Review

Remediation of soils contaminated with polycyclic aromatic hydrocarbons (PAHs)

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ARTICLE INFO

ABSTRACT

Polycyclic aromatic hydrocarbons (PAHs) are carcinogenic micropollutants which are resistant to environmental degradation due to their highly hydrophobic nature. Concerns over their adverse health effects have resulted in extensive studies on the remediation of soils contaminated with PAHs. This paper aims to provide a review of the remediation technologies specifically for PAH-contaminated soils. The technologies discussed here include solvent extraction, bioremediation, phytoremediation, chemical oxidation, photocatalytic degradation, electrokinetic remediation, thermal treatment and integrated remediation technologies. For each of these, the theories are discussed in conjunction with comparative evaluation of studies reported in the specialised literature.

Contents

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1. Introduction

Polycyclic aromatic hydrocarbons or polynuclear aromatic hydrocarbons (PAHs) are chemical compounds made up of more than two fused aromatic rings in a linear or clustered arrangement, usually containing only carbon (C) and hydrogen (H) atoms, although nitrogen (N), sulphur (S) and oxygen (O) atoms may readily substitute in the benzene ring to form heterocyclic aromatic compounds. They are produced through incomplete combustion and pyrolysis of organic matter. Both natural and anthropogenic sources such as forest fires, volcanic eruptions, vehicular emissions, residential wood burning, petroleum catalytic cracking and industrial combustion of fossil fuels contribute to the release of PAHs to the environment [1]. Several hundred different combinations of PAHs exist, but up to 28 compounds as listed in Table 1 have recently been identified as hazardous contaminants in January 2008 by the US Environmental Protection Agency (US EPA) [2]. The distinguishing feature of these toxic compounds is that they are highly hydrophobic. As such, PAHs easily adsorb onto the organic matter of solid particles, forming persistent micropollutants in the environment. Air, soil, water and vegetation all act as environmental sinks for PAHs, although a preliminary inventory of PAHs in the UK environment showed that soil was the major repository for PAHs [3].

Soils contaminated with PAHs pose potential risks to human and ecological health. The assessment of the actual risk for mutagenic and carcinogenic effects requires accurate exposure information which is extremely difficult to assess in practice [4]. Nonetheless,

as a precautionary approach, countries including the Netherlands, Denmark and Canada have stipulated soil cleanup guidelines for PAH contamination [5]. Comprehensive reviews of chemical oxidation, bioremediation and phytoremediation technologies specifically for PAH-contaminated soils are available in the literature [6–10]. To date, however, these have concentrated solely on one technology and an evaluation of all currently available soil remediation technologies for PAHs has not been explored. Thus, in this paper, the state of the art in this field will be reviewed, ranging from more widely applied technologies such as solvent extraction to new and emerging ones such as electrokinetic remediation. Table 2 shows the structure of this paper and provides the framework for the discussion that follows. The theories behind the remediation technologies will be described along with comparative evaluation of studies reported in the specialised literature. General conclusions will be drawn concerning the technologies and their present states of development.

2. Solvent extraction

In solvent extraction technology, PAHs are removed from soil using an individual solvent or mixtures of solvents. The two steps involved in the extraction of a compound from a solid matrix are desorption from the binding site in (or on) the solid matrix followed by elution from the solid into the extraction fluid [11]. Typically, mixtures of water and co-solvents or surfactants are used to extract or wash PAHs from contaminated soil. Advancements within this field include using non-toxic and biodegradable extraction agents such as cyclodextrins and vegetable oil as well as using supercritical and subcritical fluids. Table 3 summarises pertinent references on the use of solvent extraction for the remediation of PAH-contaminated soils.

2.1. Soil washing with water and organic solvents

Water and various solvents as well as mixtures of solvents have been tested at laboratory scale using a rotating shaker to remove 19 PAHs from highly contaminated soil by Khodadoust et al. [12]. Using a soil:solvent extraction ratio of 1 g:100 ml and extraction time of 24 h resulted in similar removal efficiencies of PAHs for ethanol, 2-propanol, acetone and 1-pentanol. Ternary mixtures of water, 1-pentanol, and either ethanol or 2-propanol were also tested with a

Table 1
Priority PAHs as listed by US EPA [2].

Number[a]	PAH compound	Number of rings
1	Benzo(a)anthracene	4
2	Chrysene	4
3	Benzo(a)pyrene	5
4	Benzo(b)fluoranthene	5
5	Benzo(j)fluoranthene	5
6	Benzo(k)fluoranthene	5
7	Fluoranthene	4
8	Benzo(r,s,t)pentaphene	6
9	Dibenz(a,h)acridine	5
10	Dibenz(a,j)acridine	5
11	Dibenzo(a,h)anthracene	5
12	Dibenzo(a,e)fluoranthene	6
13	Dibenzo(a,e)pyrene	6
14	Dibenzo(a,h)pyrene	6
15	Dibenzo(a,l)pyrene	6
16	7H-Dibenzo(c,g)carbazole	5
17	7,12-Dimethylbenz(a)anthracene	4
18	Indeno(1,2,3-cd)pyrene	6
19	3-Methylcholanthrene	4
20	5-Methylchrysene	4
21	1-Nitropyrene	4
22	Acenaphthene	3
23	Acenaphthylene	3
24	Anthracene	3
25	Benzo(g,h,i)perylene	6
26	Fluorene	3
27	Phenanthrene	3
28	Pyrene	4

[a] Compounds numbered 1–21 are listed on the Toxic Release Inventory reported by the US EPA National Waste Minimisation Programme while those numbered 22–28 are listed on the US EPA Priority Chemical List.

Table 2
Overview of remediation technologies for PAH-contaminated soils.

Classification	Technologies
Physical–chemical	Solvent extraction (water and organic solvents, surfactants, cyclodextrins, vegetable oil), supercritical fluid extraction, subcritical fluid extraction
Biological	Bioremediation such as on-site land farming and composting, aerobic and anaerobic treatment, phytoremediation
Chemical	Chemical oxidation with various oxidants (e.g. Fenton's reagent, ozone, peroxy-acid, $KMnO_4$, H_2O_2, activated sodium persulphate), photocatalytic degradation, electrokinetic remediation
Thermal	Incineration, thermal desorption, thermally enhanced soil vapour extraction

Table 3
Bibliographic compilation of solvent extraction studies.

Extraction agent	Soil	Process details	PAHs studied	Reference
Neat solvents 1-pentanol, ethanol, 2-propanol and acetone Ternary mixtures of water–1-pentanol–ethanol Ternary mixtures of water-1-pentanol-2-propanol	MGP soil	Rotating shaker at 24 °C, with soil:solvent (w/v): 1 g:100 ml and 24 h extraction time	Naphthalene, 2-methyl napthalene, acenaphthylene, acenaphthene, dibenzofuran, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(e)pyrene, benzo(a)pyrene, dibenzo(a,h)anthracene, indeno(1,2,3-c,d)pyrene, benzo(g,h,i)perylene	[12]
5% pentanol–10% water–85% ethanol	MGP soil	Three crosscurrent wash stages at 24 °C using rotating shaker, with soil:solvent (w/v) of 1 g:4 ml per stage and 1 h extraction time per stage	Naphthalene, 2-methyl napthalene, acenaphthylene, acenaphthene, dibenzofuran, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(e)pyrene, benzo(a)pyrene, dibenzo(a,h)anthracene, indeno(1,2,3-c,d)pyrene, benzo(g,h,i)perylene	[12]
Ternary mixtures of acetone, ethyl acetate and water	Spiked agricultural soil	Magnetic agitation with a range of soil:solvent (w/v) ratios	Naphthalene	[13]
3:1 cyclohexane:ethanol, dichloromethane, ethanol, methanol, methyl ethyl ketone, N, N-dimethylacetamide, N,N-dimethylformamide, N-butyl acetate, N-propyl acetate, toluene	Spiked sandy clay loam	Ultrasonication at 40 °C, with soil:solvent (w/v): 200 mg:30 ml and 20 min extraction time	Fluoranthene	[14]
Tween 40, Tween 80, Brij 30 and Brij 35	Spiked sandy loam soil	Rotary shaker with soil:solvent (w/v): 50 g:500 ml and 48 h extraction time	Phenanthrene	[17]
T-Maz 80, T-Maz 20, CA 620, TerraSurf 80, Dowfax 8390, sodium dodecyl benzene sulfonate, sodium dodecyl sulphate and Steol 330	Spiked Canadian river alluvium	Wrist action shaker with soil:solvent (w/v): 3 g:15 ml and 30 min extraction time	Phenanthrene	[18]
Triton X-100, Triton X-114, Triton X-305	Spiked soil	Reciprocating shaker with soil:solvent (w/v): 2 g:20 ml and 48 h extraction time	Phenanthrene, fluorene, acenaphthene, naphthalene	[19]
BCD, HPCD, MCD	MGP soil	Column extraction system. Parametric studies: temperature, concentration, soil:solvent (w/v)	Phenanthrene, anthracene, pyrene	[20]
Sunflower oil	MGP soil	Orbital shaker with soil:solvent (w/v): 150 g(or 75 g):150 ml and 7 days extraction time	Fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenz(a,h)anthracene, benzo(g,h,i)perylene, indenopyrene	[22]
Sunflower oil	MGP soil	Column percolation experiments with various combinations of stepwise additions of oil	Same as above	[23]
Sunflower oil	MGP soil	Orbital shaker with soil:solvent (w/v): 150 g (or 75 g):150 ml and 7 days extraction time Column percolation experiments with soil:solvent (w/v): 1 kg:2 l	Same as above	[25]
Peanut oil	Spiked sandy loam garden soil, spiked silt soil, creosote-contaminated soil	Orbital shaker with 3 h extraction time. Parametric studies: soil type and moisture, oil concentration, initial PAH concentration, soil pH, temperature, single- or double-extraction stages	Naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, chrysene, benzo(a)pyrene	[26]
SCCD	Spiked soil	SFE performed at temperatures of 50 °C and 80 °C and varying pressures from 230 bar to 600 bar	Naphthalene, phenanthrene, anthracene, fluoranthene, pyrene, benz(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-c,d)pyrene	[33]
SCCD	MGP soil	SFE performed at temperature of 50 °C and pressure of 200 bar for 200 min	Naphthalene, 1-methylnaphthalene, 2-methylnaphthalene, acenaphthylene, acenaphthene, fluorene, dibenzothiophene, phenanthrene, anthracene, fluoranthene, pyrene, benz(a)anthracene, chrysene, benzo(b + k)fluoranthene, benzo(e)pyrene, benzo(a)pyrene, indeno(1,2,3-c,d)pyrene dibenz(a,h)anthracene, benzo(g,h,i)perylene	[34,35]

Table 3 (*Continued*)

Extraction agent	Soil	Process details	PAHs studied	Reference
SCCD	MGP soil	SFE performed at temperature of 130 °C and pressure of 330 bar	Pyrene, chrysene, benzo(b + k)fluoranthene, benzo(a)pyrene	[36]
Subcritical water	MGP soil, pesticide-contaminated soil	Pilot scale extraction performed at temperature of 275 °C, pressure of 100 bar and flow rate of 300 ml/min for 2 h or flow rate of 600 ml/min for 1 h	Naphthalene, 2-methylnaphthalene, 1-methylnaphthalene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz(a)anthracene, chrysene benzo(b + k)fluoranthene, benzo(e)pyrene, benzo(a)pyrene indeno(1,2,3-c,d)pyrene, benzo(g,h,i)perylene	[38]
Subcritical water	Spiked sea sand	Pressurised hot water extraction performed at temperatures of 200 °C and 300 °C for 20 or 40 min	Naphthalene, fluorene, anthracene, phenanthrene, pyrene, chrysene, perylene	[39,40]

volume fraction of 1-pentanol ranging from 5% to 25% and a volume fraction of water ranging from 5% to 30%. The data obtained indicated that ethanol was a better extraction solvent for PAH removal from soil than 2-propanol. It was also shown that a ternary mixture of 5% 1-pentanol–10% water–85% ethanol used in a three-stage crosscurrent solvent washing process with contact time of 1 h per stage was capable of removing more than 95% of extractable PAHs.

Apart from solvent type, extraction efficiencies are also dependent on soil:solvent ratio. Silva et al. [13], for instance, studied the capacity of 40% acetone–50% ethyl acetate–10% water to remove naphthalene from soil at different soil:solvent ratios of 1:1, 1:2, 1:3, 1:4 and 1:8 (w/v) using magnetic agitation. For highest removal efficiency in the order of 95%, a ratio of 1:8 was necessary. In this work too, it was demonstrated that solvent regeneration could be carried out using distillation, with an approximate loss of 10%.

A number of organic solvents including cyclohexane and ethanol mixture (3:1), dichloromethane, ethanol, methanol, methyl ethyl ketone, N,N-dimethylacetamide, N,N-dimethylformamide, N-butyl acetate, N-propyl acetate and toluene have also been considered in a soil remediation study aiming at extraction of fluoranthene from contaminated soil [14]. The 3:1 mixture of cyclohexane and ethanol was found to be the most suitable solvent due to its high extraction efficiency of approximately 93% and from the point of safety.

2.2. Surfactant-aided soil washing

Surfactants are used as additives to counter the low aqueous solubility of PAHs and enhance the efficiency of soil washing/flushing using water. These amphiphilic molecules comprise of two major components, the hydrophobic or water insoluble tail group and the hydrophilic or water soluble head group. Surfactants can be classified as either cationic, anionic or non-ionic surfactants depending on the head group type. They enhance the solubility of PAHs in water by partitioning them into the hydrophobic cores of surfactant micelles [15]. The presence of surfactant micelles also decreases surface and interfacial tensions [16].

Ahn et al. [17] investigated the washing performance of four different non-ionic surfactants, Tween 40, Tween 80, Brij 30 and Brij 35 on a phenanthrene-spiked soil. It was discovered that Brij 30 had the highest washing efficiency with 84.1% phenanthrene removal at a surfactant concentration of 2 g/l. This was due to the high solubilising ability of Brij 30 for phenanthrene and its low adsorption onto soil. Subsequent selective adsorption tests indicated that phenanthrene removal by activated carbon from Brij 30 solution was only 33.9% compared to the significantly higher removal efficiencies of 54.1–56.4% with other surfactant solutions. The overall performance combining both washing and surfactant recovery steps was best with Tween 80 and Brij 35. Other non-ionic surfactants such as T-Maz 80, T-Maz 20, CA 620 and TerraSurf 80 as well as anionic surfactants such as Dowfax 8390, sodium dode-

cyl benzene sulfonate, sodium dodecyl sulphate and Steol 330 have also been shown to be effective for phenanthrene removal [18].

A recent concern raised over the use of surfactants by Zhou and Zhu [19] is that although surfactant micelles aid the transport of solubilised PAHs, they can also be adsorbed by the soil matrix and lead to PAH partitioning into immobile adsorbed surfactants which enhances the sorption of PAHs onto soils. Due to this phenomenon, the authors utilised a model to evaluate the performance of surfactant in enhancing desorption for PAHs relative to water. It was found that the efficiency of surfactants in aiding PAH desorption was strongly dependent on soil composition, surfactant structure and PAH properties.

2.3. Extraction with cyclodextrins

Cyclodextrins have been proposed as a non-toxic and biodegradable alternative to organic solvents and surfactants for removal of PAHs from contaminated soil [20]. Three cyclodextrins, β-cyclodextrin (BCD), hydroxypropyl-β-cyclodextrin (HPCD) and methyl-β-cyclodextrin (MCD) were examined for their effectiveness as PAH flushing agent. Of the three, MCD produced the highest removal efficiency followed by HPCD and lastly, BCD. At a washing solution volume to soil mass ratio of 6 and at 22 °C, PAH extraction increased linearly with increase in HPCD concentration. Similarly, a quasi-linear trend of extracted PAHs was seen with the increase in washing solution. The temperature of washing solution caused no significant enhancement in PAH extraction within the range of 5–35 °C.

2.4. Extraction with vegetable oil

Several recent studies advocated the use of vegetable oil as a non-toxic, cost-effective, and biodegradable extraction solvent. Vegetable oil is a strong sorption medium for hydrophobic compounds such as PAHs. Furthermore, its free fatty acids with molar solubility ratios for PAHs are similar to those of synthetic chemical surfactants [21]. In the works of Gong et al. [22,23], experiments were carried out to assess removal of PAHs from contaminated soils using sunflower oil. Initial extraction tests with 150 ml sunflower oil and either 150 g or 75 g of MGP soil on an orbital shaker showed that nearly all PAHs (81–100%) could be removed. Subsequent column experiments to represent in situ leaching demonstrated that more than 90% of total PAHs were removed from two samples of PAH-contaminated soils. The soil:oil ratio to achieve this removal efficiency depended on the concentration of PAHs in the soil, with up to 1 kg:4 L required for highly contaminated soil. The organic carbon content of the treated soil was restored to original level after an incubation period of 180 days. Further investigation of the influence of soil moisture on the sunflower oil extraction of PAHs from soil revealed that lesser moisture in the soil sample led

to increased removal efficiency of PAHs of [24]. Likewise to surfactant recovery, the regeneration of oil was demonstrated using activated carbon adsorption with removal efficiencies of more than 90% in batch adsorption and between 68.1% and 93.5% in column adsorption experiments [25].

Pannu et al. [26] used peanut oil to extract PAHs in an orbital shaking process. Extraction efficiencies of more than 90% were obtained for anthracene using soil:oil ratios (w/w) ranging from 39:1 to 4:1. Increasing the temperature increased the extraction efficiency of a total of 10 PAHs from spiked soil, from 51.5% at 20 °C to 81.4% at 60 °C. Similar to Gong et al. [25], activated carbon was shown to be efficient in removing anthracene from contaminated oil. It was also suggested that the remaining oil in the soil has the potential to enhance biodegradation of residual contaminants by aiding bioavailability and by being a substrate for growth of microorganisms which can biodegrade contaminants. Nevertheless, the authors raised concerns over the amount of oil required and the entrainment of oil in the bulk soil medium which reduced the efficiency of oil floatation or separation.

2.5. Supercritical fluid extraction (SFE)

SFE has been used successfully in analytical chemistry [27–29] and its application has now extended to soil remediation technology. The supercritical fluid is a fluid whereby its temperature and pressure have been raised to above its thermodynamic critical point. Therefore, the fluid exhibits a continuum of both gaseous and liquid phase properties such as liquid-like density, low viscosity, high diffusivity and zero surface tension which makes it capable of promoting opening of cavities in solid matrices and providing complete extraction of materials [30]. Organic contaminants such as PAHs which are deposited on the solid surface are extracted via dissolution while aged organic components which are absorbed into the soil particles are removed via adsorption/desorption equilibrium [31].

Carbon dioxide is typically used in SFE of contaminated soils [32]. Librando et al. [33] employed supercritical carbon dioxide (SCCD) with an additional 5% (v/v) methanol as co-solvent at an optimum temperature of 50 °C and pressure of 450 bar to remove PAHs from spiked soil. The authors reported that recovery of PAHs from both the condensation tube and the internal tube of the extractor was greater than 90%, with the exception of fluoranthene with slightly less recovery of approximately 88%. Furthermore, this SFE system was noted to provide high removal rates of higher molecular weight PAHs (four to 6 rings). Trials at a higher temperature of 80 °C showed that rapid PAH removal rates were achievable but at the expense of lower PAH removal yields. Other documented works also featured the use of SCCD to extract PAHs from contaminated soils [34–36]. Unlike other solvent extraction methods, increasing soil moisture has been found to positively affect the removal of PAHs from soil using SCCD [36].

2.6. Subcritical fluid extraction

The subcritical fluid is held in its liquid state and maintained below its critical point under high pressure and temperature. Subcritical water extraction also known as pressurised hot water extraction uses water heated from 100 °C to 274 °C under pressure to maintain it in its liquid form. As the temperature is raised, the hydrogen bonding network of water molecules weakens resulting in a lower dielectric constant and simultaneously decreasing its polarity. Thus, subcritical water becomes more hydrophobic and organic-like than ambient water, promoting miscibility of light hydrocarbons with water [37].

Work carried out by Lagadec et al. [38] focussed on the feasibility of using subcritical water to remove PAHs from soil in a pilot scale remediation unit. Water is heated along a 30 m heating coil prior to passing through an 8 L tubular extraction cell containing approximately 8 kg of contaminated soil. The optimum subcritical water extraction was reported to be at 275 °C with PAH reduction in all ranges of molecular weights from a manufactured gas plant soil sample to below negligible levels (<0.5 ppm) in 35 min. Further examination of the fertility of soil revealed that the remediated soil was healthy with positive germination and earthworm toxicity curbed to zero percent. Similarly, in another study, subcritical water extractions were conducted on PAH-spiked sand at various temperatures [39,40]. It was found that the recoveries of the PAHs were approximately 80% regardless of extraction time. The exception was naphthalene which suffered a recovery loss of 35% when extraction time was increased from 1 to 20 h due to its high volatility. Additionally, the recoveries of higher molecular weight PAHs particularly chrysene and perylene clearly increased by almost 41% with an increase of temperature from 200 °C to 300 °C. This is a result of the decrease in dielectric constant value which favours the solubility of low polarity PAHs.

3. Biological remediation/bioremediation

Biodegradation is nature's way of recycling wastes by breaking down organic or inorganic matter into nutrients using living organisms, either in the presence of oxygen (aerobic biodegradation) or without oxygen (anaerobic biodegradation). Conventionally, on-site techniques such as land farming, composting and soil piles have been employed while the more advanced ex situ methods such as the use of bioreactors provide better control of temperature and pressure to enhance the degradation process of PAHs in soil [8]. Comparative data are listed in Table 4 for on-site and ex situ aerobic and anaerobic studies.

3.1. On-site land farming/composting

In land farming, contaminated soil is periodically tilled to improve aeration and to promote soil homogeneity for biological degradation. Soil conditions are controlled by monitoring the moisture and nutrient content, frequency of aeration and soil pH to optimise the rate of contaminant degradation. Occasionally, contaminated soil are spread over with waste material or mixed with soil amendments such as bulking agents and nutrients to incorporate better degradation and oxidation process by existing microbial population.

A study by Wang et al. [41] incorporated fertilisation with 10 mg of urea and 4.3 mg of superphosphate per cm^2 area, liming with 55 mg of powdered agricultural limestone per cm^2 area and weekly tilling to a 15 cm depth with a hand shovel. With these optimum conditions, the rate of total hydrocarbon degradation increased considerably, with almost complete elimination of PAHs in 12 weeks compared to untreated soil which revealed 12.5–32.5% of higher molecular weight PAHs still present after a similar duration. In another study [42], a few hundred m^3 field unit of contaminated soil from a manufactured gas plant (MGP) site was excavated to a prepared bed land treatment unit approximately 30 cm deep. The biological land treatment of ½ to 1 year revealed that the lower molecular weight PAHs were removed to approximately 90% while there was no reduction of 5- and 6-ring PAHs.

Although the land farming process is a simple technique which requires very low cost, slight maintenance, almost none cleanup liabilities and minimal monitoring efforts, the extent of PAH biodegradation is not effective on creosote-contaminated soil which are highly toxic [41]. Treatment is limited to the superficial 10–35 cm layer of soil accessible and there exists the possibility of contaminant movement from the treatment area. The practicality

Table 4
Bibliographic compilation of bioremediation studies.

Inoculated microorganism	Soil	Process details	PAHs studied	Reference
Indigenous microorganisms	Diesel-oil-contaminated soil	Fertilisation with 10 mg urea and 4.3 mg superphosphate per cm^2 area, liming with 55 mg powdered agricultural limestone per cm^2 area and weekly tilling to a 15 cm depth	Naphthalene, phenanthrene, pyrene, mono-, di-, tri-, and tetramethylsubstituted PAH	[41]
Indigenous microorganisms	MGP soil	Prepared bed land treatment unit approximately 30 cm deep, water and nutrients supply, and tilling frequently to supply oxygen for approximately 1 year	Naphthalene, 1-methylnaphthalene, 2-methylnaphthalene, acenaphthylene, acenaphthene, fluorine, dibenzothiophene, phenanthrene, anthracene, fluoranthene, pyrene, benz(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(e)pyrene, benzo(a)pyrene, perylene, indeno(1,2,3-cd)pyrene, dibenz(a,h)anthracene, benzo(ghi)perylene	[42]
White button mushroom (*Agaricus bisporus*) compost consisting wheat straw, chicken manure, gypsum	MGP soil	170 kg dry soil mixed with 800 kg compost and water to give a soil:compost ratio of 1:4 on a wet basis. Composting in a thermally insulated composting chamber with aeration for 54 days. Additional open-air field composting for 100 days	Phenanthrene, anthracene, fluoranthene, pyrene, benz(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenz(a,h)anthracene, benzo(ghi)perylene, indeno(1,2,3-cd)pyrene	[43]
White button mushroom (*Agaricus bisporus*) compost consisting wheat straw, chicken manure, gypsum	MGP soil	88 kg dry soil mixed with 400 kg compost and water to give a soil:compost ratio of 1:4 on a wet basis. Composting in a thermally insulated composting chamber with aeration for 42 days. Additional open-air field composting for 100 days	Phenanthrene, anthracene, fluoranthene, pyrene, benz(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(a)perylene, indeno(1,2,3-cd)pyrene	[44]
White rot fungi (*Irpex lacteus*, *Pleurotus ostreatus*)	Former gasholder soil, sandy clay loam from wood treatment plant	5 g soil treated with 5 g straw substrate in incubation flasks at 24 °C in the dark for 6 weeks. Soil moisture kept constant at 15%	Phenanthrene, anthracene, fluoranthene, pyrene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenzo(a)anthracene, benzo(g,h,i)perylene, indeno(1,2,3-c,d)pyrene	[50]
Fungus (*Cladosporium sphaerospermum*)	MGP soil	7 g soil incubated in culture tubes at room temperature in the dark for 30 days. 5 kg treated in microcosm at room temperature for 60 days. Soil moisture kept at 70% of water holding capacity	Naphthalene, acenaphtylene, acenaphtene, fluorene, phenanthrene, anthracene, pyrene, benz(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenz(a,h)anthracene, indeno(1,2,3-c,d)pyrene, benzo(ghi)perylene	[51]
Microbial consortia (bacteria, fungi, bacteria–fungi mixture)	Oil-contaminated soil	5 g soil inoculated with 40% abiosalt medium and 2% of the microbial consortia shaken in culture tubes at room temperature in the dark for 30 days	Acenaphtene, acenaphtylene, napthalene, anthracene, fluorene, phenanthrene, chrysene, fluoranthene, pyrene, benz(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, dibenz(a,h)anthracene, benzo(g,h,i)perylene, indeno(1,2,3-c,d)pyrene	[52]
Earthworms (*Lumbricus rubellus*)	Spiked sandy soil	650 g soil treated with batches of 5 worms at 15 °C in the dark for 60 days	Phenanthrene, fluoranthene	[53]

Table 4 (*Continued*)

Inoculated microorganism	Soil	Process details	PAHs studied	Reference
Spent mushroom compost (*Pleurotus pulmonarius*)	Spiked garden soil	1 g soil treated with straw spent mushroom compost at 4–80 °C	Naphthalene, phenanthrene, benzo(a)pyrene, benzo(g,h,i)perylene	[54]
White rot fungus (*Phanerochaete chrysosporium*)	MGP soil	Bioreactor treatment at 39 °C for 36 days	Acenaphthene, acenaphthylene, anthracene, benzo(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(g,h,i)perylene, benzo(k)fluoranthene, chrysene, fluorene, indeno(1,2,3-c,d)pyrene, naphthalene, phenanthrene, pyrene	[55]
Shredded wheat straw cuttings and white rot fungus (*Pleurotis ostreatus*)	Spiked soil	Bioreactor treatment at 25 °C for 249 days	Fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz(a)anthracene, chrysene, benzo()fluoranthenes, benzo()pyrenes	[58]
White rot fungus (*Bjerkandera adusta* BOS55)	Spiked marsh soil	Bioreactor treatment at 30 °C for 27 days	Dibenzothiophene, fluoranthene, pyrene, chrysene	[59]
Fresh green waste compost (FGWC)	Coal-tar-contaminated soil	Bioreactor treatment at 38 °C, 55 °C, 70 °C, and variable temperature profiles for 56 days	Naphthalene, acenaphthylene, acenaphthene, fluorene, anthracene, phenanthrene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenzo(a,h)anthracene, indeno(1,2,3-c,d)pyrene, benzo(g,h,i)perylene	[60–62]
Anaerobic PAH-adapted consortium	Spiked soil	0.5 g treated with 1 ml anaerobic PAH-adapted consortium, 8.5 ml culture medium in vials. Treatment in anaerobic glove box at 30 °C in the dark for 90 days	Phenanthrene, anthracene, pyrene, acenaphthene, fluorene	[63]
Mixed bacterial consortium with acetate	Spiked soil	50 g soil treated with 220 ml solution containing PAHs, glucose, acetate, nitrate or water. Treatment in anaerobic glove box for 18 days	Biphenyl, fluorene, phenanthrene, pyrene	[64]

of this method is also heavily influenced by the surrounding conditions affecting the biological degradation of contaminants such as rainfall which is largely uncontrollable and may consequently lead to unintentional increase in time to complete remediation.

Composting, a process typically used to degrade solid waste materials, has also recently been studied as a remediation technology for PAH-contaminated soils. Mushroom compost consisting of wheat straw, chicken manure and gypsum was added to MGP soil in a thermally insulated composting chamber as reported by Sasek et al. [43] and Cajthaml et al. [44]. Optimal temperature gradient and concentrations of oxygen and carbon dioxide were controlled by aeration. Degradation efficiencies of individual PAHs after 54 days of composting in the chamber fell in the range of 20–60%, with further removal of PAHs (37–80%) found after an additional 100 days of compost maturation in an open-air field [43]. Composting was also found to degrade 3- and 4-rings PAHs more effectively than 5- and 6-rings PAHs [44].

The effects of wood ash addition as fertiliser in forests on PAH soil concentrations have been systematically investigated in a series of studies. It was demonstrated that the overlying wood ash layer on forest grounds prevented further input of PAHs from the atmosphere as wood ash has a very high PAH adsorption capacity (1169 μg/kg) and is not apparently a source of PAHs [45]. Further studies have indicated that the transfer of PAHs from wood ashes to water was extremely low due to their poor solubility in water

[46,47]. In water, PAHs have been shown to adsorp onto colloid dispersions of humic substances [48]. Therefore, ashes can be considered as stable long-term PAH reservoirs, which slowly release low levels of PAHs to runoff waters.

3.2. Aerobic bioremediation

Due to the absence of suitable endogenous microbial population and incompatible environment conditions, PAHs are naturally more recalcitrant to biodegradation and persist in the environment for years. Consequently, ex situ bioremediation techniques adapt the inoculation of PAH specific exogenous microorganisms such as bacteria and fungi.

The aerobic biodegradation process also known as aerobic respiration is the breakdown of contaminants by microorganisms in the presence of oxygen. Aerobic bacteria use oxygen as an electron acceptor to break down both the organic and inorganic matters into smaller compounds, often producing carbon dioxide and water as the final product. The genetics of PAH metabolism in aerobic bacteria has been reviewed comprehensively by Habe and Omori [49]. White rot fungus is commonly used in aerobic biodegradation due to its better degrading capability of a wider and heavier array of aromatic compounds which is contributed by the production of extracellular lignin-degrading enzymes with low substrate specificity in fungus. In a laboratory scale experimental work, two white

rot fungi, *Irpex lacteus* and *Pleurotus ostreatus* were observed to significantly degrade 3- and 4-rings PAHs with average degradation of 58–73% [50]. The ability of a Deuteromycete fungus, *Cladosporium sphaerospermum* to treat soil from an aged gas manufacturing plant has been tested in culture tubes and microcosms [51]. The results showed that the total PAH loss ranged from 21% to 26% including depletion of 5- and 6-rings PAHs after 4 weeks of incubation. Nevertheless, these degradation efficiencies achieved with fungi treatment are low when compared to solvent extraction techniques.

Apart from fungi, Li et al. [52] also revealed that the inoculation of microbial consortia made up of bacteria, fungi and bacteria–fungi mixture successfully degraded the 16 priority PAHs to different degrees of concentration. Other studies meanwhile have used earthworms [53] and spent mushroom compost [54] to treat PAHs in soils. Whilst not all microorganisms have the ability to degrade lignin, studies have revealed that rod-shaped mycobacteria has a faster growth rate on PAHs compared to other microorganisms [55]. Nonetheless, further investigations are necessary when introducing new microorganisms into a different environment since this may lead to mortality of the specialised microorganisms or movement away from the intended compounds due to their unpredictable behavioural response (negative chemotaxis) [41,56].

3.3. Aerobic bioreactor remediation

At present, many bioreactor plants are established for treatment of sewage and wastewater. Research efforts have been expended into adapting this concept for the remediation of PAH-contaminated soil. One such attempt was carried out by May et al. [57] who incubated white rot fungus, *Phanerochaete chrysosporium* in a reactor system which initially contained 3500 ml of nitrogen limited medium and 0.1% (v/v) Tween 80 surfactant to remove PAHs from a highly contaminated soil collected from a former gas work plant site. Observations at the end of the 36 days incubation period conducted at 39 °C showed that the white rot fungus was capable of reducing the total soil PAH concentration by 45% through the polymerisation process, whereby most PAHs were mainly converted to quinines. Similar bioreactor experiments using different types of white rot fungus were also executed by Richnow et al. [58] and Valentin et al. [59] who used *Pleurotis ostreatus* and *Bjerkandera adusta*, respectively.

On a similar note, Antizar-Ladislao et al. [60,61] utilised green waste compost made of foodstuff as the source of aerobic biodegradation of PAHs in contaminated soil. It was observed that the PAH removal percentage was higher compared to using white rot fungus, suggesting that the composting treatment resulted in increased generation of heat from the additional aerobic metabolism of composting matter due to the increased porosity and assimilated carbon for biomass growth in the soil slurry. Investigation of different bioreactor temperature profiles showed that the total PAHs were best removed using a constant temperature of 38 °C compared to other variable temperature treatments.

One of the advantages of the bioreactor system is the integration of controlled temperature. However, it has been demonstrated that an increase in temperature from 38 °C to 70 °C rendered the incubated microorganisms inactive leading to a reduced removal percentage of PAHs in the soil slurry [61,62]. In contrast to this, another work suggested that an increase in the incubation temperature increases the removal efficiencies of PAHs with the optimum efficiency occurring at temperatures above 75 °C [54]. This discrepancy may be due to the different compost matter employed, which may in turn lead to different microorganisms developing with dissimilar survival rates and responses to environmental warmth.

3.4. Anaerobic bioremediation

In cases when oxygen is absent or limited, biodegradation can occur anaerobically. Contrary to aerobic biodegradation, anaerobic microorganisms use other available substances such as nitrate, sulphate, iron, manganese and carbon dioxide as their electron acceptors to break down organic compounds into smaller constituents, often producing carbon dioxide and methane as the final products. Alternatively some anaerobic microorganisms can break down organic contaminants by fermentation whereby in this case, the organic contaminants act as the electron acceptors.

Primarily, anaerobic biodegradation is enforced when the degree of contamination is very high, limiting oxygen flow due to soil pore saturation or clogging of aggregates. As such, this technology is a promising remediation process for accidental oil spills as well as remediation of water submerged soil such as paddy field and swamps. In addition to that, anaerobic biodegradation is anticipated to replace aerobic biodegradation since large aeration area is not necessary which may in turn reduce total remediation cost. Furthermore, anaerobic bioremediation can treat deep underground soil since the process does not require oxygen.

Chang et al. [63] conducted a laboratory scale study using anaerobic PAH-adapted consortium culture which was incubated with spiked soil and amended with nutrients. After an incubation period of 90 days at 30 °C, it was found that the spiked PAHs were significantly degraded. Additionally the degradation of PAHs was shown to be enhanced by the addition of nutrient supplements such as acetate, lactate or pyruvate. Likewise, Ambrosoli et al. [64] achieved removal percentages in the approximate range of 30–60% for various PAHs in treating PAH-contaminated soil under denitrifying conditions by inoculating with a mixed population of microorganisms obtained from a paddy soil.

4. Phytoremediation

Phytoremediation is a relatively new in situ bioremediation method which uses plants to extract, sequester and detoxify existing environmental pollutants in particular heavy metals. Since 1991, plants have been widely studied to better understand their many endogenous genetic, biochemical and physiological capabilities to mineralise a wide variety of complex organic pollutants into non-toxic constituents such as carbon dioxide, nitrate, chlorine and ammonia [65]. To date, plants are known to enhance the remediation of soil via biophysical and biochemical processes such as adsorption of nutrients bound with pollutants, manipulation of plant uptake of pollutants by promoting a more acidic soil environment, secretion of enzymes from plants which act as surfactants to increase the bioavailability of pollutants, capability to store pollutants and sequestering them to 0.1–1% of the plant dry weight and chemical transformation of toxic elements into relatively harmless forms through their metabolism course [66,67]. Additionally, synergistic interaction between plants and microbial communities in the rhizosphere has been demonstrated to be effective for recalcitrant organic compounds [9]. Table 5 lists some bibliographic references on phytoremediation as a PAH removal technology from soil.

4.1. Phytoremediation with grass (Graminaeae)

In phytoremediation, plants are ideally chosen such that they can cover a significantly large root surface area and are capable of adapting to the conditions of the soil. From an economic viewpoint, plants that require less maintenance such as fertilising or frequent trimming are preferable. As such, feasibility studies have focussed on the *Graminaeae* family or commonly known as grass since these

Table 5
Bibliographic compilation of phytoremediation studies.

Plant	Soil	Process details	PAHs studied	Reference
Tall fescue (*Festuca arundinacea*), annual ryegrass (*Lolium multiflorum*), yellow sweet clover (*Melilotus officinalis*)	MGP soil	Soil composting or on-site land treatment followed by treatment in greenhouse for 12 months	Naphthalene, acenaphthylene, acenaphthene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthrene, benzo(k)fluoranthrene, benzo(a)pyrene, indeno(1,2,3-c,d)pyrene, benzo(g,h,i)perylene	[67]
Ryegrass (*Lolium perenne*)	Aged contaminated soil	Treatment in 5l cultivation vessels for 12 or 18 months. Average temperature was 27/12 °C (day/night) during summer and 10/5 °C during winter with cold shock for 10 days at −10 °C to simulate natural winter conditions	Naphthalene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenz(a,h)anthracene, benzo(g,h,i)perylene, indeno(1,2,3-c,d)pyrene	[68]
Grasses: *Dactylis glomerata* (cocks-foot), *Festuca arundinacea* (tall fescue), *Festuca rubra* (red fescue) and *Lolium perenne* (perennial ryegrass); legumes: *Lotus corniculatus* (birdsfoot-trefoil), *Trifolium pratense* (red clover) and *Trifolium repensm* (white clover)	Spiked soil and artificial coal-tar-contaminated soil	200 g soil treated in greenhouse at overnight temperatures minimum varied from 6 °C to 10 °C and daily maximum from 26 °C to 40 °C for 12 months	Naphthalene, fluorene, acenaphthene, phenanthrene, anthracene, fluoranthene, pyrene, benz(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenz(a,h)anthracene, benzo(g,h,i)perylene, indeno(1,2,3-c,d)pyrene	[69]
Tall fescue (*Festuca arundinacea*), switchgrass (*Panicum virgatum*)	MGP soil	1500 g soil mixed with 500 g of potting mix and treated in greenhouse for 12 months	Naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(e)pyrene, benzo(k)fluoranthene, benzo(a)pyrene, dibenz(a,h)anthracene, indeno(1,2,3-c,d)pyrene, benzo(g,h,i)perylene	[70]
Two grasses (*Panicum bisulcatum* Thunb. and *Echinochloa crus-galli*) and two legumes (*Astragalus membranaceus* and *Aeschynomene indica*)	Spiked soil	Treatment in greenhouse at 20–25 °C (day) and 10–15 °C (night). The water content was maintained at about 70% of the water holding capacity	Phenanthrene, pyrene	[71]
Red mulberry, black willow, rooted hybrid poplar, sycamore, black locust	Spiked soil	Treatment in greenhouse at ambient conditions (air temperatures range from −4 °C to 39 °C) for 12 months	Anthracene, phenanthrene, pyrene	[72]
Field crops: oat (*Avena sativa*), lupine (*Lupinus polyphyllus*) and rape (*Brassica napus* var. *Radicola*); horticultural crops: dill (*Anethum graveolens*), pepper (*Capsicum annuum*) and radish (*Raphanus sativus*); trees: jack pine (*Pinus banksiana*), red pine (*Pinus resinosa*) and white pine (*Pinus strobus*)	Spiked soil	Treatment in a growth chamber at 25 °C during a 16-h day and at 19 °C during an 8-h night for 10–14 days. The light intensity was 11,000 l×.	Pyrene	[73]
Tall fescue (*Festuca arundinacea*)	Artificial creosote-contaminated soil	Land farming for 2 weeks, followed by soil inoculation with PAH-degrading bacteria and incubation for 5 days finally phytoremediation for 100 days	Naphthalene, acenaphthene, acenaphthylene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenzo(a,h)pyrene, benzo(g,h,i)perylene, indeno(1,2,3-c,d)pyrene	[74]

species have very fibrous root systems which extend over a large surface area and penetrate deeper into the soil.

In a study by Rezek et al. [68], 15 PAHs were monitored in soil vegetated with ryegrass (*Lolium perenne*). During the cultivation of 18 months, the soil was fertilised with N–P–K fertilizer in 14-day intervals while kept at average temperatures of 12–27 °C during summer time and 5–10 °C during winter time. Analyses of the remediated soil revealed that the concentrations of all PAHs significantly decreased with an average of 50% with the exception of higher molecular weight ones including dibenzo(a,h)anthracene, benzo(g,h,i)perylene and indeno(1,2,3-c,d)pyrene. Statistical examination on the differences between PAH content after phytoremediation with regard to different soil layers showed that lower concentrations of PAHs were found mostly in the bottom layer samples of the 18 cm deep soil. This highlights the heterogeneity of PAH degradation in soil since the depth and extent occupied by plant roots are unknown and difficult to measure in actual field sites. It has also been observed that despite good germination of seedlings used for phytoremediation of PAH-contaminated soil, the subsequent growth of ryegrass was reduced when compared with the 7 other types of grass and legume species [69]. This may have been due not only to the toxicity of PAHs but also to the decline in biomass production in highly contaminated soil which reduces water and nutrients provision to plants.

Cofield et al. [70] showed that tall fescue (*Festuca arundinacea*) and switchgrass (*Panicum virgatum*) are capable of removing all PAHs with an average of 40% with the exception of indeno(1,2,3-c,d)pyrene which only had an approximate removal efficiency of 1.5% percentage. Similarly, Lee et al. [71] found that the native Korean grass species *Panicum bisulcatum* and *Echinogalus crus-galli* are both suitable candidates for phytoremediation of PAH-contaminated soil due to their robust growth and efficient extra cellular enzyme production. More than 99% degradation of phenanthrene and 77–94% degradation of pyrene were observed in soil after 80 days of treatment.

4.2. Phytoremediation with trees

Although grass have been the primary focus of phytoremediation studies, Mueller and Shann [72] suggested that trees may also have similar capabilities with their extensive root systems. Five tree species (red mulberry, black willow, rooted hybrid poplar, sycamore and black locust) were selected to represent the broad habitat range capable of removing PAHs from soil. The pot planted trees were watered and fertilised as necessary and kept ventilated in air temperatures ranging from −4 °C to 39 °C for a duration of 12 months. The overall extent of PAH loss from aged soil was compound dependent with phenanthrene as the most rapid and completely degraded PAH compared to anthracene and pyrene. Studies carried out with jack pine (*Pinus banksiana*), red pine (*Pinus resinosa*) and white pine (*Pinus strobus*) also showed positive results with 74% degradation of pyrene in soil within 8 weeks in comparison with a mere 40% or less in unplanted soil [73].

The difficulties of phytoremediation in practice lie in the measurement of phytoremediation rates, prediction of treatment durations and development of monitoring schemes [10]. To address these difficulties, effective models which include the various interactions contributing to phytoremediation can be developed.

4.3. Phytoremediation combined with bioremediation

To improve the phytoremediation treatment, Huang et al. [74] carried out a multi-process phytoremediation system consisting of land farming at a constant moisture level for 120 days followed by bioremediation with a PAH-degrading bacterial culture mixed into the soil for another 120 days and finally phytoremediation with tall fescue (*F. arundinacea*) sown directly into the soil and grown for 120 days. Prior to this however, the plant seeds were applied with plant growth promoting rhizobacteria (PGPR) to enhance plant growth and biomass production. The removal efficiency of the 16 priority PAHs in this multi-phytoremediation process was found to be at an average of 78% which is 23% more than the phytoremediation treatment by itself. Furthermore, a significant achievement of this multi-phytoremediation process was its capability to remove the higher molecular weight PAHs, particularly those with more than 5-rings with removal percentages of 32%, 42%, 43% and 58% for indeno(1,2,3-c,d)pyrene, dibenzo(a,h)pyrene, benzo(g,h,i)perylene and benzo(a)pyrene, respectively.

In another similar study, Parrish et al. [67] performed soil pre-treatment with two bioremediation methods; composting in drum reactors and on-site land farming with biosolids prior to phytoremediation with three cool season forages, tall fescue (*F. arundinacea*), annual ryegrass (*Lolium multiflorum*) and yellow sweet clover (*Melilotus officinalis*). Secondary phytoremediation treatment was subsequently carried out in a greenhouse for 12 months. The findings of this combined remediation technique are in agreement with Huang et al.'s [74] whereby significant overall reduction in PAHs were obtained especially for 4- and 5-rings PAHs.

5. Chemical oxidation

Oxidation reactions can be utilised to remediate soils contaminated with PAHs. Different types of oxidants have been investigated ranging from the more commonly studied Fenton's reagent and ozone to less common oxidants such as peroxy-acid, potassium permanganate, hydrogen peroxide, and activated sodium persulphate. Summaries of the works described here are compiled in Table 6.

5.1. Fenton's reagent as oxidant

The Fenton's reagent (Fe(II)–H_2O_2) developed in the 1980s by Henry John Horstman Fenton can be used to treat PAH-contaminated soils. Typically, the major steps involved in Fenton's reaction are as follows [75].

Hydrogen peroxide (H_2O_2) decomposition into hydroxyl radicals ($^\bullet OH$) in the presence of ferrous iron (Fe^{2+}):

$$H_2O_2 + Fe^{2+} \rightarrow \, ^\bullet OH + OH^- + Fe^{3+} \tag{1}$$
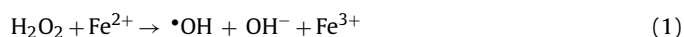
The unstable hydroxyl radicals formed are used to degrade organic compounds (RH or R) either by hydrogen abstraction:

$$RH + \, ^\bullet OH \rightarrow \, ^\bullet R + H_2O \tag{2}$$

Or by hydroxyl addition:

$$R + \, ^\bullet OH \rightarrow \, ^\bullet ROH \tag{3}$$

Flotron et al. [75] investigated the use of the Fenton's reagent to study possible desorption or degradation of fluoranthene, benzo(b)fluoranthene and benzo(a)pyrene in soil. Soil samples were mixed with water to form a solid matrix suspension prior to addition of Fe(II) solution and successive additions of hydrogen peroxide solution to instigate the Fenton oxidation. The authors observed that almost complete degradation of benzo(a)pyrene was achieved with significant degradation of fluoranthene while benzo(b)fluoranthene remained undegraded with excess concentration of hydrogen peroxide. It was also noted that several by-products, some with possible high toxicity were formed during the course of the treatment. In another study by Kawahara et al. [76], the Fenton's reagent oxidation process was utilised to treat creosote-contaminated soil from a wood-treating site. The results showed that a total of 12 PAHs increased in the range of 13–56% in the soil samples due to the weakening of the adsorptive bonds of the

Table 6
Bibliographic compilation of chemical oxidation studies.

Oxidant	Soil	Process details	PAHs studied	Reference
Fenton's reagent	Sewage sludge, agricultural soil, sediment	Magnetic stirring for 24 h	Fluoranthene, benzo(b)fluoranthene, benzo(a)pyrene	[75]
Fenton's reagent	Creosote-contaminated soil	Gyrotary water bath at 175 rpm and incubated at 25 °C in the dark	Acenaphthylene, naphthalene, 2-methylnaphthalene, benzo(a)pyrene, dibenzofuran, chrysene, benzo(b)fluoranthene, benzo(a)anthracene, pyrene, fluorene, acenaphthene, fluoranthene, phenanthrene, anthracene	[76]
H$_2$O$_2$, modified Fenton's reagent, activated sodium persulphate, KMnO$_4$, combined KMnO$_4$ and H$_2$O$_2$, combined activated sodium persulphate and H$_2$O$_2$	Contaminated sediment	Bench scale stirring	Naphthalene, acenaphtylene, acenaphtene, fluorene, phenantrene, anthracene, fluoranthene, pyrene, chrysene, benzo(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenzo(a,h)antracene, benzo(g,h,i)perylene, indeno(1,2,3-c,d)pyrene	[78]
Fenton's reagent	Artificial coal-tar-contaminated soil	Shaking at room temperature for 14 days	Phenanthrene, anthracene, fluoranthene, pyrene, benz(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene dibenz(a,h)anthracene, benzo(g,h,i)perylene, indeno(c,d)pyrene	[79]
Fenton's reagent	Contaminated soil, sand and sediment	Water bath agitation for 24 h	Naphthalene, 2-methylnaphthalene, 1-methylnaphthalene, 2,6-dimethylnaphthalene, 2,3,5-trimethylnaphthalene, biphenylene, acenaphthylene, acenaphthene, fluorene, anthracene, phenanthrene, 1-methylphenanthrene, fluoranthene, pyrene, chrysene, benz(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(e)pyrene, benzo(a)pyrene, perylene, dibenz(a,c)anthracene, benzo(g,h,i)perylene, indeno(c,d)pyrene	[80]
Ozone	Spiked soil	Ozone chamber at 13 °C in the dark for 6 h	Phenanthrene	[82]
Ozone	Field-scale tests	In situ ozonation	Pyrene, naphthalene, chrysene, phenanthrene	[83]
Ozone	Contaminated soil, sand and sediment	Ozonation at 45 °C for 4 h	Naphthalene, 2-methylnaphthalene, 1-methylnaphthalene, 2,6-dimethylnaphthalene, 2,3,5-trimethylnaphthalene, biphenylene, acenaphthylene, acenaphthene, fluorene, anthracene, phenanthrene, 1-methylphenanthrene, fluoranthene, pyrene, chrysene, benz(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(e)pyrene, benzo(a)pyrene, perylene, dibenz(a,c)anthracene, benzo(g,h,i)perylene, indeno(1,2,3-c,d)pyrene	[84]
Peroxy-acid	Contaminated soil from superfund sites	Shaking for up to 24 h	Naphthalene, acenaphthylene, acenaphthene, fluorine, phenanthrene, anthracene, fluoranthene, pyrene, benz(a)anthracene, chrysene, benzo(a)pyrene, indeno(1,2,3-c,d)pyrene, dibenzo(a,h)anthracene, benzo(g,h,i)perylene	[85]
KMnO$_4$	Spiked sandy soil	Stirring for 10, 20 or 30 min	Anthracene, benzo(a)pyrene, chrysene, fluoranthene, phenanthrene, pyrene	[86]

PAH-complex formed with soil surfaces. This suggests that Fenton's reagent may be used as a primary remediation treatment which can provide further enhancement for a more efficient secondary remediation treatment.

Modified Fenton's reagent can be used as a stronger oxidising agent to treat more recalcitrant PAHs. Here, apart from hydroxyl radicals, other highly reactive radicals are formed through the addition of chemicals such as chelating agents and/or high peroxide concentrations [77]. Experimental work using modified Fenton's reagent (catechol as chelating agent) to treat heavily contaminated sediments indicated that total PAH degradation was above 95% [78].

In the examination of role of soil characteristics in Fenton's reagent treatment, Bogan and Trbovic [79] concluded that the susceptibility of PAHs to chemical oxidation was a function of total organic content (TOC) above a threshold value of approximately 5%. For low TOC soils, oxidation strongly depended on soil porosity. Additionally, higher molecular weight PAHs tend to have stronger affinities for humic acid soil, leaving them less susceptible to the Fenton's reagent oxidation. The findings are in agreement with another work whereby it was shown that the efficiency of chemical oxidation of PAHs in soils is dependent on soil characteristics and PAH properties [80]. In this work, lower molecular weight PAHs with relatively high water solubilities were generally found to be more susceptible to Fenton's treatment than their heavier, highly hydrophobic counterparts. For two- and three-rings PAHs, organic matter, oxide content and specific surface area of soil all negatively affected the degradation process. On the other hand, degradation efficiency of 5- and 6-rings PAHs were adversely affected by the age of contamination and pH but positively correlated to degraded organic matter. This indicated that these PAHs are released and degraded when soil organic matter undergoes oxidation.

5.2. Ozone as oxidant

Ozone (O_3) can initiate indirect oxidation reactions by decomposing into OH radicals. In ozone oxidation of PAHs, PAHs undergo degradation through the direct reaction or through the radical reaction as shown by the following expressions, respectively [81]:

$$PAH + O_3 \rightarrow products \tag{4}$$

$$PAH + {}^\bullet OH \rightarrow products \tag{5}$$

In a study by O'Mahony et al. [82], ozone generated from air by electric discharge was used to remove several types of phenanthrene-spiked farm soils. The treatment of soils was carried out in an ozone chamber at a constant room temperature of 13 °C. Analyses of the treated soils showed more than 50% reduction in phenanthrene concentrations in all soils after ozone treatment for 6 h at 20 ppm concentration. It was also demonstrated that 85% phenanthrene removal could be achieved in sandy soils compared to clay soils due to its larger pore spaces, thus providing better transport of gaseous ozone through the soil matrices. Increasing moisture content was found to have an adverse effect on ozone treatment since PAHs in soil become less accessible to ozone when water occupies pore spaces. Masten and Davies [83] who also experimented with ozone as a PAH oxidising agent reported 95% removal of phenanthrene, 91% removal of pyrene while chrysene was reduced to only 50% due to its more hydrophobic nature. Similar to Fenton's reagent, a number of unidentified by-products were simultaneously discovered which were stated to be more polar than the parent compounds, thus having better biodegradability and aqueous solubility.

Comparison of Fenton's reagent and ozone oxidation in treating aged PAH-contaminated soils has been carried out by Jonsson et al. [84]. It was reported that Fenton's reagent could more effectively degrade PAHs (degradation efficiency of 40–86%) as compared to ozone (degradation efficiency of 10–70%). Degradation of lower molecular weight PAHs was more efficient using ozone as the oxidising agent while a more even degradation pattern for all ranges of PAHs resulted from the use of Fenton's reagent.

5.3. Other oxidants

Alderman et al. [85] investigated the use of peroxy-acid in a laboratory scale process. In the peroxy-acid process, it was suggested that the added organic acid reacts with hydrogen peroxide via hydrogen abstraction and hydrogen peroxide breakdown to form a peroxy-acid molecule. The peroxy-acid molecule subsequently releases a hydroxyl radical which is used to oxidise PAHs. The results of this study showed that the hydrogen peroxide:acetic acid:deionised water solution ratio of 3:5:7 (v/v/v) reduced all 14 PAHs rapidly from 5 g of soil to approximately 50%. However, a ratio of 3:3:9 (v/v/v) was necessary to produce similar results in treating 150 g of soil during the same treatment period. On a different note, Brown et al. [86] assessed the feasibility of potassium permanganate ($KMnO_4$) as oxidant to remove PAH from contaminated soil. In this study, soil was oxidised by $KMnO_4$ solutions resulted in significant reductions of benzo(a)pyrene, pyrene, phenanthrene and anthracene (72.1%, 64.2%, 56.2% and 53.8%, respectively) while high percentages of fluoranthene (86.6%) and chrysene (92.2%) remained undegraded. The observed rate of chemical reactivity of the selected PAHs during the permanganate reaction was suggested to be due to the aromatic structure of individual PAHs.

Comparison of oxidants including H_2O_2, modified Fenton's reagent, activated sodium persulphate, $KMnO_4$, as well as a combination of $KMnO_4$ and H_2O_2, and a combination of activated sodium persulphate and H_2O_2 to treat PAH-contaminated sediments has also been carried out by Ferrarese et al. [78]. The authors found that the best removal percentages (above 95%) were achieved with the use of modified Fenton's reagent, H_2O_2 and $KMnO_4$. It was also noted that the optimal oxidant dosages were considerably high, approximately 100 mmol of oxidant for a 30 g sediment sample, as sorbed PAH mineralisation requires very vigorous oxidation conditions, especially with high soil organic matter content.

6. Photocatalytic degradation

The photocatalytic degradation process uses photocatalysts to promote oxidising reactions which destroy organic contaminants in the presence of light radiation. The technology has been widely established for treatment of wastewater, and recently, its application has extended to treatment of contaminated soils. Table 7 lists the references on photocatalytic treatment of PAH-contaminated soil.

Zhang et al. [87] conducted a comprehensive study of the photocatalytic degradation of phenanthrene, pyrene and benzo(a)pyrene on soil surfaces using titanium dioxide (TiO_2) under UV light. Compared to the absence of catalyst, the addition of TiO_2 as catalyst revealed that TiO_2 accelerated the photodegradation process of all three PAHs, with benzo(a)pyrene being degraded the fastest. Nonetheless, variation in TiO_2 concentration from 0.5 to 3 wt.% did not provide any significant effect on PAH degradation. Under distinct UV wavelengths, photocatalytic degradation rates of PAHs were different. Soil pH was discovered to affect the process whereby the highest pyrene and benzo(a)pyrene degradation rates were obtained at acidic conditions, while phenanthrene was most significantly degraded at alkaline conditions. Additionally, the presence of humic acid in soil was found to enhance PAH photocatalytic degradation by sensitising radicals capable of oxidising PAHs.

Table 7
Bibliographic compilation of photocatalytic degradation studies.

Photocatalyst	Soil	Process details	PAHs studied	Reference
TiO_2	Spiked soil	Treatment in photodegradation chamber at 30 °C. Parametric studies: TiO_2 amount, soil pH, humic acid, wavelength	Phenanthrene, pyrene, benzo(a)pyrene	[87]
TiO_2	Spiked soil	Treatment in solar reactor for 6 h	Fluoranthene	[88]

Rababah and Matsuzawa [88] developed a recirculating-type photocatalytic reactor assisted by the oxidising agent H_2O_2 solution to treat soil spiked with fluranthene. It was observed that the degradation efficiency of fluoranthene was 99% in the presence of both TiO_2 and H_2O_2 compared to a lower degradation efficiency of 83% in the presence of TiO_2 alone.

7. Electrokinetic remediation

In situ electrokinetic remediation can be applied to treat low permeable soils contaminated with heavy metals, radionuclides and selected organic pollutants. The principle behind this method is the application of a low level direct current electric potential through electrodes, which are placed into the contaminated soil. Ionic contaminants are transported to the oppositely charged electrode by electromigration. Additionally, electroosmotic flow provides a driving force for the movement of soluble contaminants. Although the technology has been known and utilised for more than a decade, application to removal of hydrophobic and strongly adsorbed pollutants such as PAHs especially from low permeability soils is recent. Solubilising agents are therefore used in these cases to enhance the removal efficiency of PAHs. In Table 8, several studies on application of this technology on PAH-contaminated soils are compiled.

Reddy et al. [89] presented a series of bench scale experiments on electrokinetic remediation of aged MGP soil using different flushing agents including two surfactants (3% Tween 80 and 5% Igepal CA-720), a co-solvent (20% n-butylamine) and a cyclodextrin (10% HPCD). The experiments were conducted at 2.0 VDC/cm voltage gradient and 1.4 hydraulic gradient. The maximum electroosmotic flow was obtained with 20% n-butylamine co-solvent followed by HPCD. However, PAHs were found to be solubilised in the surfactants and HPCD enhanced systems more efficiently with

significant migration towards the cathode. The highest removal efficiency of PAHs from the soil was obtained using Igepal CA-720 surfactant. The use of HPCD at low (1%) and high (10%) concentrations for removal of phenanthrene in kaolin soil has also been studied in another work [90]. All electrokinetic tests were carried out at a periodic voltage gradient of 2 VDC/cm and neutral pH conditions at anode by addition of 0.01 M sodium hydroxide. Likewise to the previous findings [89], the migration of phenanthrene was observed to occur from anode to cathode. Phenanthrene removal was high in the case of 1% HPCD test compared to the baseline test using deionised water and 10% HPCD tests due to the high electroosmotic flow. With deionised water, phenanthrene could not be solubilised because of its hydrophobic nature, although the electroosmotic flow was relatively high.

The control of pH at the anode has been shown to affect the electrokinetic remediation of phenanthrene contaminated kaolin [91]. Controlling the pH was found to increase contaminant solubilisation and migration from the soil region adjacent to the anode, but the resulting high contaminant concentrations in the middle or cathode soil regions indicated that subsequent changes in the soil and/or solution chemistry caused deposition of contaminant and low overall removal efficiency.

8. Thermal technologies

Thermal technologies employ heat to either destroy or volatilise the PAHs in contaminated soils. Several reported works in this area are summarised in Table 9. Incineration of soil at high temperatures ranging from 870 °C to 1200 °C effectively destructs organic contaminants such as PAHs. In a remediation project funded by the US EPA, a heavily creosote-contaminated site located in Louisiana was excavated and fed into a transportable, high temperature, modular incineration plant [92]. In this project, 157,000 tonnes of

Table 8
Bibliographic compilation of electrokinetic remediation studies.

Flushing agent	Soil	Process details	PAHs studied	Reference
Surfactants: 3% Tween 80, 5% Igepal CA-720; co-solvent: 20% n-butylamine; cyclodextrin: 10% HPCD	MGP soil	Treatment in electrokinetic cell conducted at a constant voltage gradient of 2.0 VDC/cm and hydraulic gradient 1.4	2-Methylnaphthalene, acenaphthene, acenaphthylene, anthracene, benz(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(g,h,i)perylene, benzo(k)fluoranthene, chrysene, dibenz(a,h)anthracene, dibenzofuran, fluoranthene, fluorene, indeno(1,2,3-c,d)pyrene, naphthalene, phenanthrene, pyrene	[89]
1% HPCD, 10% HPCD	Spiked kaolin soil	Treatment in electrokinetic cell conducted at a constant voltage gradient of 2.0 VDC/cm	Phenanthrene	[90]
3% Tween 80, 40% ethanol	Spiked kaolin soil	Treatment in electrokinetic cell conducted at a constant voltage gradient of 1.0 VDC/cm	Phenanthrene	[91]

Table 9
Bibliographic compilation of thermal remediation studies.

Technique	Soil	Process details	PAHs studied	Reference
Incineration	Creosote-contaminated soil	Rotary kiln incinerator at 870–1200 °C	Naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fiuoranthene, benzo(a)pyrene, dibenzo(a,h)anthracene, benzo(g,h,i)perylene	[92]
Thermal desorption	MGP soil	Bench scale indirectly heated thermal desorber at maximum temperature above 450 °C	Naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fiuoranthene, benzo(a)pyrene, dibenzo(a,h)anthracene, benzo(g,h,i)perylene, indeno(1,2,3-c,d)pyrene	[93]
Thermally enhanced SVE	Lampblack-contaminated soil	Bench scale thermally enhanced SVE reactor at 250–300 °C for 35 days	Naphthalene, phenanthrene, fluoranthene, pyrene, benz(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(g,h,i)perylene, indeno(1,2,3-c,d)pyrene	[94]

contaminated solids containing PAH concentrations greater than 1000 mg/kg were successfully remediated to concentrations below 100 mg/kg. In addition to that, the total PAH concentration in the ash generated was reported to be less than 10 mg/kg. Nevertheless, there are drawbacks to the application of this technology. Firstly, moisture in the contaminated soil has to be removed either by lime addition or other methods so that combustion of the soil is more complete. Secondly, air pollution control devices should be installed to deal with the incinerator off-gases such as hydrogen chloride (HCl), sulphur oxides (SO_x), nitrogen oxides (NO_x), dioxins/furans and metal emissions.

Thermal desorption is a physical separation process applying heat to volatilise organic contaminants from waste matrices such as soil, sludge and sediments. A carrier gas or vacuum system sweeps the volatilised organic contaminants into the gas treatment system for secondary combustion or off-site disposal. In a work conducted by Renoldi et al. [93], contaminated soil from a manufacturing gas plant site was treated in a laboratory scale indirectly heated thermal desorber unit with a horizontal tubular furnace of length 68 cm and internal diameter of 3 cm. The concentration of PAHs was continuously monitored by a flame ionisation detector (FID) located at the carrier gas outlet of the reactor. After treatment at maximum temperatures above 450 °C, the concentrations of 16 PAHs reduced to below 0.05 mg/kg dry weight, which corresponded to a removal efficiency of 99.9%. However, it was noted that a few lower molecular weight compounds such as naphthalene and fluorene as well as acenaphthene remained in the treated soil at percentages of 0.2% and 1.0%, respectively. These lower molecular weight PAHs are known to form via the cracking of the higher molecular weight PAHs. Due to the high temperatures too, some oxygenated molecules such as furans and other PAHs were found present in the treated soil, formed via decomposition or oxidation of the original contaminants upon heating.

On a similar note, Harmon et al. [94] used a bench scale thermally enhanced soil vapour extraction (SVE) reactor with dimensions of 48 cm² by 30 cm depth to remediate approximately 70 kg of soil contaminated by lampblack, a carbon skeleton impregnated with oil gasification by-products. The reactor was operated for 35 days with temperatures ranging from 650 °C to 700 °C at the heating element. It was reported that temperatures ranging from 250 °C to 300 °C mobilised the majority of the 11 PAHs studied, and reduced the total PAH concentration in soil to a residual fraction of less than 100 ppm in 10 days.

9. Integrated remediation technologies

Each of the remediation technologies discussed in the preceding sections has its own strengths and weaknesses. To address the limitations of individual remediation techniques and to achieve better PAH removal efficiencies, various combinations of physical, chemical and biological treatments as shown in Table 10 can be used in conjunction with one another to treat PAH contaminants in soils.

9.1. Integrated physical–chemical treatment

Solvent extraction prior to chemical oxidation has been studied by Lundstedt et al. [95] who pre-treated aged PAH-contaminated soil with ethanol prior to Fenton oxidation. The pre-treatment was found to enhance the oxidation of strongly adsorbed PAHs especially anthracene, benzo(a)pyrene and perylene, by aiding their desorptions from the soil matrix. However, this was accompanied by an accumulation of oxidation products hence the authors suggested that the process must be further optimised before it can be applied in real situations. In another similar work, Bogan et al. [21] incorporated the use of vegetable oils to pre-treat PAH-contaminated soil prior to chemical oxidation treatment using Fenton's reagent. In this work, vegetable oils were contacted with two MGCP soils either 1% or 5% dosage (per dry weight of soil) for 2–3 h before Fenton's treatment was carried out. The findings indicated that vegetable oils can significantly enhance the effectiveness of Fenton's treatment of PAH-contaminated soils especially for high molecular weight species such as benzo(a)pyrene and dibenz(a,h)anthracene. It was suggested that the PAHs which are solubilised in vegetable oil lipids are more susceptible to free radical reactions in a Fenton chemical system. Nonetheless, the added volume of vegetable oil added needs to be carefully optimised because the use of excess lipid (above 5%) may instead consume the oxidant unproductively.

Dadkhah and Akgerman [96] performed hot water extraction concurrently with in situ wet oxidation using H_2O_2 to study the kinetics of PAHs removal from soil. In this series of small-scale semi-continuous extractions, the simultaneous pumping of H_2O_2 into the hot water reaction vessel resulted in negligible concentrations of residual PAHs in soil. Based on these results, it was suggested that this integrated method should reduce cost, making it a feasible remediation technique. Comparable studies by Kronholm et al. [39,40] using pressurised hot water extraction coupled with supercritical water oxidation revealed that the best overall extraction

Table 10
Bibliographic compilation of integrated remediation studies.

Classification	Soil	Process details	PAHs studied	Reference
Physical–chemical	MGP soil	Ethanol pre-treatment followed by Fenton's oxidation in a shaking water bath at 25 °C for 24 h	Naphthalene, 2-methylnaphthalene, 1-methylnaphthalene, 2,6-dimethylnaphthalene, acenaphthylene, acenaphthene, 2,3,5-trimethylnaphthalene, phenanthrene, anthracene, 1-methylphenanthrene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(e)pyrene, benzo(a)pyrene, perylene, dibenz(a,h)anthracene, indeno(1,2,3-c,d)pyrene, benzo(g,h,i)perylene	[95]
	MGP soil	Vegetable oil pre-treatment followed by Fenton's oxidation in a shaker at room temperature for 5 or 14 days	Fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fiuoranthene, benzo(a)pyrene, dibenzo(a,h)anthracene, benzo(g,h,i)perylene, indeno(1,2,3-c,d)pyrene	[21]
	Aged railroad tie plant soil	Hot water extraction coupled with in situ wet oxidation in small-scale semi-continuous reactor	Naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fiuoranthene, benzo(a)pyrene, dibenzo(a,h)anthracene, benzo(g,h,i)perylene, indeno(1,2,3-c,d)pyrene	[96]
	Spiked sea sand, coal gasification plant soil	Pressurised hot water extraction coupled with supercritical water oxidation	Naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fiuoranthene, benzo(a)pyrene, benzo(g,h,i)perylene, indeno(1,2,3-c,d)pyrene	[39,40]
	Spiked kaolin soil	Extraction with surfactant followed by electrochemical degradation of liquid	Anthracene, benzo(a)pyrene, and phenanthrene	[97]
	Creosote-contaminated clay	In situ electrokinetic treatment with chemical oxidation	Naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fiuoranthene, benzo(a)pyrene, dibenzo(a,h)anthracene, benzo(g,h,i)perylene, indeno(1,2,3-c,d)pyrene	[98]
Physical–biological	Coal-tar-contaminated soil	Extraction with acetone or ethanol followed by bioremediation	Naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fiuoranthene, benzo(a)pyrene, dibenzo(a,h)anthracene, benzo(g,h,i)perylene, indeno(1,2,3-c,d)pyrene	[99]
Biological–chemical	Spiked soil, industrial aged soil	Biodegradation combined with chemical oxidation with ozone	Napthalene, acenaphthene, phenanthrene, anthracene, fluoranthene, pyrene, chrysene, perylene, benzo(a)pyrene	[100]
	Artificial creosote-contaminated sand and peat	Ozonation or Fenton's oxidation followed by biodegradation	Fluoranthene, phenanthrene, fluorene, pyrene, triphenylene, benz(a)anthracene, chrysene	[101]
	MGP soil	Biodegradation combined with modified Fenton's oxidation	Naphthalene, fluorene, phenanthrene, anthracene, pyrene, chrysene, benzo(a)pyrene	[102]
Physical–chemical–biological	Aged wood impregnation plant soil	Combined soil washing–ozonation–biodegradation or soil washing–biodegradation or ozonation–biodegradation	Naphthalene, 2-methylnaphthalene, 1-methylnaphthalene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, perylene, dibenz(a,h)anthracene, indeno(1,2,3-c,d)pyrene, benzo(g,h,i)perylene	[103]

recoveries were obtained at 300 °C while the oxidation efficiencies increased with H_2O_2 concentrations and reaction time.

Solvent extraction has also been combined with electrochemical degradation for remediation of soils contaminated with PAHs. In a recent attempt, Alcantara et al. [97] used six surfactants including Brij 35, Merpol, Tergitol, Tween 20, Tween 80 and Tyloxapol to firstly extract PAH-spiked soil in an orbital shaker. Electrochemical cells were subsequently utilised to perform electrochemical oxidation of PAHs extracted into the surfactant solutions from the initial extraction. The results obtained demonstrated that all PAHs tested (anthracene, benzo(a)pyrene and phenanthrene) were almost degraded completely when electrodes of graphite or titanium were used, while the redox reactions induced by the latter electrochemical process destructed PAHs into more environmental friendly products.

Another novel integrated treatment combines electrokinetics and chemical oxidation. In this method, chemical oxidants are channelled into the anode compartment and injection wells of the electrokinetic test cell to simultaneously induce oxidation reactions directly in the contaminated soil as they migrate towards the cathode region. It has been shown that electrokinetically enhanced oxidation with sodium persulphate resulted in better PAH removal (35%) than either electrokinetics (24%) or persulphate oxidation (12%) alone although conversely, electrokinetics did not improve the performance of Fenton oxidation [98].

9.2. Integrated physical–biological treatment

Lee et al. [99] described the use of solvents (acetone and ethanol) to increase the bioavailability of PAH compounds in coal-tar-

contaminated soils prior to aerobic biodegradation in a bioreactor. Soils were firstly mixed with either solvent for 24 h and left to evaporate under normal ventilation conditions and later transferred into a reactor for biodegradation at a temperature of 21 °C. The solvent pre-treatment of soils resulted in a higher degradation rate, with approximately 90% of the total PAHs removed within 17 days in comparison to the required 35 days for biodegradation of soil without pre-treatment. The residual solvent which remained after evaporation may have been used as growth substrate leading to a higher microbial population, and subsequently revealing improvements in removal of 4- and 5-ring PAHs such as chyrsene and benzo(a)pyrene.

9.3. Integrated biological–chemical treatment

The use of ozone as post-chemical oxidation after biological treatment was performed by Derudi et al. [100] to enhance degradation of PAHs and reduce the duration of soil remediation. It was discovered that this combined biological and chemical treatment efficiently removed PAHs from both industrial aged and spiked soil with removal efficiencies larger than 90% for low molecular weight PAHs within the 3 h ozonation post-treatment. The heavier 4- and 5-ring compounds were also abundantly removed after an additional 13 h ozonation period.

Using biological remediation as a secondary step after chemical oxidation has also been demonstrated. For example, Kulik et al. [101] pre-treated sand and peat artificially spiked with creosote with either Fenton's reagent or ozone before aerobic biodegradation. In the experiments carried out, PAH biodegradability was enhanced by both chemical oxidation pre-treatments. Fenton's treatment followed by bioremediation was shown to be more effective for PAH removal in creosote-contaminated sand while ozonation prior to bioremediation was better for creosote-contaminated peat. Nam et al. [102] has also shown that simultaneous biodegradation and modified Fenton's oxidation could remove more than 98% of 2- and 3-ring PAHs and between 70% and 85% of 4- and 5-ring PAHs.

9.4. Integrated physical–chemical–biological treatment

Haapea and Tuhkanen [103] studied the feasibility of integrating soil washing, ozonation and biological treatment for the remediation of aged PAH-contaminated soil. Three different ozone doses and soil washing were experimented with different pHs in order to assess their effect on degradation and biodegradability of PAHs. The removal target of 85% could not achieved with any one of the tested methods, but was met by several combinations of the tested methods. In addition, it was observed that the consumption of ozone was 5–10 times lower in the integrated treatments of soil washing, ozonation and biological treatment than without pre-washing.

10. Final considerations

Of the remediation technologies discussed here, soil washing with water and co-solvents or surfactants can be implemented easily since the process is carried out at ambient pressure and low temperatures. Cyclodextrins and vegetable oils provide non-toxic, biodegradable and environmentally friendly alternatives to conventional solvents. In comparison to conventional soil washing, supercritical and subcritical fluid extractions are "greener" options but these entail the use of high pressure equipment. Nonetheless, solvent extraction is only a separation process which transfers PAHs onto the extract phase hence secondary treatment of the extracts is necessary.

Bioremediation and phytoremediation, meanwhile, require long treatment durations compared to all other techniques and recorded

degradation efficiencies tend to be low. The major advantages of these biological treatments is the high potential for in situ or on-site treatments and no waste treatment is required since products such as carbon dioxide, water and biomass are formed. Likewise to bioremediation and phytoremediation, chemical oxidation is able to degrade PAHs and not merely transfer them to another medium. However, concerns exist that toxic by-products may be formed during the course of treatment.

Both photocatalytic degradation and electrokinetic remediation have only recently been applied to treat PAH-contaminated soils. Successful extensions to field-scale applications will necessitate further optimisation and economic feasibility studies. Thermal technologies, on the other hand, can effectively destroy PAHs, but entail high costs due to the high temperatures and the need for treatment of the gases produced.

It has to be recognised that no single remediation technology can be the solution for all PAH-contaminated soils. Integrated soil remediation technologies which combine separation and destruction of PAHs appear to be the way forward in this technical field allowing improved removal efficiencies to be achieved. Future research should focus on a deeper technical and economic evaluation of all currently available soil remediation technologies for not only PAHs but also pesticides and chlorinated organic contaminants.

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