ABSTRACT
Polycyclic aromatic hydrocarbons (PAHs) are one of the most prevalent contaminants having toxicity, mutagenicity and carcinogenicity. Pollution caused by PAHs is a serious problem throughout the world. To solve the problem, substantial research efforts have been directed worldwide to adopt sustainable technologies for the treatment of PAHs containing soil. PAH compounds are transferred, degraded and sequestered in soils. They are relocated in the environment through volatilization, adsorption, leaching and erosion without alteration in their structure. Degradation causes alteration of PAHs structures from their original form though biological and chemical processes and sequestration occurs when PAHs are removed from bioavailable pools and stored for a long period of time. The conventional techniques for PAH removal involve excavation of contaminated soil and its incineration which are quite expensive and in many cases pollutants are transferred from one phase to another. The commonly employed biological methods for PAHs remediation in soil are landfarming, composting, bioaugmentation, biostimulation, phytoremediation etc. and chemical methods include photooxidation, ozone treatment, Fenton processes etc. This article critically reviews the updated information on various degradation methods for the clean-up of PAH contaminated soil have been critically reviewed. Sources of PAHs
The common sources of PAHs in an environment include natural as well as anthropogenic sources. Natural sources include forest fires, exudates from trees, oil seeps and volcanic eruptions. Anthropogenic sources of PAH mainly include combustion of fossil fuels, wood burning, municipal and industrial waste incineration, coal tar, coke, asphalt roads, roofing tar, discharges from industrial plants, waste water treatment plants, hazardous waste sites, coal gasification sites, smoke houses, atmospheric contamination of leafy plants, cigarette smoke etc.[11]. PAHs are formed mainly through pyrolytic processes which mainly involve incomplete combustion of organic materials during industrial and other human activities, such as coal and crude oil processing, natural gas combustion, combustion of refuse, cooking and tobacco smoking, as well as in natural processes such as carbonization.[13]. Biological strategies for remediation of PAHs
Landfarming is a commonly used, inexpensive remediation technology for PAH removal from contaminated soils.[14, 15]. The purpose of landfarming include stimulation of indigenous microorganisms to degrade PAHs via (a) addition of nutrients and a carbon source (amendments) (b) mixing soil to better distribute amendments (c) introducing oxygen into soil at depth and (d) increasing the chance of microbial contacts with contaminants.[16]. Reductions were much higher for LMW PAHs (50-80%) than for HMW PAHs (10%) after nine weeks. Hansen et al[17] evaluated the efficacy of different cultivation and maintenance schedules during bioremediation of contaminated soil containing high concentrations of polycyclic aromatic hydrocarbons (PAHs - >3 000 ppm) from a wood treatment facility. Two pilot-scale land-treatment units (LTUs) were used. Traditional landfarming practice of regular cultivation was compared with a gas-phase composting based cultivation strategy in the first treatment phase, and both the landfarming units were intensively monitored. The two strategies showed similar contaminant concentration profiles with time during the first phase. Different microbial populations were developed in the two-landfarming units. The second treatment phase involved without moisture control and nutrient delivery beyond the initial adjustments. Similar behaviour was noted for both the strategies again. GC/MS analysis of the soil samples showed that PAHs with four-ring homologues were removed. Significant reductions in leaching of low molecular weight PAHs from soil were noted after 6 and 22 months of operation. Extended treatment resulted in leaching of high molecular weight PAHs. Considerable degradation of two-, three-, four and five-ring aged PAHs was reported through the introduction of oxygen with landfarming (i.e. tillage) [18]. Composting is a remediation technique consisting of nutrient additions, moisture and oxygen control in a contained system. This technique is most commonly used for the treatment of municipal solid wastes and was demonstrated to be effective in biodegrading polycyclic aromatic hydrocarbons (PAHs) also [19,20]. The soil to compost ratios of 2:1 on a dry weight basis produced highest degradation of PAHs compared to those with higher ratios [21,22]. Potter et al.[19] used cow manure and activated sewage sludge as a bulking agent, keeping a C: N: P ratio of 100:5:1. Extensive degradation of two-, three- and four-ring PAHs during composting was noted but five- and six-ring PAHs were not degraded. The degradation of 16 USEPA-listed polycyclic aromatic hydrocarbons (PAHs) present in an aged coal tar contaminated soil amended was studied with green waste using in-vessel composting-under laboratory conditions [23]. The influence of various temperature (T:...
38, 55, and 70 °C and soil/green waste ratio (S: GW, 0.6:1, 0.7:1, 0.8:1, and 0.9:1) on dry weight basis, moisture content (MC: 40%, 60% and 80%) was investigated following 98 days of treatment. The highest removal of PAHs was observed at temperature 38 °C, S:GW=0.8:1 (75.2%) and MG (60%). In-vessel composting-bioremediation of the same coal-tar soil amended with fresh green waste compost could reduce PAH concentrations by 62% (FGWC-Site 1) and 54% (FGWC-Site 2) after 56 days at 38 °C. Thus, green waste as composting amendment instead of fresh green waste compost could serve as a better compost to achieve a higher disappearance of PAHs using a constant temperature 38 °C[24].

Removal of polycyclic aromatic hydrocarbons from soil amended with biosolid or vermicompost in presence of earthworms (Eisenia fetida) was reported [25]. Soil amended with earthworms showed increased removal of PAHs such as 91% of anthracene, 16% benz[a]pyrene and 99% phenanthrene compared to 42%, 3% and 95% in unamended soil. Biosolid and to a lesser extent vermicompost increased the removal of PAHs from soil. Therefore, application of earthworms to a contaminated site might be an environmentally friendly approach to remove PAHs from soil.

Biostimulation is a process by which the activity of the indigenous population of microbes already present at a site can be increased by addition of nutrients and/or a terminal electron acceptor (TEA). Different combinations of macro- and micronutrients were tested to enhance the bioremediation of an aged gas plant manufacturing soil (pH 7.5, organic carbon: 3.5%, and total PAH: 620 mg kg−1) through biostimulation [26]. The best nutrient combination for remediation was a low level of macronutrients with phosphorous as the dominant macronutrient in combination with high levels of micronutrients. Application of fungal substrate from commercial mushroom (Pleurotus ostreatus) production was reported for bioremediation of creosote contaminated soil. Use of spent mushroom compost (SMC) was noted to remediate PAH-contaminated soil samples which showed enhanced PAH-degrading efficiency of 82% [27]. Lee et al. [28] reported that addition of carbon in the form of pyruvate stimulated the microbial growth and accelerated the adaptation of P. putida G7 to naphthalene which enhanced the rate of in situ bioremediation. Biostimulation with linoleic acid produced by plant roots was tested for remediation of pyrene [29]. Soil spiked with pyrene and 43 different plant root extracts were tested for their ability to stimulate degradation. It was inferred that linoleic acid increased the numbers of degrading bacteria and acted as a surfactant to increase the bioavailability of the PAH. In addition, linoleic acid formed a coating on soil particles which increased the attachment of bacteria to hydrophobic sites causing their enhanced proximity to PAH compounds. Mushroom cultivation substrate (MCS) was reported as a potential remediation agent for remediation of PAH contaminated soil [30]. After two months of incubation, 32.9% dissipation of the 15 studied PAHs was observed. The results of this study suggested that MCS can serve as a cost-effective and green biostimulation agent which can provide support for the development of MCS-based biostimulation of PAH-contaminated soil.

Bioaugmentation, biostimulation, bioaugmentation and biostimulation in combination, and natural attenuation was reported [35]. Significant reduction in creosote was noted for all the treatments. However, bioaugmentation was found to be more effective for some specific polycyclic aromatic hydrocarbons (PAH) and showed the highest microbial biodiversity. The Pseudomonas genus was identified as the predominant bacteria during the creosote biodegradation processes.

The problem of removing the high-molecular-weight fraction (HMW-PAHs) from contaminated soils has been widely reported. Liadó et al. [36] reported the remediation of biotreated aged creosote-polluted soil contaminated with HMW-PAHs. The results showed that the 4-ring PAHs were degraded most by the autochthonous microbial community. Microbial community analysis of fungal and euabacterial populations showed that subbular genera viz. Chryseobacterium, Pseudomonas and Sphingobium which were concomitant with the autochthonous fungal genus Fusarium played an important role during HMW-PAH degradation in polluted soils.

A diversified approach on remediation of real industrial creosote polluted soil containing HMW-PAHs was demonstrated through biostimulation (BS) of indigenous microbial populations with a lignoclouellar substrate (LS) or fungal biodegradation with two strains of white-rot fungi (WRF) (i.e., Trametes versicolor (L.) Lamb and Lentinus tigrinus) after a 180-d pilot-scale biotreatment [37]. The impact of two mobilizing agents (MAs) viz. soybean oil and Brij 30 and bivalent manganese ions were also tested on the degradation performances of biostimulated and bioaugmented micromoscs. Highest biodegradation of HMW-PAHs (with five aromatic rings) by enhanced native microbiota was noted by means of LS amendment after 60 days of treatment. The growth of HMW-PAH degrading bacteria were specifically inhibited when non-ionic surfactant Brij 30 was amended. The concomitant LS addition with fungal inoculants failed due to the LS-promoted growth of indigenous fungal and bacterial populations. It was concluded that a lab-scale assessment of interactions between indigenous microbiota and the selected allochthonous species is necessary for implementation of bioremediation strategies.

To remove high molecular weight PAHs having 3-5 benzene rings, the potentiality of native bacteria associated with humic acids (HA), sugar cane bagasse (SCB), vermicompost (VC) and the earthworm Eisenia andrei (Eaw) were tested [38]. Isolation of bacteria was done on previous enrichment of the organic sources (OS) with mineral salts and kerosene and an average of 25 bacteria were isolated from each OS. The strain evaluation was carried out for the hydrocarbonoblastic bacteria at fixed concentration (FCH), superenant of the non-enriched OS (NES), and superenant of the enriched OS (ES). The FCHB inocula, particularly the strains provided by the HA and SCB, showed the best performance on five PAH removal under study.

Phytoremediation is an emerging on-site green remediation strategy that uses plants to reclaim contaminated soil and water containing toxic pollutants mainly through increasing microbial activity in the rhizosphere by breaking down the organic compounds in contaminated soils by metabolic processes [39]. There are reports on plant mediated PAHs degradation. The plants include Agropyron smithii Andropogon gerardii, Geranium viscosissimum, Helianthus maximiliani, Lottia perenne L. Lotus corniculata, Melilotus officinalis, Panicum coloratum and Triplolium pretense, Aster nova-anglica, Hyssopus officinalis, Panicum miliaceum (WRP), Xipho, Trametes versicolor (L.) Lamb, and Boletus gracilis and Boletus curtipespyll, Buchloe dactyloides, Dactus carota, Festuca arundinacea Schreb, Sorgum bicolor and Stenotaphrum Secundatum, Triticum aestivum [40-46]. The remediation of soil containing hydrocarbon mixture viz. n-alkanes (C10, C14-C18, C22, C24), along with pristane, hexadecane, phenanthrene, anthracene and pyrene by plant rye grass was reported [47]. The plant soil planted with rye grass lost a greater amount of a mixture of hydrocarbons than unplanted soil. It was concluded that large number of microbes and their activity in the planted soil enhanced the biodegradation of the hydrocarbons. A phenanthrene-degrading bacterial strain Pseudomonas sp. GF3 was tested for plant-growth promoting effects and phenanthrene
removal in soil artificially contaminated with low and high levels of phenanthrene [48]. Strain GF3 was able to degrade phenanthrene effectively in the unplanted and planted soils. The concentration of phenanthrene in soil in which wheat was grown was significantly lower than in unplanted soil and 62.2% and 42.3% of phenanthrene had disappeared from planted soils after a period of 80 days. The influence of sunflower rhizosphere on the biodegradation of PAHs in the soil was reported [49]. The concentration of total PAHs was found to be decreased by 93% in 90 days when the contaminated soil was cultivated with sunflowers which represented an improvement of 16% compared to contaminated soil without plants. This was the first report which analyzed the effect of the rhizosphere on autochthonous bacterial community structure from a real PAH-polluted soil. Future research can be carried out to explore the exact contribution of the direct effects of the sunflower exudates and the effects related to the ecology of soil microorganisms.

Recently, a microbial/plant combination strategy has been proposed for the successful bioremediation of an aged and heavily PAHs contaminated soil [50]. Comparative studies on three strategies viz. microbial remediation, phytoremediation, and microbial/phytoremediation were done and soil bacterial community dynamics (using a 454-pyrosequencing method), plant biomass, and activity levels of certain enzymes was monitored. Members of the phylum Acidobacteria were found to be useful indicators of the progress. The PAH removal efficiency was found to be in the order: microbial/phytoremediation > microbial remediation ≈ phytoremediation > control. The combined strategy of microbial/phytoremediation showed the removal percentage twice that of control. Inoculation of the strain Kocuria sp P10 greatly promoted PAH removal and ryegrass growth. Increase in dehydrogenase activity was noted which showed negative correlation with total PAH content. The data indicated that biodiversity of the soil bacterial community gradually increased with time and were slightly lower in control, as indicated by operational taxonomic unit (OTU) numbers and Shannon–Wiener indices. Data from a sequencing method suggested that the phylum Acidobacteria could serve as useful indicator of this process and the findings may provide new insights for the application of bioremediation and its assessment on a large scale. Fig. 1 shows the various biological strategies for PAHs remediation from soil.

**Chemical strategies for remediation of PAHs**

Among the chemical strategies, photooxidation is an important process for surface and atmospheric degradation of PAHs involving sunlight. The PAHs are directly oxidized after the absorption of sunlight radiation during direct photooxidation and they absorb radiation above 290-335 nm. Chemical transformation occurs during photooxidation and the rates of chemical transformation depend upon sunlight intensity, and overlapping spectral characteristics of solar radiation. Indirect photooxidation occurs when other substances like clay, organic matter, and inorganics absorb sunlight energy and transmit the energy to the PAHs through electron orbital interactions [51].

The photocatalytic degradation of phenanthrene, pyrene and benzo[a]pyrene on soil surfaces in the presence of TiO2 using ultraviolet (UV) light was investigated [52]. The temperature maintained in the photo chamber was 30°C. The effects of various factors, viz. TiO2, soil pH, humic acid, and UV wavelength, on the degradation performance of PAHs were studied. The photo-degradation of phenanthrene, pyrene and benzo[a]pyrene was accelerated significantly with the catalyst TiO2 and their half-lives were reduced from 533.15 to 130.77 h, 630.09 to 192.53 h and 363.22 to 103.26 h, respectively. The photocatalytic degradation rates of the PAHs were greater in acidic or alkaline conditions compared to neutral conditions. Humic acid significantly enhanced the PAH photocatalytic degradation by sensitizing radicals capable of oxidizing PAHs. The combined effect of UV irradiation and TiO2 catalysis was found to be more efficient for degradation of PAHs in contaminated soil.

The photocatalytic degradation of phenanthrene and pyrene on soil surfaces in the presence of nanometer rutile TiO2 under UV radiation was reported [53]. Soil samples were spiked with phenanthrene and pyrene, and then loaded with different dosages of nanometer rutile TiO2 (0, 1, 2, 3, and 4 wt %) and were exposed to UV-irradiation for 25 h. The results indicated that phenanthrene and pyrene on soil surfaces could be successfully degraded by the method of photocatalytic degradation in the presence of nanometer rutile TiO2. This method can serve as better choice for the treatments of PAHs.

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**Fig. 1: Application of biological techniques for remediation of PAHs in soil**

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polluted soil in the future. The photooxidation of four polycyclic aromatic hydrocarbons (PAHs), namely phenanthrene, anthracene, acenaphthene and benzo[a]anthracene were studied using solid solution GaN: ZnO before and after Pt modification as photocatalysts [54]. GaN: ZnO is a new type of oxynitride with a wurtzite-type structure which showed excellent activity for the photodegradation of PAHs. The reactivity of PAHs was decreased in the order: phenanthrene > benzo[a]anthracene > anthracene > acenaphthene. The degradation of PAHs was induced by the formation of holes and active H species in the photocatalytic system. In Fentons system, Fentons reagent treatment, peroxide at different concentrations ranging from 3 to 35% along with ferrous iron (Fe II) was used as a catalyst to oxidize organic chemicals [55]. Peroxide (H₂O₂) is decomposed into highly reactive non-specific hydroxyl radicals with the help of ferrous iron. Optimum pH needed for the reaction to occur is 3-5. If the pH is too high, iron will precipitate as iron oxides and will decompose peroxide. The iron can be artificially added with the peroxide, but if the soil has high enough iron oxides content (goethite, hematite or magnetite), addition of iron is not needed [56,57]. The decomposition process of peroxide is exothermic. The success of a Fentons system is strongly dependent on solid matrix characteristics and the contaminant availability [58,59]. Hydrophobic contaminants in aged soils are less susceptible to chemical oxidation because of their adsorption to organic material and diffusion into micropores. The presence of black carbon limits the availability of PAHs to chemical oxidation [59]. Gan et al [60] investigated the impacts of ethyl lactate (EL) based Fenton treatment on soil quality for polycyclic aromatic hydrocarbons (PAHs)-contaminated soils. Among the oxygenated PAHs (o xo-PAHs), the compound 9,10- anthraquinone (ATQ) were accumulated in contaminated soil abundantly, but lower accumulation of ATQ was reported for ethanol (EL) based Fenton treatment compared to ethanol (ET) based Fenton treatment. The EL based Fenton treatment showed both positive and negative impacts on soil physicochemical properties. The treatment was found to be most suitable for soil with native pH > 6.2 for re-vegetation.

Recently, an effective technology for the treatment of pyrene in cetylpyridinium chloride (CPC)-aided soil washing wastewater (SWW) using pyrite Fenton reaction system has been reported [61]. Pyrite Fenton system showed more enhanced degradation of pyrene compared to the classic Fenton system. Pyrene in the presence of CPC was gradually degraded by 96% in the pyrite Fenton system in 180 min at initial pH 7 whereas in a classic Fenton system, pyrene was degraded by 35% in the presence of CPC in 180 min at initial pH 3. Pyrene in presence of CPC was mainly degraded by OH radicals. This study on pyrite Fenton system could successfully degrade pyrene in the CPC-aided SWW without accumulation of toxic oxy-

pyrenes. CPC was degraded (95 %) in the pyrite Fenton system and formed carbon dioxide and ammonium as main degradation products. Therefore, it was concluded that the pyrite Fenton system can serve as an eco-friendly alternative to remediate pyrene in CPC-aided SWW without accumulating the toxic oxy-pyrenes.

Ozone treatment is the use of gaseous ozone for PAH remediation was described earlier [62] Among the technologies for the removal of PAHs, ozonation may be a good alternative, since PAHs react very fast with ozone due to their molecular structures [63]. The benefits of ozone treatment include the ability to use higher concentrations of gas compared to what could be used in the aqueous phase. Moreover, higher diffusivity of gaseous ozone facilitates the delivery of ozone to contaminated areas. In-situ ozonation has been reported as an attractive option for PAH removal at numerous contaminated sites [64,65]. The influence of gas flow-rate, ozone concentration and reaction time on remediation of soil contaminated with four PAHs viz. acenaphthene, phenanthrene, anthracene and fluoranthene was assessed [66]. Gas flow-rate showed no influence on the process efficiency and ozone concentration exerted a slight positive effect. It was concluded that reactivity of PAHs might differ in soils and liquid solvents, nature and composition of soil played an important role in influencing the reactivity. The ozonation of pyrene spiked soil (300 ppm) at various pH levels 2, 6, and 8 and three moisture contents was reported [67]. Soil pH, moisture content, and contamination age showed a significant impact on the effective oxidation of PAH. In the air-dried soils, pyrene removal efficiencies was found to increase from 95 to 97% at pH 6 and pH 8 at a dose of 2.22 mg O₃/mg Pyr. Ozone treatment for 4 h resulted 81 to 98% removal efficiencies at all pH levels. Increase in soil moisture content resulted more rapid ozone breakthrough causing reduced pyrene degradation. To compare the efficiency of PAH removal in freshly contaminated soil and aged soils, PAH contaminated soils were stored for 6 months. PAH adsorption to soil was increased with longer exposure time and required much higher doses of ozone to oxidize pyrene effectively. Anthracene decomposition in soils was studied using conventional ozonation [68] and the degree of anthracene decomposition was found depend on soil matrix, water and organic matter content. The total anthracene decomposition was studied in the two systems (sand-ozone and burned soil-ozone). In case of baked sand, anthracene was decomposed completely by simple ozonation during 15 min. In burned soil, anthracene degradation was observed during 5 min of treatment. The efficiency of ozonation was depended on the water content in treated soil samples. In the moist sand, the total decomposition of anthracene was obtained after 30 min of ozonation. The anthracene degradation in an agricultural soil (free water) was only 30% after 90 min of ozonation. Fig. 2 represents the various chemical strategies for PAHs remediation from soil.

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Fig. 2: Application of chemical techniques for remediation of PAHs in soil
CONCLUSION
Developing health based cleanup standards and remediation strategies for PAHs contaminated soils seem to be a complex and controversial task. Various strategies involving biological viz. phytoremediation and chemical methods viz. photooxidation, Fenton system and ozonation have been proposed by various researchers for the remediation of PAHs from contaminated soil. There are several drawbacks for both the biological as well as chemical methods. Among the various strategies, use of microorganisms, bio waste materials or plants may be suggested as the cost effective technology for remediation of PAHs from contaminated sites. The application of bio-nano hybrid system using nanoparticles may be tested for remediation of PAHs from soil as a new strategy.

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CONFLICT OF INTEREST
None declared.

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