Biogenic Nanoparticles and Strategies of Nano-bioremediation to Remediate PAHs for a Sustainable Future

13

Punniyakotti Parthipan, Chandar Prakash, Dhandapani Perumal, Punniyakotti Elumalai, Aruliah Rajasekar, and Liang Cheng

Abstract

Polyaromatic hydrocarbons (PAHs) are considered as dangerous contaminants in water and soil, which are highly toxic, and also carcinogenic to living organisms including humans. The concerns on the PAHs removal are increased due to the difficulties in their removal from contaminated water and soil. Bioremediation technology is the most promising, cost-effective, and eco-friendly approach to

P. Parthipan (✉)
Electro-Materials Research Lab, Centre for Nanoscience and Technology, Pondicherry University, Puducherry, India

Environmental Molecular Microbiology Research Laboratory, Department of Biotechnology, Thiruvalluvar University, Vellore, Tamil Nadu, India
e-mail: pparthibiotech@gmail.com

C. Prakash
Plant Genetic Engineering Laboratory, Department of Biotechnology, Thiruvalluvar University, Vellore, Tamil Nadu, India
e-mail: prakashtc90@gmail.com

D. Perumal · A. Rajasekar
Environmental Molecular Microbiology Research Laboratory, Department of Biotechnology, Thiruvalluvar University, Vellore, Tamil Nadu, India
e-mail: bio.dhana@gmail.com; rajasekargood@gmail.com

P. Elumalai
SCNU Environmental Research Institute, Guangdong Provincial Key Laboratory of Chemical Pollution and Environmental Safety & MOE Key Laboratory of Theoretical Chemistry of Environment, School of Environment, South China Normal University, Guangzhou, PR China
e-mail: 2elumalai79@gmail.com

L. Cheng
School of Environment and Safety Engineering, Jiangsu University, Zhenjiang, China
e-mail: clcheng@ujs.edu.cn

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remove the hydrocarbons by using potential microorganisms. Nevertheless, the existing bioremediation technology has important limitations, such as, poor efficiency of microbial communities in the field, and lesser bioavailability of pollutants. To overcome these issues, advanced nano-biotechnology could be used. In recent studies, functionalized biogenic nanomaterials have shown possible PAH removal efficiency by adsorbing/desorbing them. Also, nano-sized photocatalysts can be used for photocatalytic oxidation of adsorbed or separated PAHs. Combining these integrated approaches will make a significant impact on the bioremediation of PAH contaminants. Nano-bioremediation could play an important role in mobility, micelle formation, and increasing bioavailability, which will assist in the removal/utilization of PAHs by biological (i.e., using microorganisms) or physicochemical (i.e., photocatalysis) methods.

Keywords

Polyaromatic hydrocarbons · Bioremediation · Biodegradation · Biosurfactant · Eco-friendly · Bioavailability

13.1 Introduction

Globalization along with enormous anthropogenic actions leads to the accumulation of toxic contaminants/pollutants into the environment. These toxic contaminants are very harmful to living organisms including human beings (Behera et al. 2018). Common toxic contaminants which are making major issues to the environment are hydrocarbons (majorly from crude oil), non-degradable plastic, heavy metal accumulations, polycyclic aromatic hydrocarbons (PAHs), etc. Most of these contaminants are classified as carcinogenic and mutagenic to most living organisms (Sajid et al. 2021). Among the hydrocarbons, PAHs are classified as the most dangerous pollutants due to their impact on the environment and health issues (Sarma and Prasad 2015).

PAHs are classified as persistent organic hydrocarbons with two or more fused aromatic rings. PAHs are frequently encountered naturally or by man-made actions (Sarma et al. 2016a, b). The main source of PAHs in environments are crude oil spill, apart from this PAHs are entered into the environment by inadequate incineration of many organic materials including coal, petrol, wood, natural gas, garbage, used lubricating oil, waste incineration, petroleum spill/discharge, etc. (Sarma and Prasad 2016; Muangchinda et al. 2018; Sarma et al. 2019). PAHs from used motor oil makes an enormous impact on the environment due to inappropriate dumping into the soil. A study by Paneque et al. (2020) describes, 16 types of PAHs were identified and all these PAHs are considered to be most toxic to nature since their disposal is closely relevant to human activities, which makes the chance of inhalation by human beings very common and may perhaps cause serious health problems. Partial burning of organic materials gives out about 100 different types of PAHs, which are the primary pollutants. PAHs are found in varying levels in soil from 1μg to 300 g/kg, depending on the sources of the pollutants (Bamforth and Singleton 2005).

The life-threatening concerns regarding the PAHs is their ubiquity in air, soil, water, and aquatic sediments along with huge dwell periods in the environment (Mrozik et al. 2003). PAHs are solely responsible for the numerous health issues in human beings including cancer, nausea, anemia, abdominal pain, etc. (Chaudhary et al. 2018). Also they cause numerous antagonistic changes to aquatic living matters, including causing several adverse effects to aquatic organisms, including growth reduction (Christiansen and George 1995), endocrine modification (Meador et al. 1995), DNA mutation (Caliani et al. 2009), and deformities in larvae and embryos (Carls et al. 2008). Removal of PAHs is very difficult due to their high hydrophobicity nature, particularly in aquatic atmospheres; they habitually get adsorbed over the particulate matter for prolonged periods (Behera et al. 2018).

13.2 Remediation Technologies of PAHs: Overview

Over the years, many approaches (physical, chemical, and biological) including conventional methods to advanced technologies are used to treat the hydrophobic PAHs contaminations from soil and water sources. In brief, incineration and in-situ thermal desorption an physical methods used for the treat coal tar, wood treatment waste by volatilizing or destroying them from contamination (Gan et al. 2009). This incineration technique working at high temperatures (900–1200 °C) destroyed more than 90% of the PAHs. The major drawback of this technology is the requirement of high energy for the incinerator off-gas control devices, and also a long period (in most cases more than 3 years) along with high operational cost (Islam et al. 2012). The next one is solvent extraction/washing; this method is highly preferable for the high molecular weight (HMW) PAHs. This method is not successful as expected, since it has few drawbacks including the high hydrophobic nature of HMW PAHs, which makes it very difficult to wash, slow desorption, and low bioavailability (Pourfadakari et al. 2019). To overcome these issues, surfactants are utilized to increase bioavailability, but which makes harmful effects on the environment. Another widely used technique is chemical oxidation. This is in-situ processing technology and preferable for both low molecular weight (LMW) and HMW PAHs. In this process, PAHs are degraded after reacted with oxidants which are injected into the soil (Lemaire et al. 2013). For this purpose, various chemical oxidants have been tested including ozone and Fenton’s reagent, $KMnO_4$, H_2O_2, peroxy-acid, etc. (Cheng et al. 2016).

Among all these existing approaches, bioremediation is considered as a best alternative technology for the removal of hydrophobic PAHs. Bioremediation is accomplished great attention among the scientific and industrial sectors since it is a sustainable and green approach to treat PAHs contaminated environment (Azubuike et al. 2016). In general, bioremediation techniques are carried out in two ways such as in-situ (bioaugmentation, biostimulation, phytoremediation, and land farming) and ex-situ (using bioreactors) (Kuppusamy et al. 2016a, b). In the case of the in-situ method, degrading organisms is influenced by the physicochemical properties of the environments. At the same time for the ex-situ approach, all the parameters and conditions can be controlled, which enhances the degradation rate (Gan et al. 2009). Many factors such as cost-effectiveness, efficiency, contaminants types, complexity, time duration, and availability of resources are the major aspects that need to be considered for the selection of appropriate bioremediation methods for the removal of PAHs from the contaminated environments.

13.3 Integrated Bioremediation Approaches

Nevertheless, bioremediation is limited successive since it is a time-dependent method, high cost, low bioavailability, long duration and it is not an ideal approach for the highly contaminated environments with HMW PAHs. So, these limitations can be overcome by applying integrated approaches such as physical-chemical (for example, solvent extraction along with chemical oxidation), physical-biological (for example, solvent extraction along with bioremediation), chemical-biological (for example, chemical oxidation along with bioremediation), biological-biological (for example, enhanced bioremediation with biostimulation) and physical-chemical-biological (for example, soil washing with chemical oxidation and bioremediation) (Kuppusamy et al. 2016c). Few integrated approaches are discussed briefly here.

13.4 Electrokinetic Remediation of PAHs

One of the potential and effective integrated approaches being investigated in recent time is electrokinetic remediation. This approach is mostly applied for the treatment of the least hydraulic permeability soils. In this method, a low-intensity direct current is applied to the contaminated soil samples using appropriate electrodes. Contaminants with ionic charges transported to the oppositely charged electrode through electromigration. Besides, electroosmotic flow offers a driving power for the migration of soluble pollutants (Reddy et al. 2006). Regarding the PAHs degradation using the electrokinetic, it is not a well-established technique. The low bioavailability with the hydrophobic nature of PAHs makes it hard to separate them from soil environments using the conventional electrokinetic method. However, this problem can be rectified using the solubilizing agents (i.e., surfactants, co-solvents). At the same time, using these harmful solvents and chemical surfactants might make an adverse impact on the soil environments (Kuppusamy et al. 2016c).

13.5 Enzymatic Treatment of PAHs

Another useful approach implemented for PAHs removal is enzymatic treatment. The catalytic activity of the enzymes is an eco-friendly approach and efficient as compared to the chemical catalysts with higher reaction rates, stable at different temperature and pH ranges (Mohan et al. 2006). In a study, Wu et al. (2008) extracted laccase enzyme from a fungus *Trametes* sp. and used it to oxidize 15 priority PAHs-polluted field soils with the presence of 2,20-Azino-bis-3-ethylbenzthiazoline sulfonate as mediator. Outcomes from this study illustrated that laccase played a major role in the conversion of the toxic PAHs into the less toxic intermediate products (for example, anthracene converted as anthraquinone). If the quantity of enzyme is increased, the degradation rate is also enhanced. Recently, Perini et al. (2020) also performed laccase activity on the degradation of anthracene, benzo(a)pyrene, and naphthalene. The addition of the laccase doubled the degradation rate and converted toxic hydrocarbons into less toxic products. One of the major limitations of this method is financial constraints. This cost factor can be overcome by using advanced biotechnological approaches such as immobilization, and optimization of production conditions.

Apart from these two integrated approaches, other two methods are also existing. The first one is phytoremediation, which can be implemented using combinations of physical, chemical, and biological methods. This approach can be executed with landfarming followed by introducing potential microorganisms to degrade the PAHs and finally growing contaminants-tolerant plants in that soil. It's considered to be a good approach but removal efficiency is comparatively very less (Huang et al. 2004; Kuppusamy et al. 2016c). Another similar approach is vermi-remediation, this method is preferable for some special case, where contaminated soil has a lesser pore size (below 1μm) and there penetration of degrading microorganism is a much difficult process. In this case, PAHs are not bioavailable. In such cases, introducing earthworms makes a huge impact in the enlarging of the pore sizes, which permits degrading microorganisms to access the PAHs efficiently (Ma et al. 1995).

13.6 Nano-bioremediation

In recent times, these integrated approaches are greatly improved by introducing advanced nanotechnology and its innovations. In this technology, nano-sized materials are introduced into the contaminants to alter their physicochemical properties. This technology is implemented with other technology such as chemical methods (increasing bioavailability with the addition of surfactants) and biological methods (biodegradation). Still, many factors need to be considered in executing this approach such as the selection of toxic-free nanomaterials, biomolecules for the functionalization, and other factors. Because many nanomaterials are synthesized using highly toxic reducing agents, which need to be avoided. This problem can be sorted out by the selection of toxic-free green and biologically synthesized nanoparticles. Biogenic nanoparticles are the preferably best choice for green and sustainable nano-bioremediation.

13.7 Biogenic Nanomaterials: Synthesis, Properties, and Importance

Nanomaterials including metal and metal oxide nanoparticles (silver, gold, zinc, copper, nickel, graphene, etc.) are widely used in many applications due to their physicochemical properties. Two broad approaches such as top-down and bottom-up are most widely used for synthesis of nanomaterials. In the top-down method, large-sized bulk materials are reduced using physical methods (i.e., sonication, mechanical milling, etc.). This method is time-consuming and very difficult to obtain a uniform size of nanomaterials (Suganeswari 2011). In the bottom-up method, nanomaterials are formulated from a molecular base. Most of the common synthesis methods such as co-precipitation and sol-gel process fall under this category only. Most commonly using reducing agents such as hydrazine and sodium borohydride are classified as a highly toxic chemical, which could be accumulated as hazardous products in the environments (Wu et al. 2011; Sadhasivam et al. 2020). This problem can be overcome by utilizing eco-friendly reducing and capping agents. In recent times, it is well documented that biological reducing and capping agents such as plant extract and microbial metabolites (from bacteria, fungi, yeast, algae, etc.) is a potential alternative to the chemical reducing agents (Owaid 2019). Nanomaterials synthesized using these reducing agents are widely used in many industrial and environmental applications (Patil and Kim 2018). In this chapter, the biogenic synthesis of nanomaterials and their impact on the bioremediation of the PAHs contaminated environments are documented. For this purpose, the biogenic synthesis of nanomaterials using various biological sources is discussed in detail. In biogenic synthesis, nanomaterials can be synthesized by intracellular or extracellular methods. Comparatively, the extracellular method is easier and highly feasible, since microbial products such as proteins, amino acids, reductase enzymes, and peptides are serving as reducing and capping agents (Subbaiya et al. 2017). It is very easy to collect these kinds of bacterial metabolites from the growth medium by using a simple centrifugation method (Fatemi et al. 2018). At the same time, the intracellular method is less preferable since it requires several steps to acquire contamination-free nanoparticles, particularly this process is started with cell lysis, repetitive centrifugation/washing to separate cell debris and nanomaterials (Patil and Kim 2018).

13.8 Bacteria-Mediated Synthesis of Biogenic Nanomaterials

As earlier said, different biological sources are being tested as eco-friendly reducing agents to synthesis of different nanomaterials. The most widely tested biological source is bacterial metabolites. In most cases, the bacterium can be easily culturable and within a short time bacterium will reach their maximum growth state. Wide ranges of bacterial strains and their metabolites are employed as simple and sustainable reducing agents. Recently, Suriyaraj et al. (2019) used the *Acinetobacter* strain a zirconium resistant extremophilic bacterial strain for the synthesis of crystalline zirconium dioxide. This synthesis process is simply done by adding the starting materials into the growth medium and metabolites released into the growth medium reduced the $ZrOCl_2$ to ZrO_2. Similarly, Jha et al. (2009) synthesized TiO_2 using the *Lactobacillus* bacterial strain. The membrane-bound oxidoreductase plays important role in the bio-reduction of oxide nanoparticles.

Diverse bacterial strains are being tested for the biosynthesis of the nanomaterials. For instance, Fayaz et al. (2011) used a thermophilic bacterium *Geobacillus stearothermophilus* for the biogenic synthesis of silver (Ag) and Au nanoparticles. This strain and their metabolites reduced metal nanoparticles without any aggregation, which might be due to the production of the capping protein in the growth medium. A study by Zhang and Hu (2018) used a marine bacterium *Bacillus* strain for the biogenic synthesis of Palladium (Pd) and gold (Au) nanoparticles. Starting materials are added in the growth medium, the reduction process is occurred along with the production of the bacterial metabolites in the growth medium. In this approach, obtained nanoparticles have a uniform size (below 40 nm). A study by Srivastava and Mukhopadhyay (2013) reported the biological synthesis of selenium nanoparticles using the non-pathogenic bacterium *Zoogloea ramigera*. Selenium oxyanions were added in the growth medium as an electron acceptor along with bacterial strain. Selenium NPs were formed extracellularly with uniform size and shape. A protein secreted by this bacterium was bound over the membrane surface and it was belonging to the oxidoreductase which is playing a key role in the reduction of SeO_3^{2-} into Se^0. Also described that electrostatic interaction of proteins traps SeO_3^{2-} ions over the surface of proteins and which leads to the reduction of Se nanoparticles. Similarly, Presentato et al. (2018) also synthesized biogenic Se nanoparticles using bacterium *Rhodococcus aetherivorans*. Similarly, Wadhwani et al. (2018) used *Acinetobacter* strain for the biogenic synthesis of Au and Se nanoparticles. This bio-reduction process was mediated by the lignin peroxidase enzyme produced by *Acinetobacter* strain. In another study, Tiwari et al. (2016) used a copper-resistant *Bacillus* strain isolated from copper mine for the synthesis of copper nanoparticles (Cu NPs). Similarly, Ag NPs were biologically synthesized using *Salmonella typhirium* cell extract in bright conditions (Ghorbani 2017).

13.9 Fungi-Mediated Synthesis of Biogenic Nanomaterials

Different types of fungus are found in the environments and some of them are used for the synthesis of various types of nanomaterials. Recently, Ganesan et al. (2020) used *Periconium* species an endophytic fungus for the biosynthesis of the zinc oxide (ZnO) nanoparticles. In this study, *Periconium* biomass extract was obtained from dried biomass and the crude extract was used for the reduction purpose. A similar study by Clarance et al. (2020) used *Fusarium solani* another endophytic fungus for the biogenic synthesis of Au NPs. Polypeptides and proteins secreted by *Fusarium solani* play a key role in the reduction of the Au NPs. In a study, ligninolytic fungi *Trametes trogii* was used for the biogenic synthesis of the Ag NPs. This strain produces several ligninolytic enzymes, which are playing an important role in the bio-reduction of Ag NPs (Kobashigawa et al. 2019). Similarly, biogenic Ag NPs were synthesized using an extracellular extract of two white-rot fungi, namely *Ganoderma enigmaticum* and *Trametes ljubarsky* (Gudikandula et al. 2017). In a study, fungus *Aspergillus oryzae* was used for the fermentation of the lupin. This fermented lupin extract is directly used for the biogenic reduction of Se NPs (Mosallam et al. 2018). A study by Vago et al. (2016) used filamentous fungus belonging to the genus *Aspergillus*, *Penicillium,* and *Trichoderma* for the successful reduction of Au NPs.

13.10 Algae-Based Biogenic Nanomaterials Synthesis

Algae are classified as a photoautotrophic member of eukaryotic organisms; different types of algae are spread over in seawater globally. Algae is a potential resource for nanomaterials synthesis since it is enriched with secondary metabolites (proteins, pigments, etc.). These characteristic features make them nano-biofactories for the metallic nanoparticle's synthesis (Khanna et al. 2019). Also, algae are easily available, easily cultivable, eco-friendly, and least cost. Still, very few numbers of algae species were only explored for the biogenic synthesis of nanomaterials. Polysaccharides extracted from marine algae, namely *Pterocladia capillacae, Jania rubens, Ulva fasciate,* and *Colpomenia sinuosa* were used for the reduction of Ag NPs (El-Rafie et al. 2013). An interesting study by Pytlik et al. (2017) described the usage of *Stephanopyxis turris* a unicellular diatom for the biogenic synthesis of Au NPs. This diatom was reduced Au NPs both extracellularly and intracellularly. Similarly, Gonzalez-Ballesteros et al. (2017) used *Cystoseira baccata* a brown alga for the biogenic synthesis of Au NPs. Interestingly, synthesized Au NPs are found below 10 nm only. This brown alga extract was obtained by applying the conventional reflux method and the obtained extract was directly used for the bio-reduction. Similarly, Colin et al. (2018) synthesized Au NPs using algae *Egregia* species. In another study, iron oxide nanoparticles were biologically synthesized using brown algae *Colpomenia sinuosa* and red algae *Pterocladia capillacea* extracts (Salem et al. 2019). The polysaccharides present in these algae act as reducing and capping agents. Recently, Fatima et al. (2020) synthesized biogenic Ag NPs using *Portieria hornemannii* a red alga.

Apart from these biological sources (bacteria, fungi, and algae), some of the other microbial sources (for example some species of yeast) are also being tested for the biogenic synthesis of metal nanoparticles. Overall, these biogenic nanoparticles are considered as eco-friendly, stable at diverse environmental conditions; synthesis procedure is very simple; also there is no requirement of any harmful chemical compounds. This feature makes them a supreme candidate for many of the interdisciplinary applications from medicine to environment.

13.11 Principles/Strategies of Nano-bioremediations

In the bioremediation process, nanomaterials itself play a major role in the removal of contaminants. In some cases, nanomaterials are functionalized to perform some auctions; for this purpose, some basic methods are followed such as covalent coupling of nanomaterials surface with the ligand, the non-covalent coupling of nanomaterials surface with ligand, adsorption, and co-encapsulation. In a covalent coupling, either the nanomaterials or biomolecule binds directly through a dative bond or external bound ligand attaches nanomaterials with biomolecule using a covalent bond. In continuation into the initial interaction, some other interaction might be possible like irreversible bond formation to reversible and transient interaction based on modification, fixation, etc. (Basak et al. 2020). In the non-covalent coupling biomolecules, nanomaterials are functionalized by self-assembly redox enzyme-protein complexes (Diaz et al. 2018), dock and lock mechanism (Gong et al. 2019), etc. Another famous approach is encapsulation, in this method nanomaterials remain coated inside the capsules and also moveable. This approach is very useful for materials with higher oxidation, leaching, etc. (Gross et al. 2015). The final approach is adsorption, this method is recent technology with more advantages, more likely being applied for the nano-remediation for the affected environment.

13.12 Nano-bioremediations of PAHs

Many functionalized nanomaterials are tested for the bioremediation of PAHs contaminants from the soil and water sources. Figure 13.1 describes the overall process and steps involved in the nano-bioremediation of PAHs-polluted water. This figure clearly illustrated how integrated approaches are combined in an appropriate step for the successful removal of PAHs. In a study, Laveille et al. (2010) reported how functionalized nanomaterials react with PAHs removal. In this study, the authors used mesoporous silica to immobilize hemoglobin (Hb), since free Hb has the aptitude to oxidize about 11 different types of PAHs. But the problem associated with their use in the real-time application is their sensitivity/activity beyond pH 5 (Hb is highly active at pH 5). Most of the wastewater contaminated with PAHs are ranged from pH 6.5 to 8.5. To overcome this issue, Hb was immobilized with mesoporous silica nanoparticles using a simple adsorption method (300 mg/g). In that study also pointed out an interesting factor that free Hb activity is decreased to 47% at pH 7. At the same time, functionalized Hb showed 82% PAHs removal, which makes clear that functionalization Hb in silica nanoparticles leads to higher stability towards a broad range of pH, temperature, solvents, etc. Jin et al. (2016) used green synthesized iron nanoparticles (Fe NPs) along with bacterial strain for the removal of phenanthrene and naphthalene from aqueous solution. Initially, authors tried biodegradation alone for the removal of both PAHs, for their effort naphthalene was easily degraded completely by strain *Bacillus fusiformis.* At the same time, that capability of phenanthrene degradation by the same strain was not up to mark as they

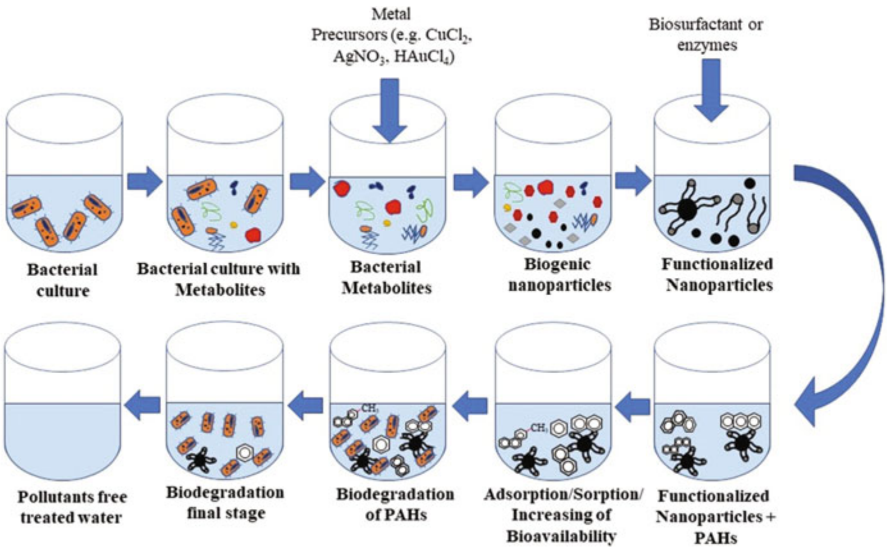

Fig. 13.1 Different steps involved in synthesis of biogenic nanoparticles and functionalization for the effective PAHs bioremediation

expected (only 28.9% removed). Further to improve the degradation efficiency tea extract reduced Fe NPs were included in the degradation systems and monitored the removal efficiency. They achieved 100% phenanthrene removal successfully using an integrated approach with bacterial strain and Fenton-like oxidization using Fe NPs.

The impact of the biosurfactant and iron nanoparticle on indeno(1,2,3-cd)pyrene (InP) biodegradation by a yeast isolate was described in an interesting report by Ojha et al. (2019). In that study, seven different isolates of yeast were applied for the biodegradation of InP. Isolates *Candida tropicalis* NN4 showed higher degradation efficiency among other isolates. Also, strain NN4 has a higher capability of biosurfactant production among other strains. Besides, iron NPs were green synthesized using mint plant leaves. Further, different reaction conditions are applied to obtain maximum removal of InP (for example with and without iron NPs and sophorolipid type of biosurfactant). Further, they added that 20 mg/L of iron NPs along with sophorolipid addition increased InP degradation up to 90%. At the same time increasing iron NPs concentration beyond 20 mg/L leads to a decrease in the degradation activity, it might be due to that higher concentration of iron NPs highly toxic to the yeast cells and may perhaps reduce their growth and development.

The use of single-walled carbon nanotubes (SWCNT) for the environmental cleanup specifically for the removal of phenanthrene in the sediment sample was done by Cui et al. (2011). In this study, they used *Mycobacterium vanbaalenii* strain for the degradation of phenanthrene. The addition of SWCNT leads to the enhanced removal of phenanthrene, it was due to that SWCNT have a higher attraction towards phenanthrene like highly hydrophobic contaminants, and the presence of SWCNT enhanced the bioavailability of phenanthrene. Also, the large surface area and high pore volume of SWCNT played important role in the sorption of phenanthrene. At the same time inclusion of dissolved organic matters (tannic acid, humic acid, and peptone) reduced the surface area by attachment of polar functional groups over the SWCNT, which reduces the sorption of phenanthrene. In a similar study, Wannoussa et al. (2015) subjected biphenyl for the biodegradation using *Rhodococcus erythropolis* with the inclusion of different metallic nanoparticles such as silver (Ag NPs), copper (Cu NPs), cobalt (Co NPs), and palladium (Pd NPs). The addition of nanoparticles alone into the degradation system leads to the agglomeration, so all the metallic NPs were anchored into the inside of microporous SiO_2 as Ag/SiO_2, Cu/SiO_2, Co/SiO_2, and Pd/SiO_2. The bacterial cultures included with Co/SiO_2 with the concentration of 10^{-4} M showed 50% higher biphenyl degradation, also improved growth and development of *R. erythropolis* strain. Further, the authors added that thermal treatment also playing a key role in the stimulating effect of biphenyl removal, since calcinated Co NPs show more effective degradation efficiency than as prepared Co NPs. Also, they summarized that the addition of Cu^{2+} or Ag^{+} ions makes a negative impact on the biphenyl biodegradation since they are toxic to the *R. erythropolis* bacterial strain than their respective metal nanoparticles anchored inside SiO_2. But the addition of Co^{2+} ions or Co NPs anchored on SiO_2 enhanced the activity of catechol 1,2-dioxygenase (a key enzyme playing a major role in the aromatic biodegradation pathway), their activity was inhibited in absence of those nanoparticles and their respective ions. This observation infers that the activity of nanoparticles and their ions are specific to each reaction condition.

In 2018, Mandal et al. (2018a) used a yeast consortium (YC04) with the combination of *Rhodotorula* sp., *Hanseniaspora valbyensis*, and *Debaryomyces hansenii* for the biodegradation of benzo[ghi]perylene with aid of ZnO nanoparticles biosurfactant. The addition of the ZnO NPs and biosurfactant into the degrading system shows improvement in the degradation efficiency with 62%. Later on, the same research group in another work used a similar concept to degrade benzo[a]pyrene. For this, they used yeast consortium (YC01) as said above but *Hanseniaspora valbyensis* was replaced with strain *Hanseniaspora opuntiae,* and the remaining two strains are the same. Yeast consortium (YC01) degraded 82.6% of benzo[a]pyrene within the 6 days of incubation period with the inclusion of biosurfactant and ZnO NPs. To obtain this much degradation efficiency growth conditions such as pH (7.0), temperature (30 °C), shaking condition (130 rpm), ZnO NPs (2 g/L), and inoculum (3%) concentrations are optimized (Mandal et al. 2018b).

In interesting integrated bioremediation, naphthalene was subjected to biodegradation using *Bacillus fusiformis*. In this study, *B. fusiformis* alone degraded about 99% of the naphthalene in 96 h of reaction time. At the same time, 59.4% of chemical oxygen demand only removed, which means that the remaining degraded metabolites still exist in the solution. For this reason, nanoscale zero-valent iron (nZVI) was applied as heterogeneous catalyst material to enhance Fenton-like oxidation of degraded products after *B. fusiformis*-mediated biodegradation process takes place (Yu et al. 2015). In a similar study, Gholami et al. (2019) used magnesium peroxide (MgO_2) nanoparticles for the nano-bioremediation of naphthalene. For this purpose, MgO_2 was encapsulated in the permeable reactive barrier (PRB) and a degradation study was conducted for 50 days and found almost complete removal within the 20 days incubation period. Microorganism responsible for this much degradation was conformed using next-generation sequencing and found *Pseudomonas putida* and *Pseudomonas mendocina*, their growth is stimulated by the addition of MgO_2 NPs in the bioremediation systems. Shanker et al. (2017) used a green approach to synthesis of iron hexacyanoferrates (FeHCF) nanoparticles. A natural surfactant rich plant *sapindus-mukorossi* was used for the synthesis of FeHCF with a size of 10–60 nm. Further, synthesized nano-sized FeHCF was used for the photocatalytic degradation of hazardous PAHs including phenanthrene, anthracene, fluorene, benzo(a)pyrene, and chrysene in both water and soil conditions. Under the solar light irradiation with 25 mg/L of catalyst concentration almost all the PAHs are fractioned into the less toxic small molecules. The degradation ranges were differed based on the PAHs for instance anthracene and phenanthrene, which were removed in the range of 80–90%. At the time benzo(a)pyrene, chrysene, and fluorene were degraded in the range of 70–80%.

Adsorption-synergic biodegradation effect of phenanthrene over the surface of multi-walled carbon nanotubes (MWCNT) buckypaper was established by Tarafdar et al. (2018). In their study, they used *Bacillus thuringiensis* bacterial strain for the degradation of phenanthrene. In general, MWCNT is highly toxic to many bacterial species but the addition of phenanthrene reduced contacts between bacterial cells and MWCNT. At the lower layer cells have to contact with MWCNT and they are disrupted, whereas at the upper layer bacterial cells are developed as a biofilm. About 93.81% of phenanthrene was degraded in presence of *Bacillus thuringiensis* and MWCNT buckypaper. This MWCNT buckypaper acts as a biological carrier or matrix which strongly supports microbial growth.

In a recent study, Wang et al. (2019) described an efficient integrated nano-bioremediation process. In that study, microbe consortium (MC) developed from sewage sludge was adjourned in the microcapsule (MI) interior space, further nano-sized photocatalyst $Ag_3PO_4@Fe_3O_4$ was anchored on the membrane of MI. These entire arrangements are called an MI-MC-photocatalyst compound system (MCS). The biocompatibility test confirmed that $Ag_3PO_4@Fe_3O_4$ makes a slight impact on soil microbe activity. This MCS degraded about 944.1 mg/kg of PAHs in 30 days, it was 49.83% higher than the control system. The addition of MCS makes a huge impact on the soil texture and microbial diversity in the contaminated areas. It also enhanced some enzyme activity more specifically dehydrogenase and hydrolase. Also, the soil toxicity was greatly decreased, which permits the germination of some seeds on the treated soil. This study clearly describes the role of photocatalyst and biodegradation process on the removal of some high molecular weight PAHs. This kind of approach and techniques facilitate sustainable environments.

Researchers from China tested the impacts and effectiveness of nano bamboo charcoal (NBC) towards the biodegradation rate of phenanthrene by bacterial strain *Sphingomonas* sp. GY2B. The addition of NBC enhanced 10.29–18.56%

degradation within 24 h of incubation and completely removed in 48 h. The addition of NBC at 20–50 mg/L enhanced the growth of *Sphingomonas* species. At the same time, increasing the concentration of NBC over 200 mg/L inhibited the growth of *Sphingomonas* strain and notable it makes a small impact in the solubilization of phenanthrene while included in low concentrations (She et al. 2016). Later on, another group of researchers focused on the role and impact of stearic acid-modified montmorillonite on the biodegradation of phenanthrene by the same bacterial strain *Sphingomonas* sp. GY2B. In the biodegradation system surface and colloidal characters of stearic acid-modified montmorillonite were altered in presence of bacterial strain, and found about 98% degradation efficiency in 2 days (Ruan et al. 2018).

Recently, Pourfadakari et al. (2019) used biosurfactants for the sorption of PAHs followed by electrokinetic oxidation for efficient removal of separated hydrocarbons. For this purpose, a halotolerant strain *Pseudomonas aeruginosa* PF2 was used for the synthesis of the rhamnolipid type of biosurfactant. This biosurfactant solution was used for the sorption of three PAHs such as anthracene, pyrene, and phenanthrene in a soil sample. Further, these desorbed PAHs were subjected to electrokinetic oxidation using the magnetite nanoparticles modified graphite. Specific pH, contact time, voltage, and electrolyte concentration are playing a key role in the removal efficiency in electrokinetic oxidation. As said, among the tested broad range of these parameters effective outcome was observed at a pH value of 5, 6 h of contact time, and applied voltage was 3 V with 25 mg/L of electrolyte concentration. These conditions show more than 99% removal efficiency of all three tested PAHs. Similarly, another recent report by Baragano et al. (2020) describes the use of commercial magnetite nanoparticles for the immobilization of PAHs in soil samples. Different concentration of nanoparticles was used such as 0.2%, 1%, 2%, and 5%. About 89% of PAHs are immobilized with 0.2% magnetite nanoparticles. After this treatment, the accumulation of iron content in the soil samples is unavoidable but the toxicity of the soil was reduced greatly.

More recently, Qin et al. (2020) used combinations of photocatalysis and biodegradation as integrated approaches for the removal. For this purpose, Cu, N-TiO_2 was coated over the polytetrafluoroethylene carriers. Microorganisms used for the biodegradation purpose were cultivated from two types of petroleum-contaminated soil (A0 and B) and biofilms are developed over the Cu, N-TiO_2 coated polytetrafluoroethylene carriers, which was further used for the photocatalytic degradation of phenanthrene. Later on, high-throughput sequencing of the 16S rRNA gene was done to find out microbial diversity in both biofilm samples and found *Lysinibacillus* as a dominant genus in the A0 sample, but in sample B genus *Pseudomonas* is more dominant. These nanocarriers enhanced the development of diverse groups of microbial strains in the biofilm sample and also these strains have actively participated in the biodegradation of phenanthrene.

Apart from these nanoscale functionalized materials, some micro-scaled materials are also used for integrated bioremediation studies. In a study, Imam et al. (2021) used rice straw biochar for the immobilization of laccase a ligninolytic enzyme, and used for the anthracene degradation. Biochar used in that study was treated with acid to make carboxyl functionality, which leads to a twofold increase in their surface area. This immobilized laccase enzyme was completely removed about 50 mg/L of anthracene in 24 h of incubations. Another study by Yang et al. (2017) used graphene oxide/Ag_3PO_4 composites as photocatalyst for the removal of three PAHs, namely phenanthrene, naphthalene, and pyrene using visible light irradiation. Within a few seconds to minutes, all the PAHs are completely removed in the solution. This much photocatalytic degradation was facilitated by superoxide radicals, photogenerated holes, and hydroxyl radicals. In a very similar manner, Cai et al. (2019) describe the use of new integrated technology called visible-light photocatalysis and biodegradation (VPCB). Efficient photocatalyst Mn_3O_4/MnO_2-cubic Ag_3PO_4 with exposed facets (MnO_x-cAP) was used in that study for the biodegradation of phenanthrene. This photocatalyst shows extraordinary degradation efficiency with 96.2% of phenanthrene removal within 20 min of reaction time. Further, elimination and mineralization were enhanced by introducing the VPCB sponge with biofilm with enriched microbial strains belonging to *Sedimentibacter, Shewanella, Acinetobacter, Comamonas,* and *Pseudomonas*. The intermediate compounds formed during the photocatalytic degradation were utilized by bacterial strains present in the biofilms. This kind of integrated approach also gives promising outcomes in PAH removal. Table 13.1 summarized the functionalized nanomaterials used for the treatment of PAHs contaminants with the mode of auction and removal efficiency.

13.13 Factors Influencing the Biogenic Nano-bioremediation Process

It’s very important to choose the correct nanomaterials for the degradation of specific hydrophobic contaminants. In some cases, the addition of some nanomaterials makes an adverse impact on the bioremediation process. For example, Zhang et al. (2018) tested the impact of carbon nanomaterials (CNM) for the mineralization and degradation of phenanthrene. In the initial period, maximum mineralization rate and mineralization efficiency were positively associated with the bioavailability of phenanthrene. Notably, the addition of phenanthrene enhanced the growth of fungi and bacteria communities and catabolic gene biomarker *nidA*. The addition of CNM suppressed the sorption rate and also makes an adverse effect on the biomass of bacterial, fungal cells, and *nidA*. These findings suggest that the selection of appropriate sorption or nano-carrier is a key feature for the successful bioremediation process.

In a study, Chaudhary et al. (2018) used silica nanoparticles (SiO_2 NPs) functionalized with four various types of cationic surfactants. These functionalized silica nanoparticles are used for the removal of naphthalene a simple and white crystalline common PAHs found in most of the contaminated areas. Among the used cationic surfactants, cetyl pyridinium bromide functionalized SiO_2 NPs showed an 85% removal percentage. This removal efficiency is 35% higher than as prepared SiO_2 NPs. In this specific study, the authors used chemical surfactants, for

Table 13.1 Different functionalized nanomaterials used for PAHs bioremediations

S. no.	Nanomaterials	Functionalized compounds/ materials	PAHs types	Mode of auction	Removal (%)	Reference
1	SiO_2 NPs	Cetyl pyridinium bromide (cationic surfactants)	13 PAHs	Adsorption	85	Chaudhary et al. (2018)
2	Mesoporous silica	Hemoglobin	11 PAHs	Adsorption	82	Laveille et al. (2010)
3	Iron NPs	Sophorolipid (biosurfactant)	Indeno(1,2,3-cd)pyrene	Biodegradation	90	Ojha et al. (2019)
4	Fe NPs	*Bacillus fusiformis*	Phenanthrene and naphthalene	Biodegradation	100	Jin et al. (2016)
5	Single-walled carbon nanotubes	*Mycobacterium vanbaalenii*	Phenanthrene	Sorption	85–95	Cui et al. (2011)
6	Ag/SiO_2, Cu/SiO_2, Co/SiO_2, and Pd/SiO_2	*Rhodococcus erythropolis*	Biphenyl	Biodegradation	80	Wannoussa et al. (2015)
7	ZnO	Rhamnolipid + yeast consortium (YC04)	Benzo[ghi]perylene	Biodegradation	62	Mandal et al. (2018b)
8	ZnO	Rhamnolipid + yeast consortium (YC01)	Benzo[a]pyrene	Biodegradation	82.67	Mandal et al. (2018a)
9	Nano bamboo charcoal	*Sphingomonas* species	Phenanthrene	Biodegradation	100	She et al. (2016)
10	Stearic acid-modified montmorillonite	*Sphingomonas* species	Phenanthrene	Biodegradation	98	Ruan et al. (2018)
11	Magnetite nanoparticles modified graphite	Rhamnolipid	Pyrene, anthracene, and phenanthrene	Desorption	99	Pourfadakari et al. (2019)
12	Magnetite nanoparticles	–	PAHs	Immobilization	87	Baragano et al. (2020)

sustainable remediation this chemical surfactant can be replaced with biosurfactant (Parthipan et al. 2017a, b, c; Parthipan et al. 2018). Biosurfactants usage in the nano-bioremediation is less documented.

Many physicochemical factors are influencing the removal percentage including the adsorbent concentration, pH, naphthalene concentration, etc. In this study, it was highlighted that increasing adsorbent dose increases the removal percentage, but concentration exceeds above 25 mg/L, adsorption steadiness of naphthalene was attained. The availability of large surface area due to the restriction in growth of nanomaterials may perhaps play a major role in this enhanced removal in presence of cationic surfactant. Similarly, decreasing the pH of the reaction condition also enhanced removal efficiency. Also, many studies have proven that physicochemical properties including temperature, pH, the concentration of catalysts or nanomaterials are playing a major role in the successful remediation of PAHs contaminated environmental samples. For this reason, some studies focus on the optimization of these parameters before proceeding to the bioremediation process (Laveille et al. 2010; Mandal et al. 2018b; Pourfadakari et al. 2019b). Also, biosurfactants are the ideal option to replace the chemical surfactant.

13.14 Conclusions and Future Directions

As discussed earlier, PAHs are considered as most toxic compounds persistent in the environment due to natural and anthropogenic reasons. The toxic nature is very harmful to aquatic organisms, even human beings are also affected due to their toxic nature. Removal of PAHs is a very basic and important necessity to make this environment eco-friendly and sustainable. Their higher hydrophobicity nature makes them very complicated compounds in the bioremediation process. Conventional bioremediation techniques are not effective and time taking process. Increasing bioavailability at the PAHs contaminated area may perhaps be useful for the PAHs utilizing/degrading microorganisms. For this purpose, integrated approaches are tried for the successful removal of PAHs from soil and water sources. Many biological molecules/compounds are playing a key role in the solubilization or degradation of PAHs, but direct delivery of these biomolecules is having many troubleshoots (active or inactive to specific pH, temperature, and other physicochemical conditions that may influence their activity). To overcome these problems, functionalized nanomaterials are introduced for the adsorption or sorption of PAHs. In some cases, nano-sized photocatalysts are used for the photocatalytic oxidation of adsorbed or separated PAHs.

However, in a sustainable point of view, very limited studies are dealing with the use of eco-friendly biogenic nanomaterials for the integrated bioremediation approaches. Still, many active biogenic nanomaterials are available or can be synthesized for nano-bioremediation. Combining nanotechnology with biotechnology will promote the expansion of "sustainable-bio-nanotechnology" approaches for the cleanup of PAHs contaminated environments. For better understanding and improvement of PAHs remediation, few technologies or approaches are needed to be considered. For instance microbiological and molecular techniques can be used for the identification of potential biosurfactant producing microorganisms. Since, biosurfactants can be used as sole compounds to enhance the bioavailability of PAHs. Highly sensible, low cost, quick detecting device or biosensors are needed to be developed to detect PAHs level and types in the environmental samples, because current methods are time-consuming analytical methods which need to be developed. Overall, very little research work is only done on the concept of biogenic nano-bioremediation, this is one of the advanced integrated approaches for the removal of PAHs pollutants. More researches need to be focused on this approach to develop sustainable and environmentally friendly bioremediation technology.

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