide energy to carry out their metabolic activities (Tang et al. 2007). Microorganisms not only play a significant role in regulating the biogeochemical cycles (Griggs et al. 2013) but also help to sustain clean air by diminishing environmental pollutants from the environment (Morris et al. 2011) keeping us healthy. Also, they protect plants from the diseases and help them to develop and grow (Pineda et al. 2017). A widespread list of the microbes that bring about bioremediation processes is available (Satyanarayana et al. 2012; Prakash et al. 2013; Abou Seeda et al. 2017).

5.2 Need of Bioremediation

Nowadays, environmental pollution is a serious issue for mankind. Remediation approaches, such as physical and chemical methods, are insufficient to alleviate contamination issues in view of the constant age of novel recalcitrant toxins because of anthropogenic exercises. Bioremediation could find a better solution to this issue. It is an eco-friendly and socially acceptable alternative to conventional remediation approaches utilizing microbes (Dangi et al. 2018).

5.3 Bioremediation of "Composting" Soils

The dynamic "composting" of soils debased with (poly) aromatic hydrocarbons (PAHs) and alkanes in combination with critical amounts of composting feedstock materials is considered as a significant bioremediation treatment approach (Antizar-Ladislao et al. 2007; Sasek et al. 2003; Semple et al. 2001; Tran et al. 2018). This approach utilizes the addition of the known amount of compost (or other organic residues) to defiled soils by improving pH, porosity, oxygen diffusion (Semple et al. 2001), and contaminant desorption (Wu et al. 2013). This is possible as composts are generally rich in nutrients such as carbohydrates, nitrogen, and phosphorus that are potentially important in accomplishing an ideal activity of pollutant degraders indigenous to polluted soils (Komilis and Timotheatou 2011; Sarkar et al. 2005). Furthermore, compost/manure contains several different microorganism populations which may degrade organic contaminants present in the environment (Scelza et al. 2007). A few examples of the utilization of "mature" manure for the application of soil bioremediation can be found in the literature. For instance, Gomez and Sartaj (2013) used "mature" manure for the bioremediation of total petroleum hydrocarbon (TPH) from the polluted soil in cold conditions.

5.4 Enzymes Used in Bioremediation

Degradation of contaminants from the environment with the assistance of microorganisms is a slow process, which diminishes the achievability of the bioremediation process in actual practice (Ghosh et al. 2017). In the past few years, to overcome these limitations, microbial enzymes harvested from their cells have been used to carry out bioremediation when contrasted with utilizing the whole microorganisms (Thatoi et al. 2014). Enzymes are proteinaceous biological macro-molecules which act as a catalyst to carry out a number of biochemical reactions involved in the pollutant degradation pathways (Kalogerakis et al. 2017). In contrast to microbes, enzymes are more specific to their substrate and versatile in nature in light of their smaller size (Gianfreda and Bollag 2002). The process of bioremediation based on purified and partially purified enzyme does not rely upon the development of a specific microorganism in the polluted environment; however, it relies on the catalytic activity of the enzyme present in the microbes (Ruggaber and Talley 2006). In insufficient nutrient soil, bioremediation can be conceivable by utilizing a purified enzyme. Enzymatic biotransformation is a safer process as toxic side products are not produced during the process.

5.5 Bioremediation of Petroleum Hydrocarbons

Microbial bioremediation is a broadly utilized method for treating petroleum hydrocarbon contaminants from the environment including both terrestrial and aquatic ecosystems (Abbasian et al. 2015; Varjani and Srivastava 2015). In the last decades, several research studies based on biodegradation of hydrocarbon pollutants have been done (Sajna et al. 2015; Varjani et al. 2015; Varjani and Upasani 2016). Microorganisms are ubiquitous in nature and play a significant role in maintaining ecosystem balance to develop a sustainable environment (Varjani and Srivastava 2015). Microorganisms such as bacteria, fungi, and algae are accounted for their capacity to degrade hydrocarbon pollutants (Wilkes et al. 2016). Bacteria are considered as primary degraders and play a crucial role in degrading petroleum pollutants from the environment (Abbasian et al. 2015; Meckenstock et al. 2016). Few examples of bacteria that act as hydrocarbon degraders include *Acinetobacter, Achromobacter, Azoarcus, Micrococcus, Arthrobacter, Brevibacterium, Flavobacterium, Corynebacterium, Nocardia, Cellulomonas, Marinobacter, Stenotrophomaonas, Ochrobactrum, Pseudomonas, Vibrio,* etc. (Varjani and Upasani 2016). Besides, fungi that play a crucial role in degrading petroleum hydrocarbon pollutant include yeast, *Candida, Penicillium, Fusarium, Aspergillus, Neosartorya, Amorphoteca, Graphium, Talaromyces, Paecilomyces, Rhodotorula, Sporobolomyces, Pichia, Yarrowia, Pseudozyma,* etc. (Sajna et al. 2015; Wilkes et al. 2016). The essential criteria needed to understand the scope and strategies of pollutant removal via bioremediation include the understanding of properties of crude oil, mechanism, the fate of oil, the concerned environment, and factors that control its rate.

5.6 Bioremediation of Agricultural Waste

Globally, every year, about 38 billion metric tons of organic waste of human, livestock, and crops are produced. Eco-friendly disposal of this waste from the environment has become a global priority. Accordingly, in recent years, much attention has been paid to develop efficient and cost-effective strategies to convert these nutrient-rich organic wastes into valuable products for sustainable land practices. With the help of microorganisms and earthworms, this can be achieved. They help in the degradation of organic matter by molding to the substrate and altering the biological activity (Dominguez 2004; Suthar 2007). Several earthworms, such as *Eudrilus eugeniae, Eisenia fetida* (Savigny), *Perionyx sansibaricus* (Perrier), and *Perionyx excavatus* (Perrier), have been recognized as detritus feeders and potentially minimize the anthropogenic waste from the various sources (Garg et al. 2006).

5.7 Types of Bioremediation

Bioremediation can be categorized into two types: In situ bioremediation and ex situ bioremediation (Fig. 5.2) (Marykensa 2011). In situ bioremediation involves treatment of pollutants, e.g., contaminated water or soil at the site of occurrence. In contrast, ex situ bioremediation involves treatment of pollutants, e.g., contaminated soil or water once excavated from its initial site (Megharaj et al. 2014).

5.7.1 In Situ Bioremediation

In this type of bioremediation, contaminated soil is treated at the site of contamination where it occurred without its removal and transportation, for example, natural

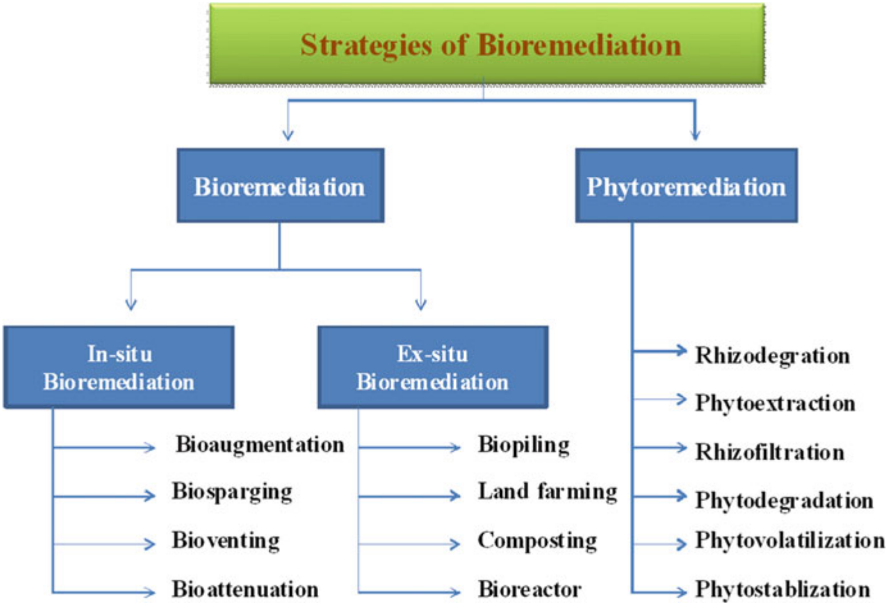

Fig. 5.2 Types of bioremediation techniques

attenuation, bio-venting, and bio-sparging. This method is considered as a natural biogeochemical process.

5.7.1.1 Bioaugmentation

It is the process of speeding up the rate of degradation of contaminants by the addition of indigenous or exogenous microorganisms to the contaminated sites containing the target contaminant. The addition of these microbial populations brings about catabolic activity and enhances the bioremediation process (Andreoni and Gianfreda 2007).

5.7.1.2 Bioattenuation

It is a set of naturally occurring phenomena used to diminish soil pollutants. It evacuates the degradation of pollutants with the help of several processes, such as by indigenous microorganisms, dispersion, chemical transformation, dilution, volatilization, and stabilization of contaminants (Guarino et al. 2017). Petroleum hydrocarbons can remain buried in soil for more than 50 years after spillage, despite treatment naturally using this strategy for remediation of TPH in freezing soil (Mair et al. 2013; Jiang et al. 2016).

5.7.1.3 Bioventing and Bio-Sparging

It is a type of bioremediation process that utilizes controlled airflow into the contaminated soil of an unsaturated zone to improve degradation activities of indigenous microorganisms. Controlled airflow rate guarantees that the contaminants get reduced because of microbial degradation instead of volatilization (Azubuike et al. 2016). Furthermore, bio-sparging is like bio-venting and aids in the movement of volatile pollutants from a saturated area to an unsaturated area (Azubuike et al. 2016).

5.7.2 Ex-Situ Bioremediation

It involves the treatment of pollutants away from the site of their occurrence. It includes excavation and transportation of contaminated soils to a protected and reliable place for their efficient treatment. On the basis of nature, severity, and geographical location of the contamination, ex situ bioremediation can be of several types. This method is a controlled remediation strategy where the treatment conditions can be overseen appropriately. A few investigations have reported the fruitful application of ex situ bioremediation methodologies for oil-polluted soil in low temperatures (Tomei and Daugulis 2013; Jeong et al. 2015).

5.7.2.1 Bio-Pile

In this process where excavated polluted soil is piled temperature and moisture control and nutrient amendments. The process involves temperature control mechanism which keeps up ideal situations even in low temperatures. This successfully helps to remediate polluted components from the cold environments also (Chemlal et al. 2012; Whelan et al. 2015).

5.7.2.2 Composting

It is the procedure of converting organic matter into humus-like non-toxic substances. During the process, active indigenous or augmented microorganisms catalyze the reaction and generate high temperature to optimize microbial activities and thus bring about degradation of the contaminants as the compost get matured (Kästner and Miltner 2016). For the successful implementation in low temperature composting can be equipped with bio-pile facilities (Sanscartier et al. 2009).

5.7.2.3 Land Farming

It is a process in which contaminated soil is spread in a bed and made accessible for biological treatment. It includes a broad range of environmental conditions, such as extreme cold and arid soil (Tomei and Daugulis 2013). Presently, for efficient degradation of pollutants, land farming methods have been improved by incorporating bioaugmentation and adding fertilizers, water, and surfactants (Jeong et al. 2015).

5.7.2.4 Bioreactor

It is a controlled system involving biological processes that can convert raw materials into useful products. In this system, a vessel (reactor) is utilized that brings about bioremediation. Bioreactors can be operated in different feed modes, such as batch, semi-continuous, and continuous. Besides, several physical (such as pH, temperature, aeration, and agitation) and biological (such as bacterial inoculums, nutrients, and substrate) parameters can be controlled in the bioreactor (Tomei and Daugulis 2013).

5.8 Phytoremediation

Though the studies were carried out in 1950s, the term “phytoremediation” was coined in 1991. Phytoremediation is a process that utilizes plants to remove contaminants from the environment (Kumar et al. 2011; Sharma and Pandey 2014). Green plants, such as herbs (e.g., *Brassica juncea*, *Thlaspi caerulescens*, and *Helianthus annuus*) and woody species (e.g., *Salix* spp. and *Populus* spp.), remove various contaminants (like heavy metals, organic compounds, and radioactive compounds in soil or water) from the environment by accumulating and transporting the contaminants via translocation (Tahir et al. 2015) (Fig. 5.3).

5.8.1 *Rhizodegradation*

Rhizodegradation occurs at a radical level of plant in a soil area called rhizosphere where biodegradation of the organic contaminants takes place. The process occurs with the help of bacteria, fungi, and yeasts. As root is a rich source of carbon and nitrogen, they expand the effectiveness of extraction and removal of contaminants (Leung et al. 2013; Liu et al. 2014).

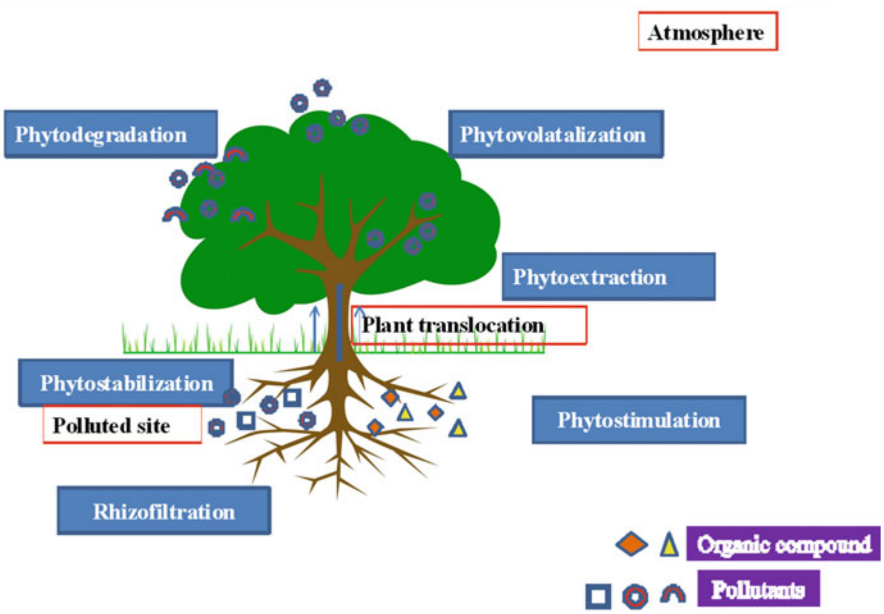

Fig. 5.3 Process of phytoremediation

5.8.2 Phytoextraction

It is an in situ strategy used for the treatment of contaminated soils (Alì et al. 2013; Van Oosten and Maggio 2014). Phytoextraction involves absorption of contaminants via roots and then their transportation and accumulation in shoots and leaves (Mahar et al. 2016; Sreelal and Jayanthi 2017). Plants engaged with this procedure should ideally have the ability to accumulate contaminants and produce high biomass.

5.8.3 Rhizofiltration

Rhizofiltration comprises biodegradation of organic and inorganic pollutants from the surface water, groundwater, or wastewater via adsorption of pollutants on the roots or around the root area (Zhang et al. 2009). This strategy is applied for the removal of heavy metals from the soil (Susarla et al. 2002) as they are maintained at the root level, and further, these elements will be harvested. The plants that are used in this process are tolerant of metal. They have a high absorption surface and tolerate hypoxia (e.g., *Salix* spp., *Populus* spp., *Brassica* spp.).

5.8.4 Phytodegradation

During phytodegradation, organic contaminants, after assimilation by the root framework, are degraded by the enzymatic activity, or they will be consolidated into the plant tissues (Alì et al. 2013; Sharma and Pandey 2014; Van Oosten and Maggio 2014). The enzymes that carry phytodegradation include peroxidase, dehalogenase, nitroreductase, nitrilase, and phosphatase (Winquist et al. 2013; Deng and Cao 2017).

5.8.5 Phytovolatilization

In this process, the contaminants are absorbed from the roots of the plant, transported through the xylem, and discharged into the atmosphere from the aerial parts of the plant in less toxic forms. The process can be applied to contaminants present in the soil, sediment, or water, particularly for organic contaminants like trichloromethane, tetrachloroethane, and tetrachloromethane (San Miguel et al. 2013) and for some high-volatile metals such as Hg and Se (Wang et al. 2012; Van Oosten and Maggio 2014).

5.8.6 Phytostabilization

The method is valuable for the treatment of Cd, Cu, Pb, As, Cr, and Zn (Zhao et al. 2016; Yang et al. 2016). The advantage of this technique consists of the changes of soil chemical composition induced by the presence of the plant itself, and such changes can facilitate the absorption or cause the precipitation of metals on the roots (Zhang et al. 2009). This process decreases contaminant versatility, avoiding movement into the groundwater and lessen the bioavailability in the food chain (Alì et al. 2013; Sharma and Pandey 2014).

5.8.7 Bioremediation of Industrial Pollution by Plants

Air pollution means "the presence of harmful or toxic substances in the atmosphere, which adversely effects on both living and non-living things." Main air pollutants are sulfur dioxide (SO_2), nitrogen dioxide (NO_2), particulate matters (PMs), volatile organic compounds (VOCs), and ground-level ozone (O_3) (Archibald et al. 2017). Bioremediation is an effective method because of its cheaper cost in comparison to different physicochemical techniques (Cheng et al. 2012; Philp et al. 2005). Exchange of gases is required by autotrophic plants for their survival; during this process, gaseous pollutants can be adsorbed/absorbed (Gawronski et al. 2017). Different policies, strategies, and models have been implemented or proposed for the removal of air pollution (Macpherson et al. 2017).

5.9 Remediation of Particulate Matters

PMs are the most hazardous pollutants in developing countries. The physical characteristics of leaves such as stomata, leaf shape, and trichomes or hairs significantly affect the collection of PM. More accumulation of $PM_{2.5}$ was reported in needle leaves than broader leaves (Terzaghi et al. 2013; Chen et al. 2017). Trichomes of the leaf have been demonstrating to high $PM_{2.5}$ accumulations. Accumulation of $PM_{2.5}$ was positively correlated with the density of trichomes of leaves and some plant with maximum hairs such as *Broussonetia papyrifera, Ulmus pumila*, and *Catalpa speciosa* were able to collect high $PM_{2.5}$ than those plants which have few hairs (Chen et al. 2017). Teper (2009) observed that needles of *Pinus sylvestris* accumulate 18,000 particles of mineral mm^{-2}. In *Hedera helix*, upper leaves received approximately 17,000 particles mm^{-2} (Ottele et al. 2010). Nowak et al. (2014) showed that trees present in the cities are responsible for the removal of fine particles from the atmosphere, which improved the quality of air and human health also. It is already demonstrated that outdoor plants can phytoremediate aerosol PM (Sæbø et al. 2012). In the period of 3 years, Popek et al. (2013) investigated that

13 woody species captured the sum amount of PMs ranging from 7.5 mg/cm^2 through *Catalpa bignonioides* to 32 mg/cm^2 through the leaves of *Syringa meyeri*.

5.10 Remediation of VOCs

The elimination of pollutants was plant-mediated; therefore, the expulsion of VOCs by the absorption of plants is through the process of normal gas exchange or absorption and adsorption with the help of plant surface (Omasa et al. 2002; Yoo et al. 2006; Ahmad et al. 2019). A hypothetical process involves aerial plant parts for the absorption of VOCs, where they can possibly enter through the Kelvin cycle, and eventually convert into amino acids through the metabolic process (Peterson et al. 2016). VOCs can undergo storage, excretion and degradation inside the plant system (Weyens et al. 2015).

5.11 Remediation of Other Harmful Gases

The concentration of atmospheric CO_2 has increased rapidly in recent decades. Contribution of CO_2 represents more than 50% of the total warming potential in all greenhouse gases (Cox et al. 2000). In the present scenario, the continuous change of climate is creating a series of problems for future generations. Various chemical and biological technologies have been introduced to remove CO_2 from the atmosphere. Many researchers have confirmed over the past few decades that plants extract CO_2 by photosynthesis (Torpy et al. 2018). Through many researches, it has been investigated that vegetative surfaces have the potential to reduce NO_2 (Chaparro-Suarez et al. 2011). Some plants can be survived in SO_2-polluted environment (Chung et al. 2010). From the air, O_3 can be removed through chemical reactions which react with reactive compounds, especially mono-terpenes that rely upon the vegetation (Di Carlo et al. 2004). Various diterpenoid organic compounds which are semi-volatile are released from the trichomes of leaves responsible for the removal of O_3 (Jud et al. 2016).

5.12 Microbial Remediation of Air Pollution and Soil

Generally, bioremediation is a process which uses the microorganisms to convert or degrade contamination into nontoxic products (Antizar-Ladislao 2010). Microorganisms such as fungi and bacteria are also responsible for bio-transforming or biodegrading pollutants into less toxic and non-toxic materials, called as microbial biodegradation (Ward et al. 1980; Ma et al. 2016). Microorganisms in the form of heterotrophs present almost everywhere, including plant shoot and roots. It has been reported that both shoots and roots are used to remediate the pollutants from the air (Weyens et al. 2015; Gawronski et al. 2017). However, a small credit has been granted to microbial activity. Bioremediation depends on the ability of microbes to breakdown the organic pollutants in the existence of optimal conditions of the environment and an adequate supply of nutrients and electron receiver (Adams et al. 2015). It should be emphasized that a soil treatment technique is not only aimed at reducing the concentrations of pollutants but also restoring the quality of soil (Epelde et al. 2010; Barrutia et al. 2011; Pardo et al. 2014). The optimum temperature typically means high levels of microbial action, which in turn possibly prioritizes increased metabolism of organic pollutants (Goiun et al. 2013).

Over the last several decades, many studies have been investigated that the microbial farming system responsible for the decrease of CO_2 from the atmosphere (Raeesossadati et al. 2014; Fernández et al. 2012). Microalgae have gained increasing interest with the recycling of CO_2 and bioremediation because of its potential to grow on non-agricultural lands and in saltwater. Weyens et al. (2010) used engineered endophytes to decrease the toxic metals and organic pollutants from polluted environments by phytoremediation. Various researchers have identified the possibility of epiphytic and endophytic microbiota, which reside on the leaves and shoots (and it is known as the phyllosphere) to remove VOCs (Khaksar et al. 2016; Sandhu et al. 2007). In addition to leaves of the plant, rhizospheric microbes also contribute to the depletion of VOCs from the internal environment (Llewellyn and Dixon 2011). Popek et al. (2015) demonstrated that trees and shrubs, forming a biofilter on the path of PM flow, have reduced the amount of PM about 50% that accumulates on the foliage of distant trees in the park. Sulfur oxidizing bacteria like *Paracoccus* and *Begiatoa* are capable of reducing sulfur compounds such as hydrogen sulfide (H_2S) to inorganic sulfur and thiosulfate to form sulfuric acid (H_2SO_4) (Pokoma and Zabranska 2015).

5.13 Role of Nanotechnology in Bioremediation of Industrial Air Pollution

Due to rapid urbanization, industrialization and increasing population pressure, are the major concerns that poses environmental pollution and human risks. Environmental pollution caused by a release of several air pollutants such as CO, chlorofluorocarbons, volatile organic compounds, hydrocarbons, and nitrogen oxide from the industries as well as other sources poses a human risk to several incurable disorders (Khan et al. 2014; Das et al. 2015; Krug 2009). Bioremediation is an eco-friendly, sustainable and economical approach that effectively restores polluted environments by utilizing microorganisms, by breaking down or transforming harmful to less toxic or non-lethal format. Meanwhile, living agents are utilized in the process of bioremediation to clean up the contaminated habitat/site, e.g., bacteria and fungi. Besides, these biomediators' advancements in science and technology gave birth to several new nanobiotechnological techniques. Nanotechnology refers to the pattern, characterization, formulation, and utilization of structures by changing shape and size at the nanometer scale (Hussain and Hussain 2015; Danish and Hussain 2019). But, due to the vast diversity of pollutants, no single bioremediation technique could serve as a "*silver bullet*" to recover the polluted environments.

5.13.1 Role of Nanotechnology in the Remediation of Toxic Gases Released from Industries

It produces novel materials with unique properties having small scale and high surface/volume ratio. These properties enable researchers to develop highly detailed and precise nanosensor appliances that significantly monitor environmental pollution. Besides, nanomaterials not only replace toxic material with a safety one but also react with impurity and degrade it into a non-lethal product (Falahi and Abbasi 2013; Chirag 2015; Ngo and Van de Voorde 2014). Also, coating technology involving nanostructures is also used to clean up such pollutants that show resistance as they possess self-cleaning features. Remediation using nanotechnology reduces air pollution in three different ways, namely adsorption of contaminants by using nano-absorptive materials, deterioration of contaminants by using nanocatalysis, and filtration/separation of contaminants by using nanofillers.

5.13.1.1 Nano-Adsorptive Materials

Nano-adsorbent could be used to clean up air pollution. Carbon nanostructures (e.g., fullerene, carbon nanotubes, graphene, and graphite) that have been used for industrial applications due to their high selectivity, affinity, and capacity (Bergmann and Machado 2015) are used as adsorbents to clean up air pollution. The addition of different functional groups to these nanostructures provides new receptive exterior sites or structure bonds for adsorption, making the process more effective by maximizing the adsorption volume of the system (Gupta and Saleh 2013; Wang et al. 2013). For example, the surface of CNTs with generous amine groups provides multiple chemical sites for CO_2 adsorption which makes CNTs ingest more CO_2 gases at low-temperature range (20–100 °C) and thus helps to reduce greenhouse gases from the environment (Su et al. 2009). Similarly, fullerene and graphene also speed up the process of adsorption to reduce greenhouse gases (Dong et al. 2015; Petit and Bandosz 2009).

5.13.1.2 Nanocatalyst Materials

The degradation of pollutants by utilizing semiconductor materials improves photocatalytic remediation by increasing surface area resulting in enhanced reaction efficiency (Özkar 2009). For example, the photocatalytic properties of titanium dioxide nanoparticles (TiO_2) are efficient to convert atmospheric contaminants such as nitrogen oxides and other pollutants into less toxic species (Shen et al. 2015). Further, TiO_2 nanoparticles are also used as an antibacterial agent. Besides, TiO_2 other nanocatalysts include nanogold-based catalysts (Singh and Tandon 2014), ZnO photocatalyst (Yadav et al. 2017), and bismuth oxybromide (BiOBr) nanoplate microsphere catalysts (Ai et al. 2009).

5.13.1.3 Nanofilters

Another approach for cleaning up air pollutants is the use of nanostructured sheets that have poured small abundance to separate contaminants from the source. Nowadays, nanofiber-coated filter media are used to filter air pollutants such as dust at industrial plants (Muralikrishnan et al. 2014). Bioaerosols, aerosols of biological origin such as viruses, bacteria, and fungi, are also air pollutants that cause many diseases such as allergies and infections. In this regard, silver nanoparticles and copper nanoparticles filters are extensively used in air filtration technology as antimicrobial agents (Lee et al. 2010).

5.14 Heavy Metals (HMs) in the Environment

Environmental pollution is one of the major challenges in modern human welfare (Ali and Khan 2017). Environmental contaminations and pollutants caused by heavy metals are a threat to the environment and are of serious concern (Alì et al. 2013; Hashem et al. 2017). Rapid industrialization and urbanization have caused contamination of the environment by heavy metals, and their rates of mobilization and transport in the environment have greatly accelerated since the 1940s (Khan et al. 2004; Merian 1984). Their natural sources in the environment are weathering of metal-containing rocks and volcanic eruptions, while industrial emissions, mining, smelting, and agricultural activities like the application of pesticides, phosphate, and other inorganic fertilizers are prominent anthropogenic sources.

According to Csuros and Csuros (2002), heavy metal is defined as “metal with a density greater than 5 g/cm^3 (i.e., specific gravity greater than 5).” The term “heavy metals” is often used as a group name for metals and semimetals (metalloids) that have been associated with contamination and potential toxicity or ecotoxicity (Duffus 2002). Very recently, we have proposed a broader definition for the term, and heavy metals have been defined as “naturally occurring metals having an atomic number greater than 20 and an elemental density greater than 5 $g \cdot cm^{-3}$”.

5.14.1 Heavy Metals: Essential and Non-essential

Regarding their roles in biological systems, heavy metals are classified as essential and non-essential. Essential heavy metals are important for living organisms and may be required in the body in quite low concentrations, but non-essential heavy metals have no known biological role in living organisms. Examples of essential heavy metals are Mn, Fe, Cu, and Zn, while the heavy metals Cd, Pb, and Hg are toxic and are regarded as biologically non-essential (Ramírez 2013; Jović et al. 2012; Rahim et al. 2016; Türkmen et al. 2009). The heavy metals Mn, Fe, Co, Ni, Cu, Zn, and Mo are micronutrients or trace elements for plants. They are essential for growth and stress resistance as well as for biosynthesis and function of different biomolecules such as carbohydrates, chlorophyll, nucleic acids, growth chemicals, and secondary metabolites (Appenroth 2010). Either deficiency or excess of an essential heavy metal leads to abnormalities or diseases in organisms. However, the lists of essential heavy metals may be different for different groups of organisms such as plants, animals, and microorganisms. It means a heavy metal may be essential for a given group of organisms but nonessential for another one. The interactions of heavy metals with different groups of organisms are much complex (Chalkiadaki et al. 2014).

5.15 Sources of Industrial Wastes in the Environment

Sources of heavy metals in the environment can be natural, geogenic/lithogenic, and anthropogenic. The natural or geological sources of heavy metals in the environment are weathering of metal-bearing rocks and volcanic eruptions. The global trends of industrialization and urbanization on Earth have led to an increase in the anthropogenic sharing of heavy metals in the environment (Nagajyoti et al. 2010). The anthropogenic sources of heavy metals in the environment are mining and industrial and various agricultural activities. These metals (heavy metals) are released during mining and extraction of different elements from their respective ores. Heavy metals released to the atmosphere during mining, smelting, and other industrial processes return to the land through a dry and wet deposition. Discharge of wastewater such as industrial effluents and domestic sewage add heavy metals to the environment. Application of chemical fertilizers and combustion of fossil fuels also contribute to the anthropogenic input of heavy metals in the environment. Regarding contents of heavy metals in commercial chemical fertilizers, phosphate fertilizers are particularly important.

In general, phosphate fertilizers are produced from phosphate rock (PR) by acidulation. In the acidulation of single superphosphate (SSP), sulfuric acid is used, while in acidulation of triple superphosphate (TSP), phosphoric acid is used (Dissanayake and Chandrajith 2009). The final product contains all of the heavy metals present as constituents in the phosphate rock (Mortvedt 1996). Commercial inorganic fertilizers, particularly phosphate fertilizers, can potentially contribute to the global transport of heavy metals (de López Carnelo et al. 1997). Heavy metals added to agricultural soils through inorganic fertilizers may leach into groundwater and contaminate it (Dissanayake and Chandrajith 2009). Phosphate fertilizers are particularly rich in toxic heavy metals. The two main pathways for the transfer of toxic heavy metals from phosphate fertilizers to the human body are shown below (Dissanayake and Chandrajith 2009):

(a) Phosphate rock⟶fertilizer⟶soil⟶plant⟶food⟶human body.
(b) Phosphate rock⟶fertilizer⟶water⟶human body.

5.15.1 Human Exposure to Industrial Wastes and Heavy Metals

Humans are exposed to toxic heavy metals in the environment through different routes including ingestion, inhalation, and dermal absorption. People are more exposed to toxic metals in developing countries. Generally, people have no awareness and knowledge about exposure to heavy metals and their consequences on human health, especially in developing countries (Afrin et al. 2015). They may be exposed to heavy metals in the working place and in the environment. Human exposure to toxic chemicals in the working place is called occupational exposure, while exposure to such chemicals in the general environment is called non-occupational or environmental exposure. Workers are exposed to heavy metals in mining and industrial operations where they may inhale dust and particulate matter containing metal particles. People extracting gold through the amalgamation process are exposed to Hg vapors. It has been reported that welders with occupational prolonged exposure to welding fumes which had significantly higher levels of the heavy metals Cr, Ni, Cd, and Pb in blood than the control have shown increased oxidative stress (Mahmood et al. 2015). Cigarette smoking is also a principal source of human exposure to Cd (Järup 2003) and other toxic heavy metals present in the tobacco leaves.

Ingestion of heavy metals through food and drinking water is a major exposure source for the general human population. Industrialization, urbanization, and rapid economic development around the globe have led to intensification in industrial and agricultural activities. Such activities may cause contamination of water, air, and soils with toxic heavy metals. Growing human foods in heavy metal-contaminated media lead to bioaccumulation of these elements in the human food chains, from where these elements ultimately reach the human body.

5.15.2 *Bioaccumulation and Biomagnification of Heavy Metals in the Human Food Chains*

Humans are omnivorous, they may be exposed to toxic heavy metals through different food items such as fish, cereals, and vegetables. Contamination of these heavy metals in freshwater bodies such as rivers, lakes, and streams leads to bioaccumulation in freshwater fish, while such contamination in agricultural lands leads to bioaccumulation in agricultural crops. Contamination of human food chains with toxic heavy metals poses a threat to human health. Certain examples from the twentieth century have shown that such contamination is a serious issue for human health. Minamata disease (MD) and *itai-itai* disease both in Japan were caused by the consumption of Hg-contaminated fish and Cd contaminated rice, respectively. Figure 5.4 depicts the transfer of heavy metals from contaminated fish to humans.

Although biomagnifications of heavy metal is a controversial issue in metal eco-toxicology, numerous studies have reported biomagnifications of heavy metal in certain food chains. In the case of biomagnifications of these metals in food chains, organisms at higher tropic levels in the food chains are at greater risk. Higher concentrations of trace metals in organisms of higher tropic levels as a result of biomagnifications can pose a health risk to these organisms or to their human consumers (Barwick and Maher 2003). To protect human health from the harmful effects of toxic heavy metals, human food chains should be constantly monitored for bioaccumulation and biomagnifications of heavy metals. However, nondestructive

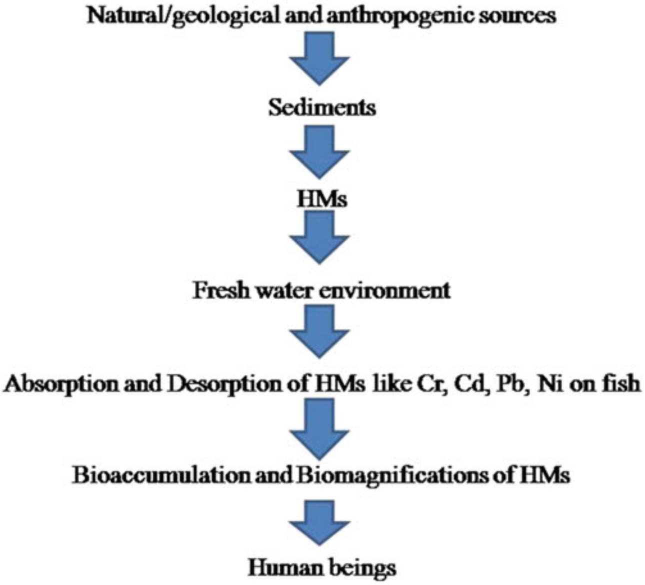

Fig. 5.4 Transfer of HMs from freshwater fish to humans in the human food chain

sampling techniques and use of environmental biomarkers should be opted to avoid loss of biota due to analysis. Furthermore, in order to avoid contamination of food chains with heavy metals, untreated municipal and industrial wastewater should not be drained into natural ecosystems such as rivers and farmlands (Balkhair and Ashraf 2016).

5.15.3 *Toxicity of Heavy Metals*

Although some heavy metals, called essential heavy metals, plays an important role in biological systems, they are generally toxic to living organisms depending on the dose and duration of exposure. It is a well-known fact in toxicology that "excess of everything is bad." Nonessential heavy metals (Cd, Pb, and Hg) and metalloids (As, etc.) may be toxic even at quite low concentrations. Essential heavy metals are required in trace quantities in the body but become toxic beyond certain limits or threshold concentrations. For some elements, the window of essentiality and toxicity is narrow. Heavy metals have been reported to be carcinogenic, mutagenic, and teratogenic. They cause the generation of reactive oxygenic species (ROS) and thus induce oxidative stress. Oxidative stress in organisms leads to the development of various diseases and abnormalities. Heavy metals also act as metabolic poisons. Heavy metal toxicity is primarily due to their reaction with sulfhydryl (SH) enzyme systems and their subsequent inhibition, e.g., those enzymes involved in cellular energy production (Csuros and Csuros). The reaction of heavy metal (M) with glutathione (GSH), (which is an important antioxidant in the body). Here, the metal replaces H atoms from SH groups on two adjacent glutathione molecules. The combination of these two glutathione molecules leads to the formation of strong bond with the metal that deactivates them for further reactions:

2 glutathione + metal ion (M^{2+}) $\longrightarrow$M (glutathione)$_2$ + $2H^+$ (3)

5.15.4 *Effects of Toxic Heavy Metals on Human Health*

Heavy metals Cd, Pb, Hg, and As deplete the major antioxidants of cells, particularly antioxidants and enzymes having the thiol group (-SH). Such metals may increase the generation of reactive oxygen species (ROS) like hydroxyl radical, superoxide radical, and hydrogen peroxide. Increased generation of ROS can devastate the inherent antioxidant defences of cells and lead to a condition called "oxidative stress" (Ercal et al. 2001). Heavy metals, including Cd, Pb, and Hg, are nephrotoxic, especially in the renal cortex (Wilk et al. 2017). The chemical form of heavy metals is important in toxicity. Mercury toxicity largely depends on Hg speciation (Ebrahimpour et al. 2010). Relatively higher concentrations of toxic heavy metals, i.e., Cr, Cd, and Pb, and relatively lower concentrations of the antioxidant element

Se have been found in cancer and diabetes patients compared to those in the normal subjects in Lahore city, Pakistan (Salman et al. 2011). We all should be aware of the potential hazards and keep in mind that studying them before applying anything in nature is one of the main challenges of future studies. New technologies are being invented throughout the year and developed/modified especially in the field of science, which can help us understand all processes better and use them very accurately in the field of bioremediation can do. Therefore, research in this area is very promising.

5.16 Conclusion

Day by day, increasing pollution threatens our health and damages the environment, affecting the sustainability of wildlife and our planet. Damage to our soil affects our ability to grow food, as summarized in our policy report on the subject of food security. Bioremediation can help reduce and eliminate the pollution we generate by providing clean water, air, and healthy soil for our generations to come.

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