Chapter 12
Vermiremediation of Agrochemicals, PAHs, and Crude Oil Polluted Land

Shivika Datta, Simranjeet Singh, Praveen C. Ramamurthy, Dhriti Kapoor, Vaishali Dhaka, Deepika Bhatia, Savita Bhardwaj, Parvarish Sharma, and Joginder Singh

Abstract Earthworms, the 'ecological engineers of the earth' have a unique capability to significantly influence the dynamics of the medium they are present in. Vermiremediation is an eco-technology that involves earthworms for remediation of contaminated soils or another medium in which they are present. The earthworms form a natural bioreactor for the decomposition of organic matter and help in nutrient recycling. It is an expanding technology which is gaining worldwide attention because of its results and cost-effectiveness. Intensification of agriculture by the indiscriminate use of agrochemicals has led to soil infertility. Plants absorb nutrients from the soil in the form of free metal ions. The agrochemicals chelate with metal ions forming stable complexes, rendering them unavailable for plant absorption. The presence of earthworms in contaminated soils is an indication that they have an ability to survive in a wide range of different organic contaminants like pesticides, herbicides, polycyclic aromatic hydrocarbons (PAHs), Polychlorinated biphenyls (PCBs), crude oil. However, earthworm survival depends at first on the concentration of contaminants. The negative connotation and cost incurred in using physical and chemical techniques for remediation of PAHs and crude oil contaminated sites have amplified

Shivika Datta, Simranjeet Singh = Equal Contribution

S. Datta
Department of Zoology, Doaba College, Jalandhar, India

S. Singh · P. C. Ramamurthy
Interdisciplinary Centre for Water Research (ICWaR), Indian Institute of Sciences, Bangalore 560012, India

D. Kapoor · S. Bhardwaj
Department of Botany, Lovely Professional University, Phagwara, India

V. Dhaka · J. Singh (✉)
Department of Microbiology, Lovely Professional University, Phagwara, India
e-mail: joginder.15005@lpu.co.in

D. Bhatia
Department of Biotechnology, Baba Farid Group of Institutions, Deon, Bathinda, India

P. Sharma
School of Pharmaceutical Sciences, Lovely Professional University, Phagwara, India

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the involvement of vermiremediation. Vermiremediation improves the quality of soil in terms of pH, electrical conductivity, metal concentration, porosity, and aeration. Earthworms mortify and aerate the substrate by acting as mechanical blenders. This splintering of organic matter alters the microbial activity, amends its physical and chemical nature by progressively reducing the C/N ratio and increasing the surface area, making it more encouraging for microbial activity and decomposition further. The earthworms thereby contribute to accelerated decomposition of contaminants; however, sometimes the pollutants get adsorbed to the vermicast due to which their dissipation is delayed, which is a huge limitation to this technology.

Keywords agrochemicals · Contaminants decomposition · Organic matter · Vermiremediation

12.1 Introduction

A wide range of terrestrial and aquatic habitats is contaminated by anthropogenic activities (Mohee and Mudhoo 2012). The ecological equilibrium is skewed due to industrialization and urbanization, increasing population pressure, and the problem is compounded by the limited stock of natural resources (Hanafi 2012). The magnitude and nature of the concern are dynamic, bringing new challenges and creating a constant lacuna in need for developing appropriate and effective technologies. Sustainable development requires environmental management and a constant search for green technologies to restore ecological equilibrium. The harmful effects of chemical fertilizers and pesticides have abstracted the interests of researchers toward organic amendments like vermicompost or use of plant growth-promoting bacteria or by the degradation of wastes by bacteria or maybe by using complexes of humic acids and metals (Scotti 2015). Large-scale industrialization has led to inappropriate, indiscriminate, and untimed disposal of wastes in agricultural fields and water bodies (Goel 2006). This leads to a sudden and massive contribution of toxic trace metals, inorganic salts, pathogens; emission of harmful gases like hydrogen sulphide, ammonia, etc.; nutrient loss in the form of nitrogen and phosphorus by leaching, runoff or erosion and several other environmental problems (Hutchinson et al. 2005). Moral et al. (2009) suggested that proper handling of organic wastes could create a new source of nutrients for agriculture, thus can alternate costly mineral fertilizers and for the production of renewable energy. Vermicompost is one such cost-effective means for the conversion of highly toxic waste into value-based products (Bhat et al. 2014). Vermicomposting is a process that is known to convert the biodegradable matter into vermicast by the help of earthworms (Fig. 12.1). This process of vermicomposting has taken the credit to increase the bioavailability of a major part of nutrients in the organic matter (Gajalakshmi and Abbasi 2008).

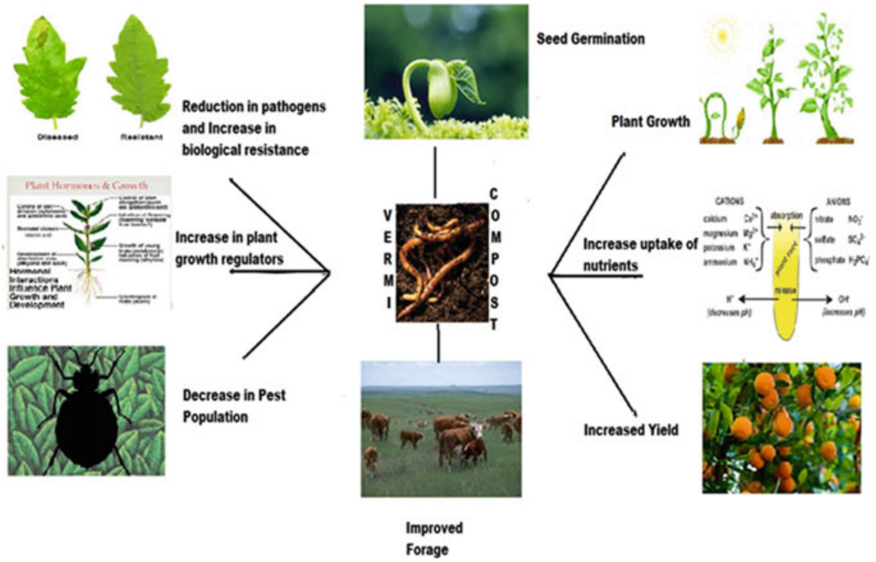

Fig. 12.1 Overview of vermicomposting

12.2 Agrochemicals: Classification, Effect on Environment, Health Hazards

The chemical products comprised of growth hormones, fertilizers, pesticides, and chemicals for the plant protection used in the field of agriculture are known as agrochemicals (Mandal et al. 2020). They involved a variety of chemicals extensively used in the field of agriculture to aid the growth of crops. To provide protection from the pests, these were manufactured as well as for the enhancement of crop yield (Ren et al. 2020). Agrochemicals concern to pesticides which consist of nematicides, herbicides, insecticides, and fungicides (Sparks 2013). Based on their mode of action and chemical structure, they are further classified into pyrethroids, organophosphorus, neonicotinoids, carbamates, and organochlorines (Xiao et al. 2017).

Although it provides many benefits in the agriculture field, agrochemicals are also found as a major pollutant widely detected in the soil (Tsatsakis et al. 2008). The numerous agrochemicals such as rodenticides, nematicides, fungicides, and other chemical fertilizers adversely affect the beneficial microbiota of the soil (Meena et al. 2016). The group of pesticides involves fungicides, insecticide, and herbicides are which function as to repel, control, or kill the life of a plant. The demand of these pesticides is constantly increasing. The pesticides have a good impact on the profit margin as well as on the crop yield, which causes them to be a significant component for agriculture (Meena et al. 2020). Though, the excessive use of agrochemicals leads to ecosystem degradation of soil microbiota (Önder et al. 2011). In agriculture, the main decreasing biotic factors are insects and weeds, which hamper the productivity and yield of the crop (Oliveira et al. 2014). Most of the insecticides and herbicides reach non-target microbes, which disturb the biodiversity of soil (Lo et al. 2015). This affects directly the microbiota of soil and soil fertility, which is a biological indicator (Santos and Flores 1995; Hussain et al. 2009). The herbicides namely 2,4-D, 2,4,5-T, Methomyl, Bensulfuron methyl, glyphosate adversely affect the *Rhizobium* species activities (Fabra et al. 1997), reduce the activity of purple non-sulphur bacteria like phosphatase and nitrogenase (Chalam et al. 1997). Which disrupts the signaling of *Rhizobium* and influences the nitrifying process (Fox et al. 2001), reduces the oxidation of methane to carbon dioxide (Arif et al. 1996), deceases the nitrogen mineralization (Subhani et al. 2000) and also suppresses the activity of phosphatase (Sannino and Gianfreda 2001).

Some fertilizers are rich in cadmium and copper heavy metals that cause toxicity in the environment of soil (Chen and Pu 2007; Kabata-Pendias and Pendias 1992). The soil consists of various enzymes. The persistent use of pesticides inhibits, decreases or increases the activity of soil enzymes viz. dehydrogenase, oxidoreductases, and hydrolases (Riah et al. 2014; Mayanglambam et al. 2005; Megharaj et al. 1999). It also alters the catabolic metabolism of the microbes (Niewiadomska 2004; Yale et al. 2017; Ortiz-Hernández et al. 2013). The major concern associated with this is water and soil pollution, causing the toxicity to animals and humans. The phosphate and nitrate compounds lead to groundwater contamination which is harmful to organisms (Aktar et al. 2009; Lamichhane et al. 2016). It also becomes a reason for the aquatic animal's death by increasing the algae growth in lakes and streams due to the overflow of fertilizers.

The exposure of agrochemical and its harmful effects on animals and humans are unavoidable (Sparks and Lorsbach 2017). It causes toxicity in the immune system, neurons, reproductive system, and also disrupts the endocrine system in humans (Mostafalou and Abdollahi 2017). Agrochemicals also play a role in disrupting the endocrine compounds of animals and humans (Luque and Muñoz-de-Toro 2020). They can mimic the interaction among the nuclear receptors (thyroid hormone, estrogen, aryl hydrocarbon, and androgen receptors) and endogenous hormones. It also interferes with the epigenetic changes and synthesis of amino acids, steroids, and peptide (Warner et al. 2020). There are different ways that agrochemicals can affect the signaling of estrogen (Vandenberg et al. 2020). A pesticide named organochlorine has properties of disrupting the endocrine in fish (Martyniuk et al. 2020). In amphibians, agrochemicals disrupt the multiple axes of endocrine, delay the metamorphosis, and influence sexual development (Trudeau et al. 2020). The endosulfan and atrazine pesticides impact the reproductive system of crocodiles (sentinels) belonging to the wetland ecosystem (Tavalieri et al. 2020). In Argentina, pesticides cause alterations of neurogenesis in hippocampal by way of disrupting the endocrine, i.e. agrochemical alters the function of the brain and hormone synthesis (Florencia and Cora 2020). Glyphosate herbicides influence female reproductive fertility. It may alter the functions of uterine and ovarian (Ingaramo et al. 2020). The agrochemical also causes obesogenic effects, for example, effects on transgenerational and development (Ren et al. 2020). They have also shown the epidemiological evidence of human obesity due to the exposure of agrochemicals.

The health risk is high to untrained farmers and their children during the usage of pesticides (Akbar et al. 2010). Many non-targeted organisms, such as small mammals, birds, and bees, suffer obliteration directly or due to the remaining traces left behind the utilization of agrochemicals (Paoli et al. 2015). Exposure of pesticides causes several health issues, for example, deformities of foetal, skin disorders, cancers, and acute poisoning (de Araujo et al. 2016).

12.3 PAHs (Classification, Effect on Environment, Health Hazards)

Polycyclic aromatic hydrocarbons (PAHs) having concerns because of their extensive occurrence, persistence, and carcinogenic characteristics in the ecosystem and human health. They are released into the environment both naturally and anthropogenically, due to the partial burning of biological resources, for instance, petroleum, tar, fossil fuels, debris, vehicular emission or other substances like plant material (Kim et al. 2013). PAHs found ubiquitously in the air, soil, sediments, aquatic ecosystems and are highly mobile in the ecosystem due to their physicochemical features and also used as air quality indicators (Baklanov et al. 2007). Sixteen PAHs are recognized as ecosystem contaminants by US EPA in accordance with PAHs abundance and harmfulness (Ghosal et al. 2016). High molecular weight PAHs, i.e. chrysene, fluoranthene, and pyrene, consisting of 4 or more rings are mostly recognized as genotoxic while low molecular weight PAHs like naphthalene, acenaphthene, fluorene, phenanthrene, consisting of 2–3 aromatic rings, are severely noxious (Abdel-Shafy and Mansour 2016). PAHs involve only C and H atoms however in some cases N, S, and O atoms added in the benzol to make heterocyclic aromatic compounds, that are generally congregated with PAHs (Alegbeleye et al. 2017). There exist various other PAHs by-products, like oxygenated PAHs (OPAHs) or nitrated PAHs (NPAHs), in addition to basic PAHs which consist of only C and H (Nováková et al. 2020).

Agroecosystems polluted with PAHs alter the agricultural soil properties, which dramatically result in a severe threat to ecosystem organisms found in that range. PAHs enter in mammals' body through breathing, skin contact, and ingestion, whereas in plants bioaccumulated via absorption from soils to roots and then transfer to various plant tissues (Veltman and Brunner 2012). PAHs are toxic to organisms when present in higher amounts in comparison to the effects range median (ERM) and harmless when lower than effects range low (ERL) (He et al. 2014). PAHs, i.e. naphthalene (NAP), fluorene (FLU), and pyrene (PYR), significantly affected the N_2-fixing bacterial organisms, which ultimately lead to a severe threat to the vigor of mangrove ecosystem by lowering the accessibility of N_2 in the mangrove regions (Sun et al. 2012). Soils which are extensively polluted with PAHs caused ecotoxic action in different plant species where the severity of the toxicity differs with the concentrations of PAHs, soil physiognomies, and the plant genotype involved (Maliszewska-Kordybach and Smreczak 2000). 1-nitronaphthalene and 1-nitropyrene affected the reproductive ability, i.e. hatchability of fish, *Fundulus heteroclitus* via lowest observed effect concentration (LOEC) of 447 μg/g and 958 ng/g, respectively (Onduka et al. 2015). Contamination of soil with PAHs caused alterations in soil characteristics, leaching and erosion, which dramatically lead to declined agricultural yield (Nwaejije et al. 2017).

Transfer of PAHs in food chains via intake of several foodstuffs is a foremost aspect of rapidly increasing concentration of PAHs in the ecosystem (Bansal and Kim 2015), and release of PAHs into the ecosystem and their toxicity to human have turned out to be a major subject of concern for researchers (Balcıoğlu 2016). The health hazards of PAHs rely upon the duration of exposure, amounts of PAHs, and the way of its intake, i.e. via inhalation, ingestion, or skin contact (ACGIH 2005; Kim et al. 2013). PAHs cause many short- and long-term health effects, carcinogenesis and also cause disruptions in the metabolism process because of their continual transfer into the food chain (Bansal and Kim 2015; Fig. 12.2). Yerba mate leaves and its hot and cold mate infusions showed carcinogenic activity, chiefly attributable to the presence of greater amounts of PAHs found in them (Kamangar et al. 2008). Acute oncogenic hazard due to PAHs has been observed in children and adults in Isfahan urban zone, entered through both PAHs dust ingestion and dermal contact (Soltani et al. 2015). PAHs cause not only cancers but various other non-genotoxic diseases also, for instance, diabetes mellitus, heart diseases (Hu et al. 2015). Nitro-PAHs caused genotoxicity by triggering severe micronuclear and nuclear aberrations in erythrocytes in comparison to control in *Pleuronectes yokohamae* fish (Bacolod et al. 2013).

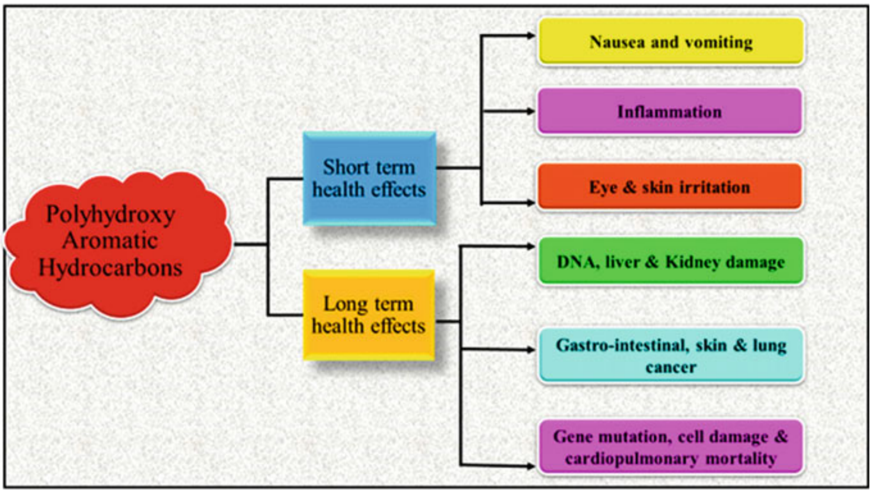

Fig. 12.2 Schematic representation of health hazards induced by PAHs (modified from Kim et al. 2013)

12.4 Crude Oil Polluted Land (Classification, Effect on Environment, Health Hazards)

Crude oil is a composite combination of organic substances which consists of hydrocarbons that differ in molecular weight and structural compounds and also contains heterocyclic molecules and some heavy metals. These biological substances include CH_4 gas, oils, crude wax, single or condensed rings and aromatic cycles like monocyclic and polycyclic aromatic hydrocarbons (Saadoun 2015). Crude oil pollution is recognized as an environmental stressor, and ecological pollutant which is released into the environment through anthropogenic activities, technical errors, transportation and storage faults, exploration and processing practices and has now become a major concern for ecosystem communities (Ivshina et al. 2015). Crude oil spills caused the devastation of fish territories in the mangrove ecosystem of the Niger Delta and also polluted the marshes and streams heavily eventually, converting them into an inappropriate habitat for fishing (Moses and Tami 2014). Total Hydrocarbon Content (THC) released from crude oil refineries resulted in altered soil chemical characteristics which ultimately lead to high noxiousness in the ecosystem (Yabrade and Tanee 2016).

In the aquatic environments, crude oil spill constructs a viscous surface slick, and H_2O-in-oil emulsion and accumulated in the aquatic habitat where it remains undecayed by microbes for a longer duration. This oil in H_2O diminished the level of O_2 in H_2O, because of the conversion of the organic moieties into inorganic substances, which dramatically lead to a decline in the biodiversity and hence, eutrophication (Onwurah et al. 2007). Waste released by crude oil refining practices discharged into marshes and the adjacent areas where it interrupts the quality of groundwater and also disrupts the health of the aquatic ecosystem (Amangabara and Njoku 2012). Crude oil adversely affected the health of various ecological niches via polluting the watercourses, canals, ponds, lakes, rivers, and mangroves (Sam and Zabbey 2018) and also resulted in deprived vigor of fish and their extinction due to abnormalities in reproductive abilities ultimately, higher mortality (Udotong et al. 2017). Petroleum hydrocarbons discharged into the water bodies and harm fish and other aquatic creatures (Clinton et al. 2014).

Wide-ranging crude oil toxicity relies upon several assets such as oil constituents and properties, weathered or un-weathered condition, contact pathway, i.e. via ingestion, skin contact, or inhalation and the oil accumulation, ultimately causes severe and long-term health problems (Ordinioha and Brisibe 2013). Crude oil pollutants disposed of refineries released into the soil and accumulated in the human body through the food chain and severely noxious to humans due to their noxious, mutagenic, and cancer-causing characteristics (Chikere and Fenibo 2018). Soil polluted with crude oil at Romanian field site resulted in high toxicity and produced carcinogenic effects where average calculated oncogenic hazard is about 1.07×10^{-5} for children and 6.89×10^{-6} for adults (Cocârţă et al. 2017). Crude oil hydrocarbons can disturb genomic stability of many creatures which eventually lead to cancer, cellular mutations, and reproductive aberrations (Short and Heintz 1997). Crude oil caused substantial upsurges in the time occurrence for numerous diseases and exerted their toxic effects by inhibiting the protein synthesis, synaptic activity, obstructs the membrane transfer process and disrupts the plasma membrane (Ordinioha and Sawyer 2010).

12.5 Global Regulations on Use of Agrochemicals, PAHs, and Crude Oil

The U.S. Environmental Protection Agency (USEPA) fixed the maximum level of contaminant (MCLs) for community water supplies to decrease the probability of undesirable health impacts from contaminated water. The maximum level of contaminant limit meets by the public supply systems. These standards are lower than levels at which diverse health effects can occur. USEPA has not fixed the maximum contaminant level limit for individual aromatic hydrocarbons, but has established MCL for total PAHs of 0.2 ppb. Currently, there are no standards for regulating levels of these toxic chemicals in private wells. USEPA requires the data of any releases of PAHs into the environment that exceed 1 pound. There are no regulations fixed for the PAH content in food items.

Different countries have set different regulations and standards for agrochemicals. They include maximum limits for pesticide residues on food, product registration requirements, and restriction for using pesticide (Fenner-Crisp 2010). Regulatory agencies have fixed the standard values for pesticide residues in air, drinking water, soil, and agricultural goods for years. Currently, more than 19,000 pesticides soil regulatory guidance values (RGV's) and approximately 5000 pesticide drinking water maximum concentration levels (MCL's) have been established by 50 and 100 nations, respectively (Fenner-Crisp 2010). Over 100 nations have provided pesticide agricultural goods maximum residue limits (MRL's) for at least one of the twelfth most commonly consumed agricultural foods. A total of twenty pesticides have been regulated with more than 99 soil RGV's, and 20 pesticides have more than 95 drinking water MCL's (Li and Jennings 2017). This research indicates that those RGV's and MCL's for an individual pesticide could differ over 7 (DDT in drinking water MCL's), 8 (Lindane in soil RGV's), or even 10 (Dieldrin in soil RGV's) (Li and Jennings 2017).

12.6 Strategies to Overcome the Harmful Effects of Agrochemicals, PAHs, Crude Oil

These compounds incite carcinogenic effects, mutagenic effects, and other toxic effects reason being they are considered as hazardous pollutants. Various strategies employed to overcome the harmful effects are divided into Chemical and Biological.

12.6.1 Chemical

They can be originated from numerous natural (such as forest fire, volcanic eruptions, oil seeps, smoke from burning of woods) and anthropogenic activities (such as the burning of fossil fuels, coal tar, oil spillage, oil leakage, petroleum refinery effluents, and automotive emissions). They are hydrophobic in nature and show low water solubility, thus can bind to the organic matter present in soil (Bourceret et al. 2018). So, it is herculean to degrade them in non-toxic form. However, there is an emergence to degrade them since they engender pernicious effects. Selection of the method to be followed is determined by the type of soil, site of contamination, the associated risk with techniques and type of contaminants. It has also been seen, epoxides and dihydrodiols produced through the process of degradation of PAHs. Epoxides and dihydrodiols are even more harmful than their parent PAHs. Owing to which, it is essential to identify intermediate PAH metabolites. So, a number of physical methods (thermal desorption, microwave heating, vitrification, air sparging), chemical methods (oxidation using ozone, Fenton's reagent) and biological methods (phytoremediation, land farming, composting) can be followed to do so. Among all these strategies, it has been found that physical and chemical methods are efficient and effective but require a high amount of energy and are cost-effective. Besides all this, they also produce secondary pollutants. These limitations of chemical and physical methods are inevitable and are the main reason for the popularity of biological methods (Redfern et al. 2019). Biological methods are eco-friendly and convert toxic pollutants in non-toxic form without producing any other harmful secondary by-product.

12.6.2 Biological Method

In the biological method, bioremediation is being carried out for over two decades. Bioremediation is a method in which microorganisms (bacteria, fungi, yeast, and algae) are employed for the degradation of PAHs (Redfern et al. 2019). Microorganisms convert the contaminants in less toxic forms by producing numerous enzymes, water, and carbon dioxide along with it as a by-product. This technique has gained so much interest all over the world because of its eco-friendly nature. Type of microorganism to be used for degradation and end products are the most challenging task for effective contaminant degradation. Factors like temperature, nutrients, metabolites, and pH also play a vital role in the process (Haleyur et al. 2019). It is of two types: in situ and ex-situ.

12.6.2.1 In Situ Bioremediation

Bioaugmentation

This technique is carried out in the soils where the number of microorganisms is less in number. So, the addition of microorganisms either exogenous or indigenous is done to the contaminated site in the bioaugmentation process. Microbes to be added are appointed on the basis of their aptness to degrade the contaminant (Haleyur et al. 2019). Both aerobic and anaerobic type of microorganisms can be used for the bioaugmentation of PAH. Factors like microorganism survival, enzymatic activity, and pollutant bioavailability are foremost for the bioaugmentation. Various studies documented the degradation of PAH in soil by bioaugmentation by using fungi and bacteria. A fungal strain *S. brevicaulis* PZ-4 has been reported to remove more than 75% of polycyclic aromatic hydrocarbon where benzo-(a)-pyrene (70–75%) and phenanthrene (more than 85%) being highest to be removed, when isolated from an aged PAH contaminated soil and incubated for 25–28 days (Mao and Guan 2016). Concurrently, *Penicillium* sp. 06, when isolated and incubated for 25–28 days, showed an oxidation effect on the petroleum-contaminated soil. It was able to oxidize 88–89% of phenanthrene in waste residues originating from the petrochemical refining industry located in Singapore. If incubated for more than thirty days, it can also oxidize more than 70% of acenaphthene, fluorine, and fluoranthene (Zheng and Obbard 2003).

Biostimulation

It involves the environmental modification by adding oxygen and nutrients such as phosphorus, carbon, and nitrogen for the stimulation of oil/contaminant degrading activity by an indigenous microorganism. These nutrients inaugurate the allowance of synthesis of required enzymes for degradation of contaminants. It has been shown that there was an increase in the microbial biomass and activity when nutrients were added in PAH contaminated soils (Roy et al. 2018), when Zucchi et al. (2003) studied biostimulation by utilizing nutrients and surfactant solution in the hydrocarbon-degrading bacterial community for crude-oil contaminated soil. They noted 40% of reduction in hydrocarbon content. Similarly, when Abed et al. (2015) conducted the study and used ammonium chloride and sodium phosphate as N and P sources during the biostimulation of oil-contaminated desert soil, investigated 15–20% increase in the oil removal efficiency. One of the most efficient organic biostimulants is inactive biomass of *S. platensis*, phycocyanin or ammonium sulfate. These biostimulants were used for the biostimulation of soil contaminated with 3–4% of diesel for sixty days. The results concluded that 64% of biostimulation of 3–4% diesel by inoculation biomass of *S. platensis* for sixty days and extracted phycocyanin of *S. platensis* was found to be most effective as it biostimulated 89% of biodiesel in sixty days (Decesaro et al. 2017).

Bioventing

In the process of bioventing, air or oxygen is endowed through wells to prompt the growth of indigenous microorganisms as growth is the most indispensable factor of microorganisms to perform remediation. This technique has been extensively used for the remediation of the soils that are contaminated by petroleum hydrocarbons (Singh and Haritash 2019). A pilot-scale experiment was performed at Reilly Tar and chemical corporation site in St. Louis Park, Minnesota for the bioventing of 15.3 m^2 area, which included pyrene, benzo-(a)-anthracene, and fluoranthene. Ensue the completion of bioventing the results indicated, 20–24% reduction in six-membered ring PAHs, 15–20% reduction in five-membered ring, 30% reduction in four-membered ring, 45–50% reduction in three-membered ring, and 60% reduction in two membered rings PAHs (Alleman et al. 1995). When bioventing treatment of artificially contaminated soil by phenanthrene was done for seven months, 90–95% of phenanthrene was removed. Under conditions of carbon/nitrogen/phosphorus = 100:20:1 and humidity = 55–60% (Rodriguez et al. 2017).

12.6.2.2 Ex-Situ Bioremediation

Land-Farming

Land-Farming comprise the excavation, transportation of contaminated soil to the land-Farming site and then spreading over the prepared bed. Later tilling is done in order to provide aeration. It is the simplest technique for remediation of contaminated soil. Microorganisms degrade the contaminants by oxidation, a metabolic process. In South Africa, land-Farming of creosote contaminated soil was done and in six months and found that naphthalene, phenanthrene, fluorine, and anthracene (low molecular mass) were degraded. On the other hand, for the remediation of high molecular mass PAHs land farming was done for another ten months, and 75–88% of four-five membered rings PAHs were remediated (Atagana 2004). Not only PAHs but petroleum hydrocarbons such as trimethyl benzenes and diesel range organics can also be degraded by land farming (Katsivela et al. 2005).

Composting

Composting is a process in which both thermophilic and mesophilic microorganisms are used to degrade the organic contaminants at elevated temperature (60 °C). Microorganisms release the heat amidst the process which ameliorates the solubility of the contaminants. Scrutinization on spent mushroom compost was conducted for bioremediation of soil contaminated with PAHs in which the degradation of phenanthrene, naphthalene, and benzo-(a)-pyrene was observed after 48 h at 75–80 °C (Lau et al. 2003). The thermally insulated chamber was used for the remediation of soil contaminated with PAHs. Mushroom compost, consisting wheat straw, gypsum, and chicken manure was also used in it. This experiment was carried out for fifty days. In the end, 50–60% of compost was noticed. After another hundred days, 40–80% of aromatic hydrocarbons were eliminated (Sasek et al. 2003). For intensification of PAH's bioavailability coal tar, diesel, coal ash contaminated soil was mixed with compost (Wu et al. 2013).

Phytoremediation

It is a process that involves the employment of green plants and ally microorganisms to remove or degrade the PAHs or any type of contaminant. It is a cheaper and more convenient way to remediate the contaminants. Techniques like phytoextraction, phytostabilization, phytotransformation, rhizodegradation can opt for the remediation of soil (Kathi and Khan, 2011). Plants have the aptitude to secrete enzymes such as dioxygenase, monooxygenase, dehydrogenase, and hydrolase that assist in the remediation of contaminants (Cristaldi et al. 2017). It has been concluded that different types of plants such as *T. repensm* (white clover), yellow sweet clover (*M. officinalis*), *F. arundinacea,* and ryegrass (*L. multiflorum)* have the capability to degrade the PAHs such as fluoranthene, chrysene, naphthalene, and anthracene (Rezek et al. 2008). Contaminant nature, soil properties, type of plant, and bioavailability of the contaminants are various factors that can affect the phytoremediation process. A pot culture experiment was conducted for the remediation of petroleum hydrocarbons by using different species of plants, i.e. *M. sativa*, *E. purpurea, F. arundinacea.* All these plants removed the TPH, including polar compounds, aromatic hydrocarbons, and saturated hydrocarbons consequently (Liu et al. 2012). Various techniques, such as electrokinetic treatment or bioremediation, can be followed for the enhancement of phytoremediation. It is possible to boost up the remediation of anthracene or phenanthrene from the soil by electro-phytoremediation with *B. rapa* (Cameselle and Gouveia 2019). It took the choice of best remediation technology, environmental conditions, type of soil, toxicity to achieve highly efficient phytoremediation.

12.6.3 Remediation by Chemical Methods

It is a productive way to remove lethal waste from the soil at the location of oil spillage. Soil matrix mainly determines the efficiency of this method. In this method, Fenton's reagent is employed, which is a mixture of ferric ions and hydrogen peroxide. It carries out the oxidation as hydrogen peroxide is a strong oxidizing agent; it produces hydroxyl ions (Goi et al. 2006). On the other hand, ferric ions act as a catalyst. The effect of hydroxyl ions destroys contaminants. Fenton's reagent helps in remediating oil from the soil by lowering the pH of soil. It is the simplest and most efficient method for remediation of oil from the soil, but it has some drawbacks, i.e. very costly, time-consuming. Besides this, the transfer of contaminated soil to the disposal site is also a big issue.

12.6.4 Remediation by Bioremediation

Bioremediation is a biological and traditional method to remediate the harmful contaminants by using living organisms (bacteria, plants, and fungi). Employing this method for remediation of crude oil is efficient because it is environment friendly and cheap at the same time (Siles and Margesin 2018). Hydrocarbon concentration, soil characteristics, and pollutant constituents determine the efficiency of this method.

12.6.5 Remediation by Rhizoremediation

It is a method which assists plant microbes for remediation. Microorganisms that are present in the soil enhance the tendency of a plant to remediate crude oil by forming a cooperative nexus with one another. This cooperative nexus between soil microbe and plant is called rhizoremediation in which plants give space, and other required environments to the microbes and microbes degrade the contaminants in return. Lately, rhizoremediation is being the most efficient and cost-effective technique to remediate crude oil from the soil. Mainly it occurs naturally but can also be initiated by the addition of specific microbes (Kang et al. 2020). In a study, conducted on the wheat plant under hydroponic conditions concluded that more than 20% of the oil was eliminated by wheat seedlings from media and when associated with *Azospirilum* this ability increased by 25–30%. Bioremediation of soil contaminated by oil can be done by using yellow alfalfa in the association with *Acinetobcter sp.* Strain SS-33 which improved efficiency of remediation by 35% as compared to alone alfalfa which was 30–34% and *Acinetobacter* sp. S-33, which was 30–33%. Thus it was analyzed by fractional contaminants that plant–microbe association is very efficient technology in the clean-up of aromatic hydrocarbons from the soil (Muratova et al. 2018).

12.7 Vermicomposting in Bioremediation

12.7.1 Garden, Kitchen, and Agro Waste

According to Bouwman (2007), a number of tests have been developed to determine the effect of pollutants on earthworms, the reason being that earthworms are an essential ecological component of many soils (Bouwman 2007). That is why a lot of focus has deviated upon the possible role of vermiculture in solving the problem associated with waste disposal. Garden waste can be converted into manure by vermicomposting (Shah et al. 2015). Empty fruit bunches when mixed with cow dung and subjected to vermicomposting converts it into nutrient-rich organic fertilizer (Lim et al. 2014). According to another study, the cast from the earthworms produced by the ingestion of agricultural waste contains plant nutrients and growth-promoting substances in an assimilated form (Sinha et al. 2009). This increased level of nutrients can be attributed to the enzymatic and microbial activity of earthworms, and the results advocate that post-vermicompost samples derived from agricultural waste contain a fairly higher level of major and micronutrients in comparison to the initial levels of nutrients. The enzymatic and microbial activity of the earthworms contributes to this increased level of nutrients. Suthar (2009a) also reported the vermicomposting of post-harvest residues of some local crops like wheat, millets, and a pulse and concluded that agro waste could be converted to some value products like vermicompost which have the potential to be used for sustainable crop production (Suthar 2009a). Singh and Kalamdhad in 2013 also recycled temple waste that included floral offerings through vermicomposting through *Eisenia fetida* and a comparison was made with vermicompost from kitchen waste and farmyard waste (Singh and Kalamdhad in 2013). The maximum biomass was found in temple waste vermicompost, and also temple waste vermicompost showed an increase in the length of root, shoot; a number of secondary roots and total biomass when compared with kitchen waste and farmyard waste. Suthar (2007a, b) vermicomposted agriculture waste, farmyard manure, and urban solid waste with an earthworm, *Perionyx sansibaricus*. The decrease in organic carbon, C:N ratio; also the increase in NPK, plant metabolites in the end product and growth pattern of *P. sansibaricus* in different organic waste resources indicate that this species can be efficiently used for recycling of wastes with a low-cost input (Suthar 2007a, b).

12.7.2 Heavy Metal Reduction from Soil

Pathma and Sakthivel (2012) also suggested that vermicompost can potentially be used in sustainable agriculture and also can effectively manage wastes from agriculture, industrial, domestic, and medical sector which tends to be at high risk for both life and environment. The sewage sludge having high nutritive value for plants can be utilized as fertilizers after the elimination of heavy metals (Suthar 2009b;

Bettiol 2004). Singh and Kalamdhad (2013) reported the feasibility of earthworms in the reduction of metal toxicity and to increase the nutrient profile in water hyacinth vermicompost for sustainable land improvement practices. The bioavailability and leachability were marginally reduced by the vermicomposting of water hyacinth by *E. fetida*.

12.7.3 Municipal Sewage Waste

Earthworms are an important ecological part of many soils. Treatment of wastewater and sludge also utilize earthworms (Kaushik and Garg 2004). The municipal sewage waste by vermicomposting can be effectively converted to nutrient-rich, and eco-friendly biofertilizer (Mishra et al. 2014). Thus, if municipal sewage waste is managed in an appropriate manner, then it not only mitigates the negative effects, but it could help in meeting the demand of ecology and economy. Vermicomposting municipal biodegradable wastes at home are the best possible method for waste disposal. In terms of economy and impact on the environment, the most effective way to deal with solid waste is to reduce domestic waste at the source itself (Pirsaheb et al. 2013a, b, c). Vermicomposting of sewage sludge also resulted in a reduction in C:N ratio, total organic carbon (TOC) but increases in EC, total nitrogen, potassium, calcium, phosphorus, indicating sewage sludge could be converted to a good quality fertilizer. Khwairakpam and Bhargava in 2009 also vermicomposted sewage sludge and observed an increase in EC, N, K, Ca, Na, P; also, the heavy metals Cu, Mn, Pb, and Zn were now in permissible limits thus indicating that recycled sewage sludge through vermicompost can be used as an effective fertilizer.

12.7.4 Tannery Industry

The tanning industry is spread all over India and a major part in Tamil Nadu and Uttar Pradesh (Ravindran and Jindal 2008). It is one of the highly polluting and growth-oriented industries, and it generates tones of wastes in the form of rawhide (and skin) trimmings (Ozgunay et al. 2007). Tannery industries release not only organic material which forms a source of valuable nutrients on decomposition but also metals and pathogens and other toxin components which genuinely may put the environment to greater risks (Contreras-Ramos et al. 2004; Ganesh Kumar et al. 2009). The effluents from the tanning industry are high in organic and inorganic dissolved and suspended solids along with proclivity for high oxygen demand. The tanning activities lead to unpleasant odor that ensues from the decomposition of ammonia, solid protein waste, hydrogen sulphide, and volatile organic compounds. Most of the chemicals used in processing remain unabsorbed and thus are discharged into the environment. Tannery sludge can provide a nutrient supplement for crops after proper remediation as it contains plant nutrients like nitrogen, phosphorus, iron, zinc, and copper.

A successful attempt to recycle tannery sludge into manure through vermicomposting by *E. fetida* was made by Hemelata and Meenambal (2005). Another study evaluated the amendment of tannery sludge by vermicomposting. Results inferred an increase in nutrient content, lower C:N ratio and lower electrical conductivity which could be used as manure depicting that vermicompost could be considered as an effective technology for production of value-added products using tannery sludge as an input (Vig et al. 2011).

12.7.5 Improving Forage Quality

In a study reported in 2014, pre-composting prior to vermicomposting contributes for a powerful design for management of ruminant manure. This reduces the environmental pollution from ruminant production and can be effectively used as a feed supplement to ruminants (Nasiru et al. 2014). Further, the vermicast produced can be used as a good fertilizer. Vermicompost also increases the green fodder and dry matter in the case of sorghum (*Sorghum bicolor* (L.) Moench) (Sheoran and Rana 2005). Forage sorghum (*Sorghum bicolor* (L.) Moench) was produced by vermicompost and farmyard manure integrated with inorganic fertilizers (Sheoran and Rana 2005).

12.8 Vermicompost: Mechanism

Microorganisms primarily accomplish the task of biochemical decomposition of organic matter, but earthworms are the critical drivers of the process because they graze on microbes and stimulate their decomposer activity (Aira and Domínguez 2009; Monroy et al. 2009; Gomez-Brandon et al. 2011a, b), and in addition to this, they also increase the surface area available for microbes to act upon after decomposition of organic matter (Dominguez et al. 2010). The mechanism of converting ‘garbage into gold’ is very well studied and is comprised of the following steps (Fig. 12.3):

1. Ingestion of the substrate by the earthworms.
2. The grinding ‘gizzard’ located next to worm’s mouth, helps in mincing of the ingested substrate and leads to an increase in the surface area of the substrate, which facilitates for microbes to act upon (Chan and Griffiths 1988).
3. Enzymes, along with the microflora of the worm’s gut, digest the substrate further as it passes through the body.
4. The formation of the substrate as ‘vermicast’ which is microbially much more active than the ingested one.

Almost any industrial or agricultural organic material can be subjected to vermicompost, but out of the few may be toxic to be used directly for the earthworms

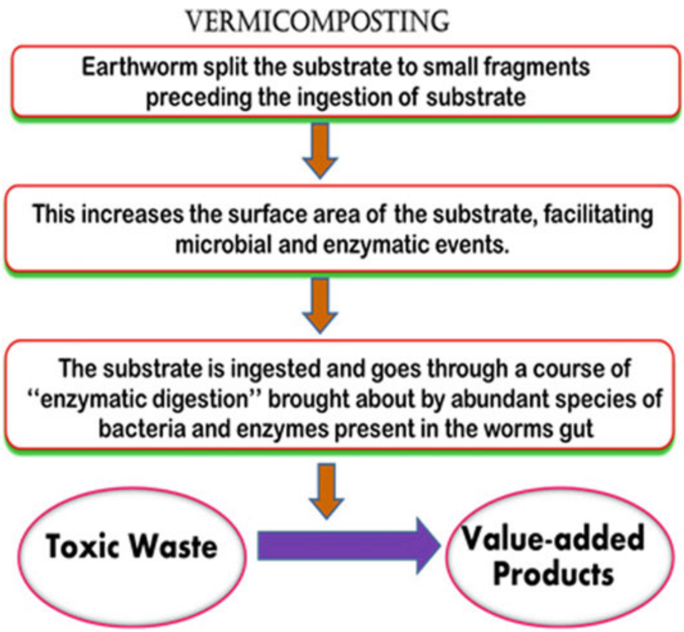

Fig. 12.3 Mechanism of conversion of toxic waste into value-added products by vermicomposting

and thus require a pre-processing. (Gajalakshmi and Abbasi 2008). This preliminary process can be in the form of washing, pre-composting, macerating or mixing. Precomposting facilitates vermicomposting (Tognetti et al. 2007) because it is a thermophilic phase and kills most pathogenic organisms which make sure that earthworms survive and grow well and also ensure pathogen-free vermicompost (Dominguez and Gomez-Brandon 2012).

Unlike composting where the substrate has to be tossed regularly to maintain aerobic conditions, in vermicomposting the earthworms take over the roles of both turning and maintaining the organics in an aerobic condition, eliminating the need for mechanical aeration (Misra et al. 2003; Sinha et al. 2010).

12.9 Conclusion

The waste material from various industries serves as a rich source of nutrients, proteins, and energy that should not be wasted by mere disposal in dumps or landfills. Rather, their immense energy should be utilized in one form or the other. Here, comes the role of vermicomposting which not only utilizes the wastes that would otherwise be problematic for the society but also converts and recycles that waste supplying the valuable nutrients back to the soil maintaining ecological sustainability. The post-vermicompost matter could be largely utilized as organic amendments in agriculture.

Thus, this solves the problem of waste disposal and equally benefits agro systems. Future research should be directed to increase the understanding of the impacts of organic fertilizers on soil microbial processes and nutrient cycling and disentangling the influence of different factors such as crop species, soil type, and compost properties, in order to increase crop yields under sustainable production systems. The combination of modern microbiological techniques with the knowledge of soil ecological processes would provide a unique opportunity to improve agronomical practices. The goal is to use and optimize the biological resources already existent in the soil and optimize fertilizer management to maximize yields while reducing environmental impacts.

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