Synthetic Nanoparticle-Based Remediation of Soils Contaminated with Polycyclic Aromatic Hydrocarbons

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Contents

Abstract

Polycyclic aromatic hydrocarbons (PAHs) are recognized as potent mutagens or carcinogens and are listed as priority pollutants by the European Commission (EC) and United States Environmental Protection Agency (USEPA). PAHs enter in soil accidentally or through the intended combustion of various kinds of fuels. Invariably after their release a large amount of the PAHs persist in the roadside and agricultural soils. They reach the soil mainly as atmospheric fallout after their release into the environment. The vehicular exhausts, domestic burning, and cigarette smoke also contribute toward their entry into the open environment. Waste generated from the petroleum and coke manufacturing industries further adds to the pollution load onto the environment. The presence and the persistence of PAHs in the soil affect the innocent biota and cause unprecedented damage to the ecology of the area. The deleterious effects to a large extent will depend upon the decay rate and the toxicity of the PAHs and their metabolites. The application

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of nanoparticles to remediate soils contaminated with PAHs has been widely studied in the last decade. The present study will provide a comprehensive overview of various kinds of nanoparticles such as polymer-based and carbon-based material, metal oxides, and nanoscale zero-valent iron utilized for the degradation of PAHs in soils. In order to keep a proper track of the environmental impact of the release of these compounds, the present study on their decay profiles in the soil ecosystem under varying environmental conditions is highly significant.

Keywords

PAHs · Carcinogens · Agricultural soils · Nanoparticles · Decay profiles · Persistence

Introduction

Exploding urbanization and industrialization often combined with improved standards of living have resulted in deleterious effects on the quality of the environment. Due to a large-scale increase in pollution, present-day society is facing several environmental issues which are growing in size and complexity and threatening the survival of mankind on earth (Abdel-Shafy and Mansour 2016). In developing countries, the increasing growth of human population, exploitation of resources, and rapid industrialization are responsible for degradation of existing environmental components. India is a very typical example of developing nation receiving significant pollution from various sources due to rapid industrialization and urbanization. Constant efforts are being made by the Indian government as well as other agencies to decrease air, water, and soil pollution but these are not enough until every human being participates actively and cooperates to build a pollution-free environment (Pathiratne et al. 2010).

One of the most vital components for supporting life on earth is considered as soil. Soil regulates planetary processes to ensure life as well as serves as indispensable medium for food production and growth of flora on earth (Abhilash et al. 2012; Banwart 2011; Hodson 2010). The different processes which are regulated by soil to support life are biodiversity maintenance, ecosystem restoration, biogenic gas regulation, pollutant detoxification, earth's climate, water cycle, and biogeochemical cycles (Gil-Díaz et al. 2014; Abhilash et al. 2013). In order to maintain environmental and earth balance, it is necessarily required to manage soil health. Agricultural as well as food production are also safeguarded by soil (Lal 2015).

With large-scale industrialization, atmospheric air, water reservoirs, and soil ecosystems are getting polluted with undesirable organics and inorganics. Out of these, the organic pollutants are larger in number than the inorganic ones and their number is continuously increasing. A large number of these pollutants exist for longer duration in the environment and are known as persistent organic pollutants (POPs). POPs are organic compounds such as pesticides, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and polybrominated diphenyl ethers (PBDEs) which are resistant to degradation and have adverse effects on environment as well as human health. POPs are transported across international boundaries far from their sources, even at places where they have never been used. The fate and behavior of organic pollutants in aquatic and terrestrial environment are of paramount importance due to their key role in the biological cycles. Pollutants, particularly persistent organic pollutants, once released into the environment may accumulate in the food products (Nasreddine and Parent-Massin 2002; Ahmed 2003; Fontcuberta et al. 2008; Polder et al. 2010; Qin et al. 2011; Fierens et al. 2012) and ultimately find way into human body (Li et al. 2008; Çok et al. 2012). Among the POPs, polycyclic aromatic hydrocarbons (PAHs) belong to a major category. These are of major concern because of their ubiquity, mutagenicity/carcinogenicity, bioaccumulative nature, and ability of transportation to longer distances as well as in food chain. These pollutants are getting deposited on surface aquatic and terrestrial bodies in large quantities through various anthropogenic activities resulting in ecological imbalance.

Role of Nanomaterials in PAH Removal from Soil

Polycyclic aromatic hydrocarbons (PAHs) are recognized to be potently carcinogenic as well as mutagenic in character. These are also identified as priority pollutants by the USEPA and EC. PAHs are introduced into the aquatic and terrestrial systems as a result of both natural activities, namely forest fire and volcanic eruption, as well as anthropogenic activities like incomplete combustion of fuels, cigarette smoke, vehicular traffic, fumes, and wastewater releases from various industries. PAHs may also be contributed by oil spillage and tire abrasion (Gonzalez et al. 2006; Ravindra et al. 2007). PAHs contributed by industrial and domestic waste play a significant role in deterioration of the urban aquatic and terrestrial bodies. Due to the persistent characteristics of PAHs, these can undergo atmospheric transport for dispersion in environment and may deposit in soil at shorter as well as longer distances. These pollutants are thus capable of long-range atmospheric transport affecting pristine regions far from their source of origin. The direct contact with contaminated air, water, or soil causes their exposure to humans. The human exposure to PAHs is higher through soil in comparison to air or water (Agarwal 2009). Urban areas are more contaminated as compared to the rural areas due to high vehicular traffic and increased industrialization. Industrial sources include burning of fuels such as coal, wood, gas, oil, and processing of raw materials. Different group of researchers has monitored the levels of PAHs in soil (Malawaska and Wilkomirski 2001; Skrbic et al. 2005; Yang et al. 2002; Xing-Hong et al. 2006), sediment (Soclo et al. 2000; Nikolaou et al. 2009; Christensen and Bzdusek 2005), and air (Masih et al. 2010; Liu et al. 2014) in different parts of the world. Reports are also available on the presence of PAHs in various water and wastewater systems (Wlodarczyk-Makula 2005; Olenycz et al. 2015; González et al. 2012).

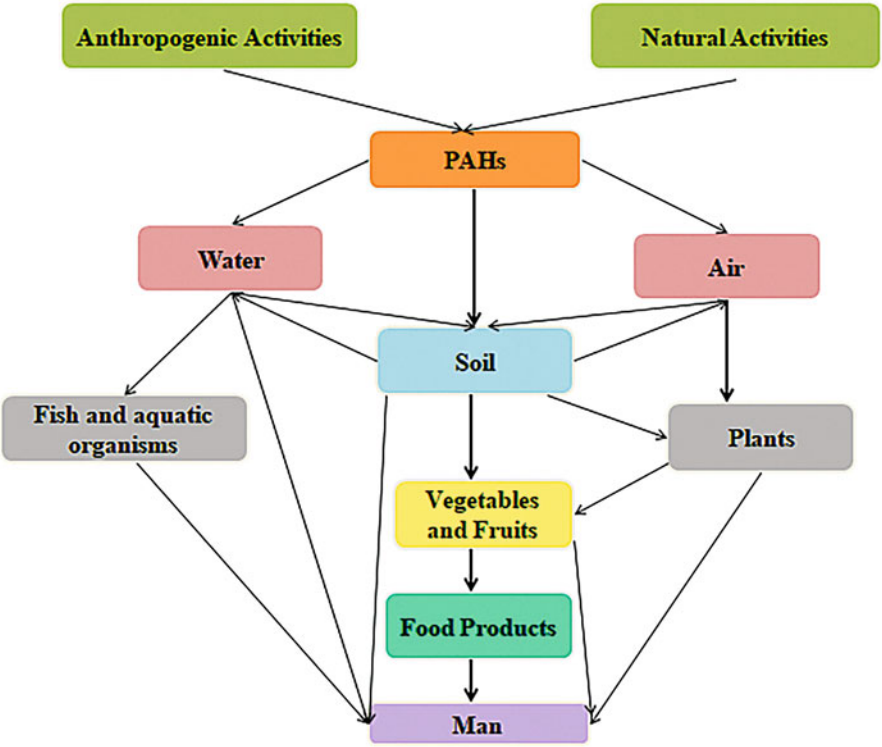

Fig. 1 Interrelated network of PAHs in the environment

The release of PAHs is an unavoidable output of the various industries but this results into a long-term hazard to the environment. The agony of the industrial plants is that on one side there are pressures to expand and modernize the plant, whereas on the other hand the units are being closed down due to poor environmental management. PAHs reach to environment through various anthropogenic activities and cause air, water, and soil pollution depending on their persistence in different matrices. PAHs present in all the segments of environment are inherently toxic and accumulate in the food products by atmospheric deposition from air, translocation in plants through contaminated soil, and in seafood through polluted water. Moreover, the food products also get contaminated during the cooking processes such as grilling and roasting (Chung et al. 2011). PAHs settle down on soil and water surface through atmospheric fallout from air. On the other hand, PAHs being volatile reach air through evaporation from soil or water. Human beings are exposed to PAHs through inhalation of polluted air, consumption of contaminated food or water, and dermal contact with impaired soil. The fate of PAHs and their interrelated network in the environment is illustrated in Fig. 1.

The environmental presence of PAHs is concerned owing to their carcinogenic/mutagenic properties and their capability of toxic effect exertion (Qiu et al. 2011; Xia et al. 2011; Wester et al. 2012; Cheng et al. 2013; Schellenbergera et al. 2013). Because of their hydrophobic nature and low vapor pressure, PAHs tend to accumulate in the soil. PAHs pollution has been widely used to assess the potential impact of anthropogenic activities on soil surfaces because their occurrence in the soil is closely linked to urban activities. In each forthcoming year, the contamination and pollution in soils is increasing, which leads to the reduction in agricultural land for production of food. It is a challenge to grow more food for the increasing population in the decreasing landscape. Simultaneously, the challenge is to prevent soil from environmental contamination and restoration of polluted soil. Therefore, the study of PAHs degradation on soil surface and their toxic potential is of utmost significance in the present situation.

PAHs enter in soil accidentally or through the intended combustion of various kinds of fuels. Invariably after their release a large amount of the PAHs persist in the roadside and agricultural soils. They reach the soil mainly as atmospheric fallout after their release into the environment. The vehicular exhausts, domestic burning, and cigarette smoke also contribute toward their entry into the open environment. Waste generated from the petroleum and coke manufacturing industries further adds to the pollution load into the environment. The presence and the persistence of PAHs in the soil affect the innocent biota and cause unprecedented damage to the ecology of the area. The deleterious effects to a large extent will depend upon the decay rate and the toxicity of the PAHs and their metabolites. The persistence, no doubt, is primarily determined by the chemical nature but is significantly affected by the nature of the medium and the environmental factors like temperature, humidity, and pH. The interaction of PAH with a medium like soil is more complicated than with water. The persistence of PAHs in the soil may vary from a few hours to many years depending on its type (Howard et al. 1991). Fate and behavior of PAHs in soil depend upon many factors like degradation rate, uptake by the soil microorganisms

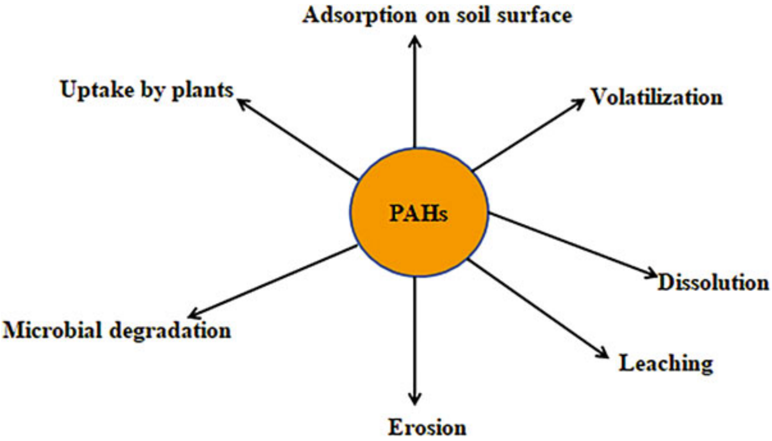

Fig. 2 Fate of PAHs in soil environment

or plants, adsorption on organic matter and clay, leaching with the downward percolation of water, and volatilization (Fig. 2).

In order to prepare soil suitable for production of crops and agriculture as well as to vanish PAH contamination, explorations of a number of technological innovations have been investigated. Among different technological innovations, the application of synthetic nanomaterials for degradation of PAHs in contaminated soils is one of the most suitable techniques due to their superiority in the capacity to degrade the PAHs. Their high degradation capacity creates nanoparticles (NPs) an ideal material to decontaminate soil from PAH pollution (Souza et al. 2020; Riding et al. 2015; Peikam and Jalali 2018).

The materials with sizes in the range 1–100 nm in at least one dimension are referred as nanomaterials. In the field of remediation, nanoparticles (NPs) become more advantageous compared to bulk phase due to their specific characteristics such as high catalytic efficiency, enhanced magnetic properties, and high surface-to-volume ratio (Gupta et al. 2011). The NPs degrade the contaminant faster than bulk phase along with generation of smaller amount of toxic by-products due to their greater surface reactivity and high surface area (Bhattacharya et al. 2013). In order to decontaminate polluted sites, the application of various nanomaterials such as metal oxides, biometallic particles, dendrimer enzymes, nanoscale zeolites, and carbon nanotubes is in vogue (Mehndiratta et al. 2013).

The nanomaterials in different categories such as polymer-based nanomaterials, carbon-based nanomaterials, metal oxides, and nanoscale zero-valent iron have been utilized for PAH remediation from contaminated soil (Mazarji et al. 2021). The summary of different categories of nanomaterials has been illustrated in the following discussion.

Nanoscale Zero-Valent Iron (nZVI)

The remediation of PAH-contaminated soils has been conducted using the widely employed nanomaterial, nanoscale zero-valent iron. The reactivity of nZVI toward PAHs is high due to the smaller size. Various researchers have utilized nZVI for the degradation of PAHs in soils (Table 1).

Chang et al. (2007) investigated the degradation of PAH pyrene utilizing nZVI as well as microscale ZVI (mZVI). The surface area (33.5 m^2 g^{-1}) for nZVI was higher than mZVI, leading to higher degradation of pyrene in presence of nZVI. The study suggested that the cumulative effect of particle size and surface area was responsible for the variation in rate of reaction. Chang and Kang (2009) also demonstrated remediation of pyrene-contaminated soil by nZVI. The variation in oxidation-reduction potential as well as pH by nZVI was compared to mZVI. The researchers observed production of hydroxide with rise in pH up to 8.5 from an initial pH of 5. At the same time, a rapid decrease in oxidation-reduction potential was observed up to −700 mV from +400 mV, suggesting domination of reduction conditions. Pardo et al. (2016) conducted column studies for nZVI-activated persulfate reaction to examine its efficiency and effectiveness. It was found that the removal of PAHs

Table 1 Remediation of PAH-contaminated soils using nZVI

Nonmaterials used	Target pollutants	Remarks	References
ZVI	Pyrene (PYR)	The pseudo-first-order rate constant for nZVI was 0.24 min^{-1}. The study suggested that the cumulative effect of particle size and surface area was responsible for the variation in rate of reaction	Chang et al. (2007)
nZVI	PYR	Study suggested that the involvement of nZVI particles created strong reduction conditions and increased the removal percentage of pyrene from soil	Chang and Kang (2009)
nZVI catalyzed persulfate in column condition	ANT, PHE, PYR, and BaP	The removal of PAHs was higher under optimum conditions. However, in order to avoid radical scavenging, nZVI may be applied in moderate doses only	Pardo et al. (2016)
nZVI with biochar	All PAHs	Biochar and nZVI together were useful to reduce the PAH contents of soil. However, further studies suggested that sorption properties of biochar are mainly responsible for PAH reduction	Oleszczuk and Koltowski (2017)
nZVI, C-nZVI, and mZVI-activated persulfate	PAHs	The PAH removals were 69.14% 62.78% and 82.21% for persulfate activated with mZVI, C-nZVI, and nZVI, respectively	Song et al. (2018)
nZVI coated with sugar esters, sorbitan monolaurate, and polyacrylic acid	PAHs	The suitable surfactant for PAH removal from soil was sugar esters, which are biodegradable and non-tic in nature. After oxidation and degradation of PAHs, finally three main products, 1,5-diphenyl-1,4-pentadiyn-3-one, fluoranthene and 9-methylene-9H-fluorene, were produced	Sun et al. (2022)
nZVI coated with carbon	ANT	After 0.5 h, 51.6% anthracene was removed from the soil, which was further increased to 76.4% after 12 h. The study of mechanism of degradation indicated that $O_2^{\bullet -}$ and $^1O_2$ were the main species responsible for the anthracene degradation	Li et al. (2022)

was higher under these conditions. However, in order to avoid radical scavenging, nZVI may be applied in moderate dose only. Oleszczuk and Koltowski (2017) investigated the application of nZVI along with biochar to degrade PAHs in soil.

The study indicated that biochar and nZVI together were useful to reduce the PAH contents of soil. However, further studies suggested that sorption properties of biochar are mainly responsible for PAH reduction. Song et al. (2018) utilized various ZVI such as commercial micron-sized ZVI (mZVI), stearic-coated micro/nanostructured ZVI (C-nZVI), and micro/nanostructured ZVI (nZVI) for the activation of persulfate and removal of PAHs. The PAH removal efficiencies of persulfate activated with mZVI, C-nZVI, and nZVI were 69.14%, 62.78%, and 82.21%, respectively, after a period of 104 days. The pH of the soil was also found to be decreased due to decomposition of persulfate and release of H^+. Sun et al. (2022) applied nZVI modified with sugar esters, sorbitan monolaurate, and polyacrylic acid for the remediation of soil contaminated with PAHs, where $KMnO_4$ was taken as oxidant. It was reported that the suitable surfactant for PAH removal from soil was sugar esters, which are biodegradable and non-tic in nature. The researchers reported that after oxidation and degradation of PAHs, finally three main products, 1,5-diphenyl-1,4-pentadiyn-3-one, fluoranthene, and 9-methylene-9H-fluorene, were produced. Li et al. (2022) employed nZVI coated with carbon to activate persulfate and degrade PAH anthracene in soil. The results suggested that after half an hour of reaction 51.6% anthracene was removed from the soil, which was further increased to 76.4% after 12 h. The study of mechanism of degradation indicated that $O_2^{\bullet -}$ and $^1O_2$ were mainly responsible species for the anthracene degradation. Moreover, the soil component in the form of MnO_2 facilitated the formation of $^1O_2$. The usefulness of nanoscale zero-valent iron in persulfate and Fenton-like processes is shown in Table 1.

Metal Oxides

In the last decade, a large number of metal oxides have been investigated for the degradation of PAHs. Among the applied metal oxides, different forms of iron oxide and titanium oxides were studied prominently. The characteristics of metal oxide–catalyzed PAH degradation are summarized in Table 2.

Wen et al. (2003) studied the photodegradation of pyrene in aqueous solutions in presence of TiO_2. The results revealed the occurrence of hydroxylation, ketolysis, and ring-open reactions for the formation of intermediates. The solution pH had a little effect on photodegradation rate of pyrene. Zhang et al. (2008) studied photodegradation of phenanthrene, pyrene, and B[a]P on soil surfaces in the presence of TiO_2 under UV irradiation. The effect of various parameters on the degradation was observed.

Photodegradation of pyrene on solid phase of iron oxide was investigated by Wang et al. (2009). The results revealed that the rate of photodegradation of pyrene is in the order: goethite > hematite > maghemite > lepidocrite. First-order rate kinetics were observed for the degradation of pyrene. It was also observed that iron oxides along with oxalic acid may initiate photo-Fenton-like mechanism under UV irradiation in the absence of additional H_2O_2. The degradation was also studied in red soil contaminated with 09 h PAHs using α-FeOOH along with oxalic acid for a

Table 2 Metal oxides for decontamination of PAHs-contaminated soils

Nonmaterial	Target pollutants	Remarks	References
TiO_2	PYR	Occurrence of hydroxylation, ketolysis, and ring-open reactions for the formation of intermediates. The solution pH had little effect on photodegradation rate of pyrene	Wen et al. (2003)
TiO_2	PHE, PYR, and B[a]P	Phenanthrene, pyrene, and B[a]P were degraded on soil surfaces in the presence of TiO_2 under UV irradiation	Zhang et al. (2008)
Fe_3O_4	PYR	The rate of photodegradation of pyrene is in the order: goethite > hematite > maghemite > lepidocrite. First-order rate kinetics was observed for the degradation of pyrene. It was also observed that iron oxides along with oxalic acid may set up photo-Fenton-like mechanism under UV irradiation in the absence of additional H_2O_2	Wang et al. (2009)
Rutile TiO_2 and anatase TiO_2	PHE and PYR	In both cases, photodegradation rate followed pseudo-first-order rate kinetics and the rate increased with the increasing concentration of H_2O_2 and humic acid and intensity of light	Dong et al. (2010a, b)
Iron oxides	B[a]P	The results suggested that degradation of BaP was enhanced due to goethite in all soils. The addition of oxalic acid further increased the decay rate due to involvement of Fenton-like mechanism without H_2O_2	Gupta and Gupta (2015a)
Iron oxide	PYR	The results suggested that the PAH pyrene in soils was successfully decayed in the presence of goethite NPs into smaller fragments, which are nontoxic in nature	Gupta and Gupta (2015b)
Akaganeite	PHE	The rate constant for phenanthrene degradation was 6×10^{-3} h^{-1} with nano-rods of akaganeite (4%). The possible decay profiles for phenanthrene degradation in soils were also demonstrated	Gupta (2016)
Fe_3O_4 and α-FeOOH	ANT	The degradation of anthracene was faster using α-FeOOH compared to Fe_3O_4	Gupta et al. (2017)
Iron nano-oxides	PYR	After 6 h of Fenton's process, 93% pyrene decay was reported	Jorfi et al. (2013)
Photo-Fenton catalyst (α-FeOOH)	PAHs	After irradiation of 480 μW cm^{-2} UV light for 12 h, various PAHs degradation was in the range 12–22%	Wang et al. (2009)

(continued)

Table 2 (continued)

Nonmaterial	Target pollutants	Remarks	References
g-C_3N_4/Fe_3O_4 as visible-light-driven photocatalyst	PHE	92% photodegradation of phenanthrene was achieved by g-C_3N_4/Fe_3O_4	Wang et al. (2019)
Fe_2O_3	16 PAHs	The degradation of PAH involves photocatalysis as well as photolysis. Quick volatilization influences medium and low molecular weight PAHs BaP photodegradation was higher (71%) in the presence of Fe_2O_3 than in the absence of Fe_2O_3 (50%)	Marquès et al. (2020)
Potassium zinc hexacyanoferrate nanocubes	ANT, PHE, FLU, CHR, and BaP	Under sunlight, at neutral pH, maximum degradation of PAHs was observed. The rate of degradation becomes slower in soil than in water due to soil organic content. The degradation of smaller PAH, PHE, and ANT was in the range 80–93%, whereas the degradation of high molecular weight PAH, BaP, CHR, and FLU was in the range 70–80%	Shanker et al. (2017a)
Iron hexacyanoferrate	BaP, CHR, FLU, PHE and ANT	The prepared NPs work as photocatalyst cum adsorbent in the order: dark < UV light < sunlight	Shanker et al. (2017b)
TiO_2-based zinc hexacyanoferrate	PHE, ANT, and FLU	After 24 h irradiation of sunlight, FLU, PHE, and ANT were undergone 82, 84, and 86% degradation, respectively	Rachna et al. (2019)
TiO_2	12 PAHs	The study suggested that the removal efficiency in industrial soil was increased due to presence of metal oxide, TiO_2	Eker and Hatipoglu (2019)

time interval of 12 h. The degradation of PAHs was in the range of 12.2–21.8% (Table 2).

Dong et al. investigated degradation of phenanthrene and pyrene on soil surfaces using rutile TiO_2 (Dong et al. 2010a) and anatase TiO_2 (Dong et al. 2010b) as photocatalysts under UV irradiation. In both cases, photodegradation rate followed pseudo-first-order rate kinetics and the rate increased with the increasing concentration of H_2O_2 and humic acid and intensity of light. Barzegar et al. (2017) achieved the degradation of pyrene by using nanoscale Fe_3O_4 through sonolysis-assisted Fenton-like process. The removal of pyrene was 98% with 0.066 min^{-1} as pseudo-first-order rate constant under optimum conditions (Table 2). Along with the spiked soil samples, real samples containing chrysene (CHR), phenanthrene (PHE), acenaphthene (ACE), fluoranthene (FLU), and pyrene were also investigated, achieving a percentage removal in the range of 37.7–85.2%. In the spiked soil, the removal of pyrene was also examined using a mixture of Fe_2O_3 and Fe_3O_4 (nanoform). The efficiency of pyrene removal at neutral pH was found to be >90% on application of Fenton-like reaction (Jorfi et al. 2013).

The doping of metal oxide NPs with other photocatalysts was also found to be popular among the environmentalists throughout the world. Photocatalytic degradation of phenanthrene was performed using TiO_2 nanostructure doped with iron. The electron trap ability, band gap, and specific surface area were observed to be improved due to doping. Under alkaline conditions, the degradation efficiency of catalyst for PHE was greater than neutral and acidic conditions. The percentage degradation was >80%, which was attributed to the generation of (Fe^{3+}-ligand) complex and $^{\bullet}OH$ under strong oxidizing conditions (Table 2). The amount of phenanthrene was diminished to 40 and 20 mg kg^{-1} without and with photocatalyst, respectively, from an initial amount of 60 mg kg^{-1} after a period of 2 h (Theerakarunwong and Phanichphant 2016).

The phenanthrene-contaminated soil was treated with the photocatalyst g-C_3N_4/Fe_3O_4 under visible light. At a pH near 7, the degradation of phenanthrene (200 mg kg^{-1}) under visible light irradiation of 2 h was >90% (Wang et al. 2019). The degradation of phenanthrene was also examined under UV light using iron oxide nano-rods as photocatalyst by Gupta (2016). The rate constant for phenanthrene degradation was 6×10^{-3} h^{-1} with nano-rods of akaganeite (4%). The possible decay profiles for phenanthrene degradation in soils were also demonstrated. The study of intermediates and their persistence clearly indicated the complete degradation as well as removal of phenanthrene from contaminated soils.

The photocatalyst Fe_2O_3 was employed to investigate decay of 16 PAHs in soil for a period of 28 days under optimum conditions. The presence of photocatalyst Fe_2O_3 significantly enhanced the degradation of BaP, phenanthrene, and fluoranthrene, whereas the degradation of dibenzo(a,h)anthracene (DBahA) and benz(a)anthracene (BaA) was reduced with the presence of photocatalyst (Marquès et al. 2020) (Table 2). Chien et al. (2011) indicated that total organic carbon as well as soil texture may affect the degradation of pyrene. The researchers utilized 100–392 nm TiO_2 particles in red, alluvial soil, and quartz sand under sunlight to achieve 32, 23, and 78% pyrene degradation in respective soils (Table 2). Shanker et al. (2017a) used nanocubes of potassium zinc hexacyanoferrate to degrade BaP, CHR, FLU, PHE, and ANT along with irradiation of sunlight. Green method of synthesis using *Sapindus Mukorossi* was employed to prepare the photocatalyst. The degradation of smaller PAH, PHE, and ANT was in the range of 80–93%, whereas the degradation of high molecular weight PAH, BaP, CHR, and FLU was in the range of 70–80%. Compared to aqueous conditions, the PAHs diffusion on organic carbon was slow, which makes the decay process more difficult. The same group of authors, Shanker et al. (2017b), demonstrated the synthesis of green nanoparticles of iron hexacyanoferrate to degrade BaP, CHR, FLU, PHE, and ANT. The prepared NPs work as photocatalyst cum adsorbent in the order: dark < UV light < sunlight. Rachna et al. (2019) established the framework of TiO_2-zinc hexacyanoferrate for PAH degradation under visible light. The results reveal that nanocomposite's positive surface and PAHs were interacted due to cation-π complexes. After 24 h irradiation of sunlight, FLU, PHE, and ANT were undergone 82, 84, and 86% degradation, respectively.

Gupta and Gupta (2015a) studied the degradation of BaP in the presence of different forms of synthesized iron oxides and reported fastest degradation with goethite NPs. Goethite NPs were applied for degradation of BaP in soils of varying pH under UV irradiation. The results suggested that degradation of BaP was enhanced due to goethite in all soils. The oxalic acid addition further increased the decay rate by involvement of Fenton-like mechanism without H_2O_2. The study also demonstrated the degradation pathways and persistence of intermediate degradation processes. A smaller PAH pyrene was also observed as intermediate during the degradation of BaP. In another study, Gupta and Gupta (2015b) demonstrated the decay of PAH pyrene in soils with goethite under UV irradiation. The results suggested that the PAH pyrene in soils was successfully decayed in the presence of goethite NPs into smaller fragments, which are nontoxic in nature. Gupta et al. (2017) synthesized Fe_3O_4 and α-FeOOH NPs and applied for degradation of anthracene. It was observed that the degradation of anthracene was faster using α-FeOOH compared to Fe_3O_4.

The metal oxide nanomaterials combined with plant materials form a more efficient photocatalyst for remediation of PAHs. Włóka et al. (2019) used *Brassica napus* L. and *Phalaris arundinacea* L. in combination with SiO_2 NPs to remediate PAHs. The reduction in PAH toxicity was reported due to the presence of SiO_2 NPs. Eker and Hatipoglu (2019) studied the photodegradation applications for remediation of PAHs in industrial soils. The study suggested that the removal efficiency was increased due to presence of metal oxide, TiO_2. The application of UV radiations reduces 86–90% PAH content from polluted soils.

In the light of above discussion, it is well established that highly reactive radicals are generated by persulfate and Fenton's process for mineralization of PAHs in soils. Moreover, the pH of soil plays an important role during degradation of PAHs.

Other Synthesized Materials

Materials Based on Carbon

Carbon-based nanomaterials are one of the most promising materials for remediation of various environmental contaminants. Due to surface functionality, excellent thermal conductivity, and greater surface area, graphene is applied for decay of organic pollutants globally (Huang et al. 2012). Due to occurrence of strong π-π interactions, high surface area, and dispersibility, nano-sulfonated graphene have prominent affinity toward various PAHs. The removal of PAH decreases with the increase in ring size under optimum conditions (Gan et al. 2017). Alhendal et al. (2022) removed PAHs using hybrid sol–gel sorbent, aramid-wrapped CNT. In soil samples, the affinity of sorbent was increased due to hydrophobic and hydrophilic interactions as well as π–π stacking.

In case of silt loam and sandy loam, multiwalled carbon nanotubes (MWCNTs) showed sorptive characteristics for naphthalene, fluorene, and phenanthrene. The study reported three times higher sorption of studied PAHs onto MWCNTs as compared to silt loam and sandy loam (Li et al. 2013a). In another study, the same

Table 3 Carbon- and polymer-based nanomaterials for PAHs-contaminated soils

Nonmaterials used	Target pollutants	Remarks	References
Aramid-wrapped CNT	PAHs	The affinity of sorbent was increased due to hydrophobic and hydrophilic interactions as well as π–π stacking	Alhendal et al. (2022)
Multiwalled carbon nanotubes (MWNTs) for sorption	Single PAH	Three times higher sorption of studied PAHs onto MWCNTs as compared to silt loam and sandy loam	Li et al. (2013a)
Carbon nanotubes (CNTs)	NAP, FLU, PHE, and PYR	The hydrophobic properties, micropore volume, and surface area are main factors, governing PAH mobility in column mode	Li et al. (2013b)
Nanocomposites based on chitosan and metal oxides	PHE and ANT	Higher degradation of anthracene than phenanthrene was due to lower stability of anthracene. GC-MS analysis suggested the formation of by-products which are relatively safe as well as smaller than parent compounds	Rani and Rachna (2020)
APU particles	PHE	APU particles behave similar to Triton X-100 reagent, but it is better due to its cross-linked structure, leading to lower adsorption tendency onto aquifer sand	Kim et al. (2003)
Fabricated fibrous membranes carrying laccase	B[a]P, FLU, PHE, and BaA	The effectiveness of remediation for benzo[*a*]pyrene, benz[*a*]anthracene, fluoranthene, and phenanthrene were 72.5%, 79.1%, 93.2%, and 95.1%, respectively	Dai et al. (2011)
Cu_2O/Polylactic acid composite	FLU	Under visible light irradiation, >65% of PAH, fluoranthene was found to be degraded	Xu et al. (2020)

researchers reported smaller mobilities of studied PAHs due to occurrence of higher sorption capability of carbon nanotubes. Retention in mobility of PAHs was observed during their leaching in presence of carbon nanotubes in column mode. The hydrophobic properties, micropore volume, and surface area are main factors, governing PAH mobility in column mode (Li et al. 2013b). A few of the carbon-based nanomaterials for remediation of PAHs are summarized in Table 3.

Polymer-Based Nanomaterials

The remediation of PAHs has also been demonstrated using polymer-based nanomaterials. The urethane acrylate nonionic chain was employed through the chemical cross-linking route to fabricate amphiphilic nanoscale polyurethane (APU) particles. The results reveal that APU particles behave similar to Triton X-100 reagent, but it is better due to its cross-linked structure, leading to lower adsorption tendency onto aquifer sand (Kim et al. 2003). Rani et al. (2020) degraded carcinogenic PAHs using nanocomposites based on chitosan and metal oxides. The natural surfactant *Azadirachta indica* was used to synthesize nanocomposite via green method.

Under direct sunlight, phenanthrene and anthracene were decayed exponentially (>90%) with photocatalyst in 12 h. Higher degradation of anthracene than phenanthrene was due to lower stability of anthracene. GC-MS analysis suggested the formation of by-products which are relatively safe as well as smaller than parent compounds. Dai et al. (2011) employed different fabricated fibrous membranes carrying laccase to investigate the removal of shoal soil contaminated with PAHs. The core of the structure was composed of laccase, which is responsible for degradation of PAH and nanofibers cause PAH adsorption, whereas mass transfer was performed by pores on the shell. The effectiveness of remediation for benzo[*a*]pyrene, benz[*a*]anthracene, fluoranthene, and phenanthrene were 72.5%, 79.1%, 93.2%, and 95.1%, respectively. The half-lives for PAHs were 1.25–12.50 h (membrane adsorption) or 17.9–67.9 h (free laccase), while using the fibrous structures these become much shorter, i.e., 0.003–1.52 h. In the overall reaction, the rate-limiting steps were internal diffusion and superficial adsorption, as suggested by third-order reaction kinetics. The triple-phase distribution and kinetics propose synergistic effect between degradation and adsorption. In a recent study, Xu et al. (2020) fabricated nanofibers of Cu_2O/polylactic acid, consisting of Cu_2O NPs and biodegradable polymer, polylactic acid. Under visible light irradiation, >65% of PAH, fluoranthene was found to be degraded using Cu_2O/polylactic acid nanofibers (Table 3).

Mechanism of PAH Degradation Using Synthetic NPs and By-Products Identification

The NPs generally have a band gap between the conduction band and the valence band. Upon irradiation of synthesized NPs with radiation of suitable wavelength, an electron-hole pair is generated due to transfer of an electron from valence band to conduction band. The electron combines with oxygen (O_2) to produce $O_2^{\bullet -}$, whereas the hole combines with water molecule to form $OH^\bullet$ radical and H^+ by splitting. The H^+ combines with $O_2^{\bullet -}$ to produce H_2O_2, the produced H_2O_2 combines with iron oxide to demonstrate Fenton-like mechanism (Shanker et al. 2017a; Gupta and Gupta 2015a; Wang et al. 2009). The generated H_2O_2 molecule also produces $OH^\bullet$ radical, which is responsible for the initiation of degradation mechanism. The $OH^\bullet$ radical combines with the PAH molecule and generates another radical. It is well established that radicals are short lived and undergo fragmentation or combination to form different entities. Generally, the molecule undergoes fragmentation to smaller molecules, which further converted to even smaller counterparts, leading to mineralization of environmental contaminant. The degradation process and generation of $OH^\bullet$ radical is summarized in Fig. 3. Several photocatalytic studies also reported the by-products generated after degradation of PAHs in the presence of photocatalysts. Shanker et al. (2017a) proposed the production of malealdehyde, o-xylene, 2-methylhex-3-enoic acid, 2,4a-dihydro-1H-cyclopenta[cd]indene, 2-hydroxycyclohexa-1,3-dienecarboxylic acid, 2,3-dimethylbenzoic

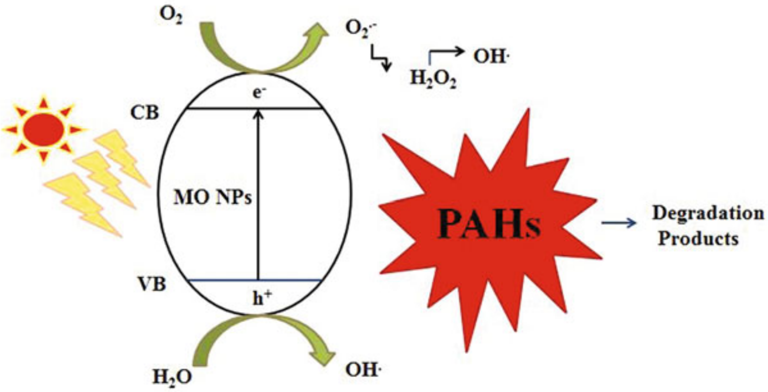

Fig. 3 Photocatalytic degradation process in presence of NPs

acid, and 2-hydroxy-1-naphthoic acid using iron hexacyanoferrate NPs and potassium zinc hexacyanoferrate nanocubes under visible light (Fig. 4).

Similarly, Gupta and Gupta (2015a) proposed the degradation of BaP in different soils contaminated with PAHs. The degradation of BaP in neutral soil produces benzo[a]pyrene-4,5-dione, cyclopenta[d,e,f]chrysene-4-one, 5-hydroxybenzo[a] pyrene, and 1,2-epoxypyrene. In case of basic soils, the degradation of BaP produces 4,5-dihydroxybenzo[a]pyrene, cyclopenta[d,e,f]chrysene-4-ol, benzo[a]pyrene-4,5-ketol-7,8-dihydrodiol-9,10-epoxide, and 1,2-dihydroepoxypyrene. In acidic soils, along with several other degradation products, smaller PAH pyrene was observed. Gupta and Gupta (2015b) identified different degradation products of pyrene in different soils. The intermediate generated in neutral soils are 1-hydroxypyrene, 3,4-dihydroxy-3,4-dihydrophenanthrene-4-carboxylic acid, 3,4-dihydrophenanthrene-4-carboxylic acid, 3-(1-hydroxy-2-naphthalenyl)-2-propenal, and 1,2-naphthalenedione. In basic soil, intermediate phenenanthrene-4-carboxylic acid was observed. In acidic soils, the intermediates 6-hydroxy-4H-cyclopenta[def]phenanthrene-4-one, 2-hydroxypyrene-4,5-dione, 4Hcyclopenta[def] phenanthrene-4-ol, and phenanthrene-4-carboxylic were examined. Due to appearance of different chemical environment, the degradation products were of different persistence as well as different nature and size. The studies on the identification of metabolites of benzo[a]pyrene and pyrene reveal that the photodegradation of the PAHs occurs through oxidative mechanism.

The metabolic pathways seem to be complex and different metabolites were observed in soils with different pH. During photodegradation of benzo[a]pyrene, metabolite benzo[a]pyrene-[4,5]-dione (m/z 283) was observed in neutral and acidic soil due to full oxidation of benzo[a]pyrene, while in case of basic soil metabolite 4,5-dihydroxybenzo[a]pyrene (m/z 285) was observed due to partial oxidation of benzo[a]pyrene. The metabolite 9-hydoxybenzo[a]pyrene-7,8-dione was observed in neutral soil only and in acidic or alkaline soils, it oxidized further to benzo[a] pyrene-4,5-ketol-7,8-dione-9,10-epoxide (m/z 331). In acidic and basic soils,

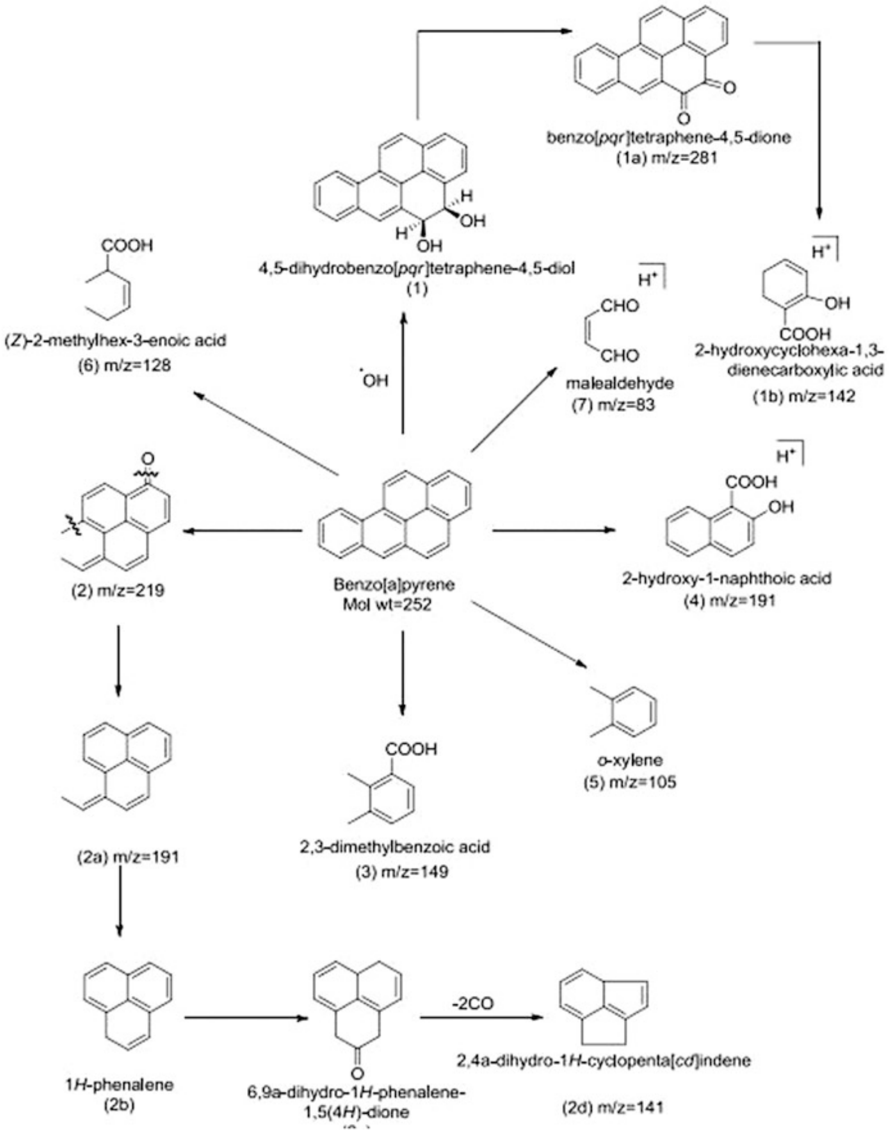

Fig. 4 Degradation of B[a]P using iron hexacyanoferrate NPs and potassium zinc hexacyanoferrate nanocubes. (Reprinted from original article by Shanker et al. (2017a) after permission through RightsLink)

metabolite 5-hydroxybenzo[a]pyrene was persistent after 120 h, but was not observed in neutral soil after 120 h. In acidic soils, benzo[a]pyrene was converted to smaller PAH pyrene.

In case of pyrene, metabolites corresponding to naphthalene and its derivatives are persistent in basic and neutral soil, but in acidic soil, hydrogenated phenanthrene was persistent. The degradation pathways thus indicate that the mutagen pyrene is degraded efficiently in presence of goethite into smaller nonmutagenic/non-carcinogenic hydrocarbons. Photodegradation studies further reveal that the metabolites of benzo[a]pyrene and pyrene, reported to be toxic, such as diones, diols, and epoxides, disappear in all the three soils after 120 h. Thus, the study provides an efficient method for the remediation of PAH-contaminated soil surfaces.

Theerakarunwong and Phanichphant (2016) reported phenanthrene degradation under visible light in presence of Fe-doped TiO_2. The degradation of phenanthrene was initiated by attack of generated $OH^{\bullet}$ radical to the K-region phenanthrene molecule. The main by-products formed during the decay process were 1,4 Napthoquinone and heptadecane. Wang et al. (2019) demonstrated on the basis of ESR analysis that not only $OH^{\bullet}$ radical but also $O_2^{\bullet-}$ causes the degradation of PAH. The two types of radicals were generated by solar light irradiation of g-C_3N_4/Fe_3O_4 in their study. Gupta (2016) described the proposed mechanisms for the decay of phenanthrene in acidic, basic, and neutral soils using akaganeite nano-rods under UV irradiation. In case of acidic soils, nontoxic and simpler intermediates such as phenylmethanol, phthalic acid, pyrocatechol, salicylic acid, and open-chain compounds were reported at the later part of reaction. In neutral soils, simpler intermediates were 9H-fluoren-9-ol and benzoic acid. In basic soils, the simpler intermediates were pyrocatechol, 2,5-dihydroxybenzoic acid, 2-hydroxybenzaldehyde, or benzoic acid. The simpler intermediates were also reported to disappear at the time of completion of reaction. The degradation in the three types of soils occurs through loss of CO group, loss of oxygen, oxidative ring opening, and oxidation cleavage. The study concluded that phenanthrene degradation with akaganeite nano-rods depends on soil characteristics. It was also suggested that the identified intermediates may serve as data bank to different toxicological studies.

Conclusions

Polycyclic aromatic hydrocarbons are globally distributed and persistent environmental contaminants. The extent and seriousness of the potential hazards due to these pollutants have already been defined by various environmental agencies such as USEPA and EC by categorizing them as priority pollutants. Among different technological innovations for their remediation, the application of synthetic NPs for remediation of PAHs in the contaminated soils is one of the most suitable techniques due to their superiority in the capacity to degrade the PAHs efficiently. Their high degradation capacity creates nanoparticles an ideal material to decontaminate soil from PAH pollution. The current chapter reports the application of various NPs based on carbon, polymer, metal oxides, and nanoscale zero-valent iron. It was observed that different types of nanoparticles degrade the PAHs efficiently in varying soils. Among different iron oxides, the rate of photodegradation of pyrene was in the order: goethite > hematite > maghemite > lepidocrite. In the spiked soil, the removal of pyrene was also examined using a mixture of Fe_2O_3 and Fe_3O_4 (nanoform). The removal efficiency of pyrene, at neutral pH, was found to be >90% on application of Fenton-like reaction. The nanocubes of potassium zinc hexacyanoferrate degrade smaller PAH, PHE, and ANT up to an extent of 80–93%, whereas the same photocatalyst degrades high molecular weight PAH, BaP, CHR, and FLU up to an extent of 70–80%. The mechanism of degradation suggests that the decay process occurs through oxidative mechanism. The major species responsible for degradation was found to be $OH^{\bullet}$, whereas based on ESR analysis it was also concluded that $O_2^{\bullet-}$ can also cause the degradation of PAH. The pH of the soil plays a significant role in the degradation process. A large number of intermediate and by-products have been proposed by diverse researchers, which may serve as a data bank for various toxicological studies in future.

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