



Review

Application of vegetable oils in the treatment of polycyclic aromatic hydrocarbons-contaminated soils

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ABSTRACT

A brief review is conducted on the application of vegetable oils in the treatment of PAH-contaminated soils. Three main scopes of treatment strategies are discussed in this work including soil washing by oil, integrated oil-biological treatment and integrated oil-non-biological treatment. For each of these, the arguments supporting vegetable oil application, the applied treatment techniques and their efficiencies, associated factors, as well as the feasibility of the techniques are detailed. Additionally, oil regeneration, the environmental impacts of oil residues in soil and comparison with other commonly employed techniques are also discussed.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are one of the most widespread organic pollutants in soil. They are mainly formed from anthropogenic processes, as by-products of incomplete combustion of carbon-containing fuels such as coal, petroleum and their related products. The severe contamination of PAHs in soil is commonly associated with industries such as gas manufacturing, coke production, wood preserving and petroleum refining.

The accumulation of PAHs in soil can lead to the contamination of the food chain, which then cause direct or indirect exposure to humans. PAHs may also transport to air and groundwater through evaporation, leaching and migration. PAH concentrations ranging from 1 µg/kg to over 300 g/kg have been reported in soils and sediments from both contaminated and uncontaminated sites [1]. The presence of PAH compounds in soils is an issue of concern due to their carcinogenic, mutagenic, and tetratogenic properties [2]. In 2008, 28 PAHs have been identified as priority pollutants by the National Waste Minimization Programme, a project which is funded by US Environment Protection Agency [3].

Commonly employed remediation technologies for treating PAH-contaminated soils include soil washing or solvent extraction, bioremediation and chemical oxidation. In all PAH remediation techniques, a major influencing factor is the tendency of PAHs to adsorb tightly to organic matter in soil due to their hydrophobic nature. This renders them less susceptible to desorption, as well as biological and chemical degradation. In addition, prolonged aging time in contaminated soil promotes the sequestration of PAH molecules into micropores and increases the recalcitrance of PAHs towards treatment [4]. Hence, consideration has to be given to the desorption, dissolution and availability of PAHs to added chemicals in developing effective remediation techniques. An interesting advancement in the field of soil remediation for hydrophobic organic compounds is the inclusion of vegetable oil in various technologies. Vegetable oil offers multiple applications in soil remediation, ranging from its utilisation as a solvent to physically extract PAHs to its usage as soil amendment to enhance biological and non-biological treatments. To date, comprehensive reviews of remediation technologies specifically for PAH-contaminated soils have been reported in the specialised literature [5–9]. Previous works have either concentrated solely on one technology or evaluated various technologies for removal or destruction of PAHs in soils. Hence, this review is focussed on the application of vegetable oils in the treatment of PAH-contaminated soils which appears not to have been fully explored. In this paper, three main scopes of treatment strategies including soil washing using vegetable oil, integrated oil-biological treatment and integrated oil-non-biological treatment are reviewed, with an emphasis on the theoretical arguments supporting vegetable oil application. The applied treatment techniques are discussed from various aspects including removal efficiency, associated factors and feasibility of techniques. Comparison of remediation techniques which utilise vegetable oil with other commonly employed techniques is also included. Table 1 compiles the pertinent bibliographies studies in this field and forms the framework for the discussions in this review.

2. Physical extraction

2.1. The role of vegetable oil in desorption, solubility and extraction of PAHs

The addition of vegetable oil onto the soil matrix can be classified as a co-solute or co-solvent or solvent depending on the oil/water/soil ratio. At significant concentrations, vegetable oil acts as an immiscible organic liquid which affects the behaviour of hydrophobic contaminants including PAHs sorbed onto the soil matrix through competitive, cooperative or solvency effects [10]. Competitive and solvency effects would reduce the sorption of hydrophobic contaminants onto the soil, whereas cooperative effect would enhance the sorption. Competitive effect typically occurs when the addition of immiscible liquid such as oil is relatively small in quantity. In this case, the oil competes with the organic contaminants for the bounding sites of the soil, hence promoting desorption of contaminants from the soil matrix. Cooperative effect occurs when the immiscible oil contributes to the organic matter in the soil matrix and creates bounding sites for the organic contaminants to bind onto and sink into the soil matrix [11]. When the quantity and polarity of the immiscible liquid oil is large enough to dissolve the hydrophobic contaminants, this results in the solvency effect whereby the contaminants would be desorbed, dissolved and extracted from the soil matrix [12,13]. The effect which will be dominant is dependent on the interactions between the multi-components in the soil matrix.

The propensity of PAHs towards lipid phase than aqueous phase was clearly observed through the transfer of PAHs into the lipid tissues of marine aquatic life from contaminated sediment and the measured solubility of PAHs which was 4–5 orders of magnitude higher in oil phase than in aqueous phase [14]. Vegetable oils are complex mixtures of numerous organic compounds, which are largely composed of triglycerides (93–99%) with smaller amounts of phospholipids, free fatty acids, unsaponifiables, and tocopherols [15]. Their physical properties resemble mineral oil and they are categorised as light non-aqueous phase liquids (LNAPLs). The partition of hydrophobic compounds into this non-aqueous phase liquid is in many ways comparable to sorption onto soil organic matter.

Chiou [16] determined the partition coefficients for 38 different hydrophobic organic compounds in triolein–water systems (K_{triolein}) and found them to be slightly greater than the octanol–water (K_{ow}) coefficient when the $\log K_{\text{ow}}$ of the compound was ≤ 5.10 . When the $\log K_{\text{ow}}$ of the compound was ≥ 5.58 , K_{triolein} was found to be slightly smaller than K_{ow} . Since the soil adsorption coefficient (K_{oc}) of a PAH is always smaller than K_{ow} [17] and the K_{triolein} greater than K_{ow} until $\log K_{\text{ow}}$ exceeds 5.58, it can be expected that the partition of a PAH would favour the vegetable oil phase than the soil organic phase for $\log K_{\text{ow}}$ up to 5.58 or higher. The dissolution or desorption of PAHs when vegetable oil is added to soil has been observed through increasing soil toxicity [18]. Additionally, the inclusion of oil dissolves the soil organic material that binds PAHs, which then acts as a co-solute which enhances the capacity of oil to extract PAHs from contaminated soil.

Zemanek et al. [19] studied the partitioning of PAHs in the presence of a hydrophobic oil/water/soil system. The direction of partitioning of PAHs from aqueous phase to oil phase was more pronounced for low molecular weight (LMW) PAHs than high molecular weight (HMW) PAHs. In contrast, the direction of par-

Table 1
Bibliographic compilation of studies on the application of vegetable oils in PAH-contaminated soil treatments.

Reference	Oil type	Treatment description	Oil:soil	Water: soil	Spiked ^d or Field ^b soil	% of PAHs removed (% enhanced) ^c	Other parameters studied	Comments
<i>Physical extraction</i>								
[29]	Peanut oil	Batch extraction by oil slurry system.	2.5% (w/w) 2x ^d (5% w/w)	0.75:1 0.75:1	S S F S	90.0–92.0 91.4 83.7 90.0	Soil type, moisture content, temperature, oil concentration, PAHs concentration	Offers fast remediation of heavily contaminated sites. Most suited to sites which pose severe health and environmental risks whereby the curbing of pollutants spread is critical.
[24]	Sunflower oil	Batch extraction by oil/slurry/polystyrene foam particles system 1. Batch extraction by oil only 2. Oil regeneration with activated carbon	1:1 (v/dw) or 2:1 (v/dw)	Field moist	F	81–100	Dissolution kinetics, oil/soil ratio, PAHs size	
[26]	Sunflower oil	Batch extraction by oil only	1:1 (v/dw)	Field moist	F	67.2	Dissolution kinetics, moisture content, PAHs concentration, PAHs size, oil:soil ratio, mass balance	
			2:1 (v/dw)	Air dried Field moist	F F	90.2 81.5		
		Column extraction by oil/oil only	2x ^d (1:1 v/w)	Air dried Field moist	F F	97.0 65.6		
[25]	Sunflower oil	Column extraction by oil only	2x ^d (1:1 v/w)	Air dried Field moist	F F	96.3 >90	Contact time (flow rate), volume of oil, PAHs concentration, PAHs size, biodegradation of oil residue	
			4x ^d (1:1v/w)	Air dried	F	>90		
<i>Integrated oil-biological treatment</i>								
[91]	NA ^e	Oil amended biodegradation with by white-rot fungi in soil slurry system	5% (w/dw)	5:1	F F	36 83	Surfactant, removal of various vegetable oils, % inoculation	In situ techniques involve low cost and offer long-term soil recovery. Suitable for remediation of sites for future agricultural use.
[14]	Rapeseed oil	Two sequential: 1. Biodegradation in bioslurry reactor by mixed inoculated microbes. 2. Two-liquid-phase (oil/water/soil) extraction.	- 26.7% (v/dw)	10:1 5.4:1	F -	44–64 85–94 (3 rings:+30) (5 rings:+41)	Partitioning study, oil:soil ratio, partitioning time, multiple extractions, microbial analysis, post-bioslurry degradation, post-bioslurry-surfactant treatment	Ex situ techniques remediate within reasonable treatment durations. Suited to sites requiring remediation to meet clean-up standards.

Table 1 (Continued).

Reference	Oil type	Treatment description	Oil:soil	Water: soil	Spiked ^a or Field ^b soil	% of PAHs removed (% enhanced) ^c	Other parameters studied	Comments
[77]	Peanut oil	Oil amended biodegradation by mixed inoculated microbes in bioslurry reactor	0.2%	2:1	F	54.4–96.5 (PHE: +21.4) ^f (BAP: +27.4) ^f	% oil, PAHs concentration, HMW versus LMW PAHs, log colony forming unit, pure culture versus mixed culture	
		Combination of oil and activated carbon (1%) for biodegradation in aqueous mixed bacteria culture	0.1%	-	S	45.2 (ANT: +10.1) ^f		
[62]	Rapeseed oil	Biodegradation by <i>Rhodococcus sp.</i> on oil-amended soil	1% (w/w)	60% of WHC ^g	S	22.6–61.2 (PHE: –9.9) ^f (BAP: –2.5) ^f	Degradation in liquid culture, biosurfactant production and effect, PAH-degrading strain identification, the use of PAHs as sole carbon source	
[58]	Rapeseed oil	Biodegradation by <i>R. wratislaviensis</i> on oil-amended soil	1% (w/w)	60% of WHC ^g	S	43.8–99.0 (PHE: –32.8) ^f (BAP: +42.0) ^f	Biotic versus abiotic degradation, mineralisation, microbial activity, surfactant production	
[92]	Rapeseed oil	Two-sequential: 1. Biodegradation by mycobacterium. 2. Oil-amended abiotic treatment.	1% (w/w)	60% of WHC ^g	S	85–99 (PHE: +0.1) ^f (BAP: +39.5) ^f	Isolation, identification and characterisation of PAH-degrading microorganism, degradation in liquid culture.	
[78]	Soybean oil	Composting by white-rot fungi on oil-amended soil.	2.5% (w/w)	0.15:1	S	75–100 (PHE: +11.1; +19.3) ^{f,h} (BAP: +22.2; +24.2) ^{f,h}	Impact of mobilizing agent on fungal growth, activity of enzyme, microbial density, composition and diversity of bacteria	
[93]	Canola oil	Biodegradation by adapted mixed culture on oil-amended soil slurry	0.1% (w/dw)	4:1	F	No reduction	PAHs bioavailability, PAHs in supernatant, oil concentration in soil	
[39]	Canola oil	Biodegradation by adapted mixed culture on oil-amended soil slurry	1% (w/dw)	4:1	F	5.6–6.8 (FLT +10,+35) ^f (BAP: –2, –2.5) ^f	PAHs bioaccessibility, biodegradation of LMW versus HMW PAHs, biodegradation of oil	
<i>Integrated oil-non-biological treatment</i>								
[99]	Palm Kernel oil, corn oil	Fenton reaction in oil-amended soil slurry	5%	5:1	F	20–46 ⁱ	Abiotic versus biotic, incorporation of CaO ₂	Rapid, destructive, and insensitive to external disturbance. Suited to sites requiring immediate remediation.

^a Spiked soil (S).

^b Field soil (F).

^c % enhanced = % removal of PAHs in oil-amended soil – % removal of PAHs in unamended soil; (+): enhance and (–): depress.

^d Multiple extractions.

^e NA: not available.

^f ANT: anthracene; BAP: benzo[a]pyrene; PHE: phenanthrene.

^g WHC: water holding capacity.

^h % enhanced by *Irpex lacteus*; % enhanced by *Pleurotus ostreatus*.

ⁱ Data estimated from graph.

tititioning for HMW was mainly from soil organic matter (SOM) to oil. This was expected since HMW PAHs have lower water solubility compared to LMW PAHs.

The solubility of PAHs in oil is dependent on the type of oil. PAH solubility in oil reduces with increasing molecular size and water solubility of the compounds. Reported values for the solubility of phenanthrene, anthracene, fluoranthene and pyrene in rapeseed oil were 94 g/l, 4 g/l, 65 g/l and 57 g/l respectively with the total of 220 g/l [14]. These values were much greater compared to solubility in silicone oil (phenanthrene: 5 mg/l; pyrene: 2 mg/l) [20]. On the other hand, free fatty acids solutions have solubility ratios for PAHs (phenanthrene and pyrene) which are very similar to those of synthetic chemical surfactant [21,22], as do esterified fatty acids derived from coconut oil [23].

2.2. Oil/soil extraction system

Gong et al. [24–26] used sunflower oil as a sole extraction solvent for highly PAH-contaminated field soil. According to the authors, the use of sunflower oil, rapeseed oil and soybean oil resulted in similar extraction efficiencies although the data was not shown. In batch systems, the ratio of oil:soil of 1–2:1 (v/w) gave rapid dissolution of PAHs within 1–3 days (LMW and HMW PAHs respectively) with 67–100% removal for the contamination range of 1254.8–5400 mg/kg. Using column systems, the oil:soil ratio increased to 4:1 to give more than 90% removal for highly contaminated soil with 4721 mg/kg PAH concentration. For lower PAH soil concentration of 724 mg/kg, an oil:soil ratio of 2:1 was necessary to give 80% removal. Under the best proposed combination of air-dried soil with oil:soil ratio of 2:1 in the batch study, the molecular weight of PAHs was found to have no influence on the mass transfer rate. The removal efficiencies of HMW PAHs were consistently higher than their LMW counterparts irrespective of the individual PAH concentrations. This was considered to be advantageous since other conventional remediation techniques often face difficulties in removing HMW PAHs.

The kinetics of dissolution from the batch studies fitted well to an empirical first order model proposed by Woolgar and Jones [27]. This takes the form of $C_0 = C_e [1 - \exp(-kt)]$ whereby C_0 is the PAH concentration in the oil phase at time t , k is the mass transfer coefficient that measures the propensity of PAHs existing in each phase, C_e is the equilibrium oil phase PAH concentration indicating the particular extraction efficiency and t is the contact time with oil. During the initial phase, solubilisation was found to be rapid (within 24 h), followed by a phase of slower dissolution, which was in line with the kinetics of dissolution for common chemicals [28].

2.3. Oil/water/soil extraction system

Pannu et al. [29] used an oil/water extraction system to extract PAHs from contaminated soil. The oil used was 4 orders of magnitude less than the sole oil extraction system proposed by Gong et al. [24–26]. The study proposed the addition of 75% water to form an oil/water/soil slurry. For PAH concentrations of 100 mg/kg or below, a single extraction using 2.5% (w/w) oil would be enough whereas for higher concentrations of 1000 mg/kg or above, a double extraction using 5%+5% (w/w) oil was needed to achieve 91.4% and 83.7% removal in spiked and field soils respectively. The authors also studied the addition of absorbent polystyrene to the extraction system, and managed to reduce the oil dosage to one order of magnitude lower (0.25% instead of 2.5%). The separation of oil phase was achieved by floatation of the cellular foam.

2.4. Associated factors

The increase in water content reduced the extraction efficiency in the sole oil extraction system [25] but enhanced the extraction efficiency of the oil/water extraction system [29]. In the former, the inhibition effect was more obvious in column than in batch extraction process. The contradictory findings could possibly be due to the difference in extraction solvent [30], soil compounds [31] and extraction mechanism [32].

The volume of oil applied is dependent on the extent of contamination. Higher concentration of PAHs in soil required greater amount of oil for extraction [25,29]. However, for moist soil, too high an oil:soil ratio (2:1) was demonstrated to reduce the mass transfer rate of PAHs, which might be due to the reduction of contact sites between oil and contaminants [26].

Soil characteristics are another factor to be considered in the extraction of PAHs. Silt/clay soil retains more PAHs than sandy loam soil. The organic matter associated with larger particle size soil fractions was significantly less effective as a sorbent compared to that associated with finer particle sizes [33].

A pH within the range of 4–8 gave the highest oil recovery of more than 90% from soil whereas at pH of 6–7, the PAH extraction efficiency was highest [29]. High temperature, proper mixing and longer contact time (i.e. longer agitation in batch extraction or lower flow rate in column extraction) increased the rate of mass transfer, and led to the improvement in extraction efficiency [24,25,29,34]. Cold temperatures were less favourable for extraction due to the higher oil viscosity and slower metabolic rates.

Multiple extractions resulted in higher removal efficiencies than a single extraction [29]. This can be attributed to Fick's law of diffusion which states that fresh solvent increases the PAH concentration gradient and hence promotes the mass transfer and increases the extraction rate. In the case of multiple extractions, the extraction duration was shown to be of minor importance [14].

2.5. Feasibility

The potential of using vegetable oil as solvent in soil washing to remove PAHs is evident from the series of experiments described. This technique can be applied in situ and ex situ, and is convenient for highly contaminated soil urgently needing remediation. However, due to the high quantity of oil used in the case of sole oil extraction, the regeneration and reuse of the oil is essential from an economic and environmental point of view. This may ultimately involve multiple remedial steps and higher cost. Additionally, vegetable oil extraction is only able to transfer the PAHs onto a different phase but not destroy these pollutants. As for oil/water extraction, the aqueous solution needs to be cleaned up of the oil. This can be achieved by biodegradation if the amount of PAHs is limited. High concentrations of retained oil in the soil can also negatively affect the ecology. The quality of soil may deteriorate hence limiting future reuse of the treated site. Nevertheless, soil extraction with vegetable oil is still more environmentally friendly compared to extraction with volatile solvents or chemical surfactants.

3. Integrated oil-biological treatment

The main disadvantage of biodegradation is that it is a time-consuming process. For instance, the reported half lives for phenanthrene in soil ranged from 16 to 126 days while for benzo[a]pyrene, the half lives ranged from 91 to more than 1400 days [35,36–38]. Bioavailability is one of the most important factors limiting bioremediation rate [39]. In order to degrade organic compounds, the degrading microbes or their extracellular enzymes require physical contact with the compounds [40]. To attain this

contact, conventionally the compound must be water-dissolved [41,42] and located at the advecting-water layer outside the soil pore or in a soil pore with a pore neck greater than 0.3 μm [43]. However, the aqueous concentration of PAHs is so small that the contribution of biodegradation in the aqueous phase can be considered to be negligible. With regards to this, Robinson et al. [44] have suggested that for compounds with low water solubility, biodegradation occurs predominantly in the organic matter of soil phase or sorbed phase substrate that can be easily desorbed.

3.1. The role of vegetable oil in enhancing biodegradation

3.1.1. Enhanced mass transfer through physiochemical process

PAHs especially those with HMW are tightly bound to the soil hence the direct usage of bioremediation in the soil phase is limited. In contrast, the inclusion of oil promotes desorption of PAHs from the soil phase and sorption onto the oil phase, thereby enabling effortless biological uptake due to easy desorption from oil/water interface or oil/soil interface. Coating of soil particles with vegetable oil may also help in diffusive movement of PAHs especially since fatty acid is able to diffuse into small micropores that are inaccessible to bacteria cells [45]. Considering that diffusion is a dynamic process, this fatty acid may act as carrier to transport the PAHs out from the micropores, making them available for biological uptake. The potential of vegetable oils in this role can be observed from their common usage as carriers for hydrophobic herbicides in soil [46].

Although the partition of inaccessible hydrophobic contaminant molecules into the oil phase was proven to significantly increase contaminants biodegradation [39], the extent of increase in bioaccessibility was strongly dependent upon the strength of contaminants sorption towards soil constituents and soil organic carbon. For instance, lower biodegradation was found on oil-amended manufactured gas plant (MGP) soil compared to preserved railroad sleeper soil, suggesting that the vegetable oil induced PAH mobilisation was limited to less strongly bound contaminants [39].

Scherr et al. [39] reported that maximum oil degradation occurred with the highest increase of PAH content in the water phase. They also suggested that biodegradation of canola oil and/or its metabolic by-products might also contribute to the observed mobilisation effects and possible subsequent biodegradation of otherwise unavailable contaminants from soil particles. The observed mobilisation effects were small but statistically significant.

3.1.2. Increased surface area for microbial contact

Several mycobacteria (a group of gram positive bacteria) are capable of adjusting the composition of mycolic acids (C80–C90 fatty acids) of their cell walls to be more hydrophobic [47]. This may offer better contact of microorganisms with oil droplets or adhesion to oil droplets, hence favouring the uptake of pseudosolubilised substrate or substrate dissolved in oil droplets, such as PAHs for biodegradation [48,49]. The enhancement of biodegradation, due to the better attachment of the microorganisms on various surfaces including hydrophobic solvent [48], crude oil [49], surfactant [49] and polymer membranes [50] has been reported. Delivery of the encapsulated PAHs in oil droplets to membrane-bound enzymes is possible since the increase of biodegradation and utilisation of alkane encapsulated in liposomes as a growth substrate by a *Pseudomonas* strain has been observed [51]. The change of mycolic acid on the cell wall was also proven to facilitate the mineralisation of pyrene [52] and anthracene [53]. The mineralisation of pyrene was found to be 8.5 times higher in paraffin oil augmented cells than in the aqueous phase [54].

In adapting to the hydrophobic compounds or substrates such as PAHs or vegetable oil, the PAH degrader usually has the ability to form biofilms at the interface of the aqueous and hydrophobic phases that facilitate the direct uptake of these substrates [55]. Biofilm-mediated biodegradation has been found to be more effective than planktonic bacteria remediation since cells growing within a biofilm have higher chances of adapting to different environments and surviving [56]. Besides that, the oil surface area is also important in the sense that biodegradation occurs at the oil–water or oil–soil interface.

3.1.3. Reduced surface tension by oil components

The phospholipids, fatty acids and neutral lipids present in the vegetable oil can contribute to the surfactant effect [57]. Similar to surfactants, these lipid compounds are amphiphilic, i.e. containing hydrophobic and hydrophilic portions that reduce the free energy of the system by replacing the bulk molecules of higher energy at an interface. This interface is present at the boundary among immiscible substances including the hydrophobic phase of the contaminants and aqueous phase. The lipids weaken the interfacial tension and change the properties of an interface. This promotes the mobility and the displacement of the contaminants and subsequent desorption from the soil matrix. One study showed that the surface tension of the sterile soil dropped immediately after the addition of rapeseed oil, indicating that the oil itself served as a surfactant [58]. The decrease in surface tension increased with increasing oil concentration. With addition of 1% rapeseed oil, the surface tension was reduced from 71 mN/m to 56.7 mN/m.

Conversely, Yi and Crowley [45] stated that the addition of linoleic acid (10 mg/ml) slightly above the critical micelle concentration (CMC) inhibited pyrene degradation in liquid medium. The pyrene might have occluded within micelles which were inaccessible to bacteria cells. Higher levels of linoleic acid in soil required for the promotion of pyrene degradation also reflects the increase of required concentration due to adsorption of the surfactant to soil particles [45]. Varying effects of different surfactants on PAH degradation in soil have also been reported [49,59,60].

3.1.4. Enhanced biosurfactant production

The addition of vegetable oil to enhance the production of rhamnolipid-type biosurfactant has been demonstrated using the genus *Pseudomonas*. A probable reason for this tendency is that *Pseudomonas* is lipase positive which facilitates the assimilation of fatty acids contained in vegetable oil fractions [61]. Rapeseed oil [62], babassu oil [63], canola oil [64], corn oil [64], olive oil [65,66], soybean oil [64,66], palm oil [65], coconut oil [65], sunflower oil [66] and castor oil [66] have all been shown to promote the production of surfactant by *Pseudomonas* bacteria.

The production of biosurfactant is highly related to the type of substrate [62]. Olive oil and rapeseed oil were found to be the best carbon source for biosurfactant production compared to hexadecane and glucose [61]. In addition, olive oil, palm oil and coconut oil were also discovered to be able to stimulate the production of rhamnolipid by *P. Aeruginosa* [61]. Rhamnolipids produced by *P. Aeruginosa* strains are among the most effective surfactants for the removal of hydrophobic compounds from contaminated soils [67]. They have low average minimum surface tension of 30–32 mN/m, high average emulsifying activity of 10.4–15.5 U/ml filtrate and low CMC of 5–65 mg/l [67]. Palm oil was the best compared to olive oil and coconut oil in lowering surface tension. Shorter chain fatty acids resulted in higher biosurfactant activity while higher unsaturated fatty acid promoted higher oil displacement activity and rhamnose content [65]. Glycerol, as another main hydrolysis product of oil, did not facilitate biosurfactant production [65]. Both rapeseed oil [62] and olive oil [68] have been utilised by *Gordonia* sp. to induce emulsification. In this case, the presence of both oil

and extracellular biosurfactant were responsible for the formation and stabilisation of foam [68].

Induced biosurfactants may be able to facilitate the uptake of PAHs after their pseudosolubilisation, enhance the removal of PAHs from soils and accelerate their biodegradation [69]. Deschênes et al. [70] also reported that rhamnolipids could enhance the solubilisation of 4-ring PAHs more significantly than 3-ring PAHs and with efficiencies 5 times higher than the anionic surfactant sodium dodecyl sulfate (SDS). Moreover, the uptake of biosurfactant-solubilised molecules was measured to be faster than the uptake of truly dissolved (i.e. monodisperse) molecules. Many biosurfactant are constituents of cell envelopes [71], which indicates the interaction of biosurfactant micelles with cell membranes and the possibility of a fusion between micelles and cells. This inevitably eases the uptake of PAHs.

Nonetheless, biosurfactant production under environmental conditions is not common [72]. Pizzul et al. demonstrated the production of biosurfactant by *Rhodococcus wratislaviensis* in oil-amended aqueous culture [62], but no biosurfactant activities were observed when inoculation was carried out on oil-amended PAH-contaminated soil [58]. Johnsen et al. [55] suggested that the release of biosurfactant was a way for hydrophobic cells of microbes to leave hydrophobic surfaces such as PAHs (or oil), for instance when the cells at the bottom of the biofilm became oxygen-limited. This process was likely to occur in oil-amended soil.

3.1.5. Extra carbon and energy source

The biological degradation of PAHs, as outlined by Johnsen et al. [55], can serve three different functions: (a) assimilative biodegradation that yields carbon and energy for the microorganism and goes along with the mineralisation of the compound, generally accompanied by the growth of the microbes (b) intercellular detoxification process that render the PAHs water-soluble and hence their excretion and (c) cometabolism which is the degradation of PAHs by the non-specific enzymatic reactions, without the production of energy and carbon for the organism metabolism. LMW PAHs are frequently used as the sole source of carbon and energy for microbial growth and maintenance [73] while mineralisation of more than 3 aromatic rings is less common [74] and in some cases only possible in the presence of other substrates or co-substrates [75]. Bacteria capable of utilising 5-ring or more PAHs as a sole source of carbon and energy have so far never been demonstrated. Hence, all reported biotransformation of PAHs occurred under cometabolic conditions and by only a few bacterial species (such as *Mycobacterium* sp. and *Sphingomonas* sp.) and mixed microbial cultures [76].

The addition of vegetable oil increased the biodegradation of phenanthrene in liquid cultures of actinomycetes (bacteria), even in cultures that do not use phenanthrene as the sole carbon source [62]. This showed that vegetable oil could act as primary carbon and energy source to induce cometabolic degradation of phenanthrene. In contrast, Pannu et al. [77] reported the addition of 0.1% of peanut oil facilitated the growth on *C. testosteroni* (bacteria). More studies are needed to elucidate the use of vegetable oil as an extra carbon source in enhancing PAH degradation by bacteria.

For PAH degrading white-rot fungi, the use of vegetable oil could significantly serve as an extra carbon and energy source to support fungi growth, either in the soil system [78] or liquid cultures [79,80]. This is of particular significance since 5-ring and above PAHs are mainly degraded by fungi through their non-specific extracellular enzyme.

The soil bacteria are generally thought to be carbon and energy-starved [55] and thus the addition of oil may be one of their carbon sources to maintain biomass rather than promoting growth. It is also possible that copiotrophic soil bacteria which grow rapidly in the presence of easily degradable substrate like vegetable oil

colonise the surrounding of vegetable oil droplets [81]. As PAH-degrading bacteria are assumed to be oligotrophic [55], they are suppressed by such rapidly growing, opportunist soil microbes.

Some studies have suggested that the degrading organisms may prefer vegetable oil over PAHs as an energy source. In one such study [58], it was reported that the mobilisation of PAHs by vegetable oil lowered the affinity of degrading microorganism to substrate as evident from a longer lag phase for phenanthrene degradation by autochthonous microflora after oil addition. In this case, the explanation given was that the microorganism only started using the PAHs as substrate after the degradation of oil. This shift of substrate towards vegetable oil was supported by the significant decrease of mineralisation over percent of biodegradation for the PAHs tested, i.e. ^{14}C -phenanthrene, ^{14}C -pyrene and ^{14}C -benzo[a]pyrene in the presence of 1% (w/w) rapeseed oil or in 30% (v/v) rapeseed oil emulsion [58,81] whereas the reduction in the presence of 0.1% (w/w) rapeseed oil was not significant [58].

3.1.6. Initiation of degradation by MnP-mediated lipid peroxidation

Pizzul et al. [58] observed that rapeseed oil tremendously enhanced degradation of anthracene and benzo[a]pyrene but with accompanying accumulation of anthraquinone. This was explained by the release of extracellular lignin-degrading enzymes, manganese peroxidase (MnP) from microbial systems that triggered lipid peroxidation of unsaturated fatty acids in the oil which led to the production of PAH-oxidising radicals. The accumulation of anthraquinone as metabolites was proof of this as anthraquinone is the main metabolite of anthracene in the MnP system.

MnP is a common enzyme released by white-rot fungi and litter-decomposing fungi. The MnP-mediated lipid peroxidation and the radicals generated have been comprehensively explained by Wanatabe et al. [82] and the process is depicted in Fig. 1 [82]. In this system, the abstraction of hydrogen atom by the peroxy radicals to generate a hydroperoxide is the rate-limiting step of vegetable oil peroxidation. The rate constant for this rate-limiting step depends primarily on the strength of the carbon-hydrogen bond being broken. The strength of a carbon-hydrogen bond next to a carbon-carbon double bond is lower and the hydrogen can be removed easily. Thus oils containing double bonds are more susceptible to lipid peroxidation. Vegetable oils containing high percentage of unsaturated fatty acids are expected to react more readily than less unsaturated oils [83]. On the other hand, unsaturated lipid in the form of monoglyceride is more efficient in the MnP-mediated lipid peroxidation degradation than their fatty acid counterpart or fatty acid-based surfactant.

In both in-vitro and in-vivo studies, the simple MnP system of lignin peroxidase (LP) is only able to oxidise PAHs with ionisation potential less than 7.5 eV (e.g. benzo[a]pyrene and anthracene). However, in the presence of lipids, the occurrence of MnP-mediated lipid peroxidation via unsaturated fatty acids or their derivatives enabled substantial decrease of all PAHs, included those with high ionisation potential [84], poor bioavailability (benzo[g,h,i]perylene and indeno[1,2,3-cd]pyrene) [84], as well as complex PAH mixtures (creosote) [85].

Lipid peroxidation can also be initiated by ions such as Mn^{2+} and Mn^{3+} as well as photooxidation of vegetable oil [34,86]. Once initiated, this oxidation process can continue independently, through propagation and sufficient oxygen supply. Even though biological processes may be involved at the beginning of the process, abiotic processes predominate in the transformation of compounds during the whole process.

Although studies have indicated that lipid degradation enhanced PAH degradation, PAH mineralisation did not seem to be enhanced by the process. It has been reported that even though the degradation of benzo[a]pyrene was 72.8% compared to an una-

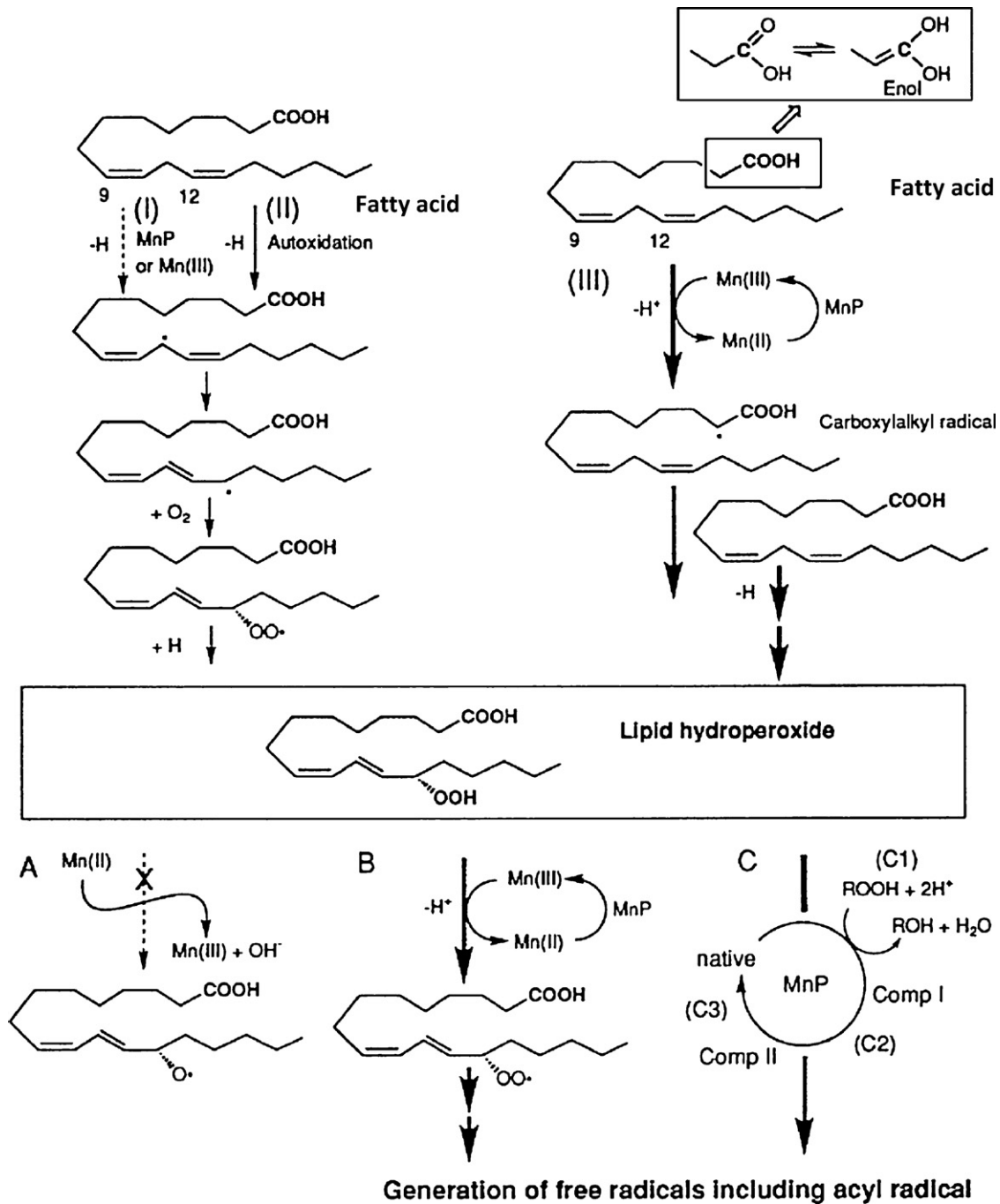


Fig. 1. MnP-mediated lipid peroxidation schematic diagram (adapted from [82]). The lipid peroxidation can be initiated by MnP lignolytic enzyme or by photolysis. Once initiated, the process will propagate independently. The radicals produced are able to oxidise PAHs at various kinetic rates.

mended control with 30.8% degradation, the total mineralisation was approximately 9% [58]. Bezalel et al. [87] suggested that the complete mineralisation of HMW PAH requires a combination of lignolytic enzyme and non-lignolytic enzymes. The addition of vegetable oil may result in a deficiency in this combination.

3.1.7. Enhanced PAH degrading enzyme production

Soybean oil was shown to be able to promote the production of phenoloxidase enzyme (laccase) by white-rot fungi by five-fold compared to the no added oil control on a basal nutrient medium [88]. Laccase is also an extracellular enzyme that is able to degrade PAHs. Certain laccase mediator systems are even better in degrading PAHs compared to peroxidase (such as MnP and LiP) [89].

However, Leonardi et al. [78] reported that depending on the fungi, the laccase activity in soybean amended soil can be enhanced or reduced (*I. Lacteus* and *P. Ostreatus* respectively).

3.1.8. Selective enrichment of PAH degrading microbes

Yi and Crowley [45] stated that linoleic acid was the main phytochemical in plant species that stimulated PAH degradation. This was proven by the direct addition of linoleic acid and sodium linoleate into the soil which acted as a powerful stimulant of pyrene and benzo[a]pyrene degradation. In contrast, other fatty acids such as oleic acid, linolenic acid and palmitic acid had no effects on PAH degradation. Overall 46–57% of pyrene removal was achieved in 20 days of incubation compared to the unamended

control with 15% removal. A slightly longer period was required for benzo[a]pyrene compared to pyrene. After investigation, the gram positive mycobacteria was found to be the predominant group responding to linoleic acid which suggested the possibility of selective enrichment of this PAH degrading bacteria in soil in the presence of linoleic acid.

3.2. Sequential bioslurry treatment with post-two-liquid phase (TLP) extraction

Berg and Mattiasson [14] proposed a two-step remediation of PAH-contaminated soil comprising firstly biodegradation by PAH degraders in a slurry bioreactor for 30 days followed by abiotic extraction of the residue PAHs with rapeseed oil in a TLP slurry system using 7.5 ml of rapeseed oil for 28 g soil (around 26% v/w). Total PAH removal efficiencies within the range of 85–94% were obtained. The efficiency of biodegradation which decreased with increased molecular weight was compensated by the high affinity of all PAHs for the oil phase of the system.

The abiotic extraction followed the following steps: (1) suspension of soil particles on oil droplets, (2) partition of contaminants from the particles into the oil phase, and finally (3) the dilution of contaminated oil by fresh oil in multiple extractions or the continuous levelling out of the contaminants over the oil matrix in a single extraction. The efficiency of the treatment was dependent on many factors including the amount of oil used, the shaking intensity and pollutants composition. The authors also demonstrated that among the three tested post-bioslurry treatments, vegetable oil extraction was superior to commercial surfactant washing and biodegradation for subsequent removal of PAHs.

The advantage of the TLP system in increasing the mass transfer rates of the contaminants into the aqueous phase efficiently has long been recognised by researchers [20,54,90]. The use of vegetable oil in the TLP system is advantageous in the sense that vegetable oil is biodegradable whereas the residues of conventional non-biodegradable oil or immiscible liquid in treated soil may cause problems in reuse of soil.

3.3. Bioslurry treatment

Pannu et al. [77] described the effects of vegetable oil addition on the mixed bacteria inoculated PAH-contaminated weathered soil. The presence of 0.2% (w/w) of peanut oil stimulated the degradation of PAHs in a soil slurry system (2:1 water:soil ratio), whereby 96% of phenanthrene, 74% of anthracene, 65% of pyrene and 70% of benzo[a]pyrene were degraded after 24 days of incubation at 30 °C. In another study by Scherr et al. [39], biodegradation was conducted at 20 °C in the presence of 1% (v/v) canola oil in mixed culture inoculated soil slurry (20 ml water:5 g soil). The addition of oil increased the PAH accessibility up to 4 rings, but had no effect on 5 and 6 rings. Removal efficiencies of 78.7% and 23.9% were obtained for former railway sleeper preservation site soil within 105 days and former MGP plant within 98 days respectively. Bogan and Lamar [91] also carried out a similar biodegradation in a soil slurry system (20% dry wt.) with white-rot fungi. The addition of 5% (w/w) vegetable oil resulted in total removal efficiencies (13 PAHs) of 36% and 83.3% after 35 days, in coking plant soil and MGP soil respectively.

3.4. Solid phase composting

Leonardi et al. [78] were the only ones who studied treatment of PAH spiked soil using maize stalks previously colonised with white-rot fungi and incubated at 24 °C under dark and moist conditions (15% water). The addition of 2.5% (w/w) soybean oil enhanced the

degradation of 7 spiked PAHs with total removal efficiencies within 75–100% after 42 days.

3.5. Sequential *in situ* biotic and abiotic treatment

Pizzul et al. [92] proposed an *in situ* two-step sequential treatment comprising biodegradation followed by oil addition to promote abiotic degradation. The system inoculated with indigenous PAH degrading microbes was given a lag time of 2 weeks for the degradation of LMW PAHs. Subsequently, this was followed by the addition of 1% (w/w) of oil for the microbes to stimulate the abiotic degradation, which was the release of radicals from lipid peroxidation to oxidise the recalcitrant HMW PAHs. High PAH removal efficiencies of 85–99% were achieved within 34 days. On the contrary, the abiotic process initiated by photooxidation or fungal enzyme was not observed by Scherr et al. [39]. This could possibly have been attributed to the differences in soil and type of vegetable oil or as reported by Leonardi et al. [78], the depression of MnP production by the oil.

3.6. Associated factors

The concentration of added vegetable oil is the main factor which dictates its effects on biological treatment and the associated biological-initiated abiotic treatment of contaminated soils. Vegetable oil additions ranging from 0.2% (w/w) to 5% (w/w) have been used as co-substrates to enhance biotransformation of PAHs by 11–68% under optimised conditions [14,39,77,78,91]. Here, the simultaneous provisions of oil and nutrients can magnify the ability of microbes to degrade PAH contaminants. Nonetheless, other studies indicated that vegetable oil addition into soil treatment resulted in either an inhibition effect [62] or no significant effect [93]. Above the optimised oil addition concentrations, degradation efficiency reduced [77], showed no significant changes or slight enhancement [39]. Excessive amounts of primary carbon source can inhibit biodegradation of the contaminants resulting in insufficient energy in the microorganisms to cometabolically degrade the pollutants [94].

Under optimised oil concentrations, the efficiency of oil-amended biodegradation was not affected by the PAH concentration, however, above certain PAH concentrations, metabolites accumulation from cometabolism of PAHs might cause cytotoxicity and reduced biodegradation [77]. Apart from PAH concentration, the size of the PAH compounds and ageing of PAH-contaminated soil are factors to be considered in soil remediation. The majority of the studies reported that oil amendment favoured the biodegradation of HMW PAHs more than LMW PAHs [77,78]. In aged contaminated soils, contradictory findings on oil addition effects on HMW PAHs have been published [39,77].

3.7. Feasibility

The first two biologically integrated techniques discussed above involved the use of bioreactors. The disadvantages of this are the transportation of soil to special facilities and subsequent waste water treatment, which entail relatively high capital investment and subsequent high operating costs [95]. Slurry bioreactors only need small additions of vegetable oil to enhance degradation of PAHs due to optimum mixing conditions within the reactors. This minimises the environmental hazards as no oil recovery is required. However, experimental results have shown that the performances of oil-amended bioslurry treatments were inconsistent and poorer compared to the sequential treatment of bioslurry with post-TLP extraction especially for HMW PAHs. The drawback of the post-TLP extraction is the relatively high percentage of oil addition.

Solid phase composting is a simpler process compared to bioslurry treatment. No recycling of water or oil phase is needed. However, poorer mixing inevitably means higher oil addition is required and possible inconsistent degradation rates. In the case of in situ sequential treatment, only a small amount of oil is added at the latter stage to initiate subsequent abiotic PAH degradation. Likewise to bioslurry reactors, this minimises the environmental risks and no oil recovery is necessary. The process can be applied in situ thus making it economically feasible. Nonetheless, its in situ performance is highly dependent on environment, geology and microbial factors, unlike the ex situ bioreactor treatment which benefits from tighter monitoring and control. Additionally, in situ oil amendment can create higher difficulties in oxygen and water diffusivity. In unamended soil, the effective oxygen distribution for desirable rates of bioremediation extends to a soil depth range of only a few centimetres to approximately 30 cm, although depths of 60 cm and greater have been effectively treated in some cases [96]. To date, only a few successful field-scale applications of bioaugmentation exist. A thorough study of the contaminated site is essential before the implementation of in situ techniques.

4. Integrated oil-non-biological treatment

Fenton treatment is the only non-biological process that has been integrated with vegetable oil treatment. Fenton reaction is an established chemical oxidation technique which is used to remediate PAH-contaminated soils. However, removal efficiencies are always limited by poor availability especially at in aged contaminated soil, except in cases where high concentrations of Fenton reagent are used to directly oxidise the PAHs on the organic soil surfaces without desorption. This can be uneconomical and harmful to the ecosystem of soil matrix. Organic solvents [97] and surfactants [98] have been applied to overcome the availability problem in Fenton treatment. Recently, vegetable oil was proposed as an environmental friendly alternative to conventional solvents and surfactants to promote the extractability of PAHs, and their subsequent removal from soils.

Since HMW PAHs favour the oil phase more compared to LMW PAHs [17,99], higher desorption of HMW PAHs into oil phase can be expected. Although Fenton reaction occurs in the aqueous phase, the Fenton reagents hydrogen peroxide (H_2O_2) and iron (II) ions (Fe^{2+}) are diffusible through the core structure of lipids [100], thereby generating in situ OH^\bullet radicals to oxidise the PAHs. Wu et al. [101] showed that free-radical based reactions can be preferentially localised to such vegetable oil structures. In addition, in a study on micellar-exchange dynamics of hydrophobic compounds with the aqueous phase, it was found that both the entrance and exit rates of PAHs were likely to be far higher than biodegradation rates [102]. Hence, the mass transport of PAHs between these micelles and the aqueous phase can also enhance the Fenton reaction occurring in the aqueous phase.

The OH^\bullet radicals generated by the Fenton reagent in the aqueous phase can initiate lipid peroxidation on polyunsaturated fatty acids or phospholipids in vegetable oil [103]. This lipid peroxidation is similar to that involved in MnP-mediated lipid peroxidation which occurs in white-rot fungi or litter-decomposing fungi. The radicals produced can oxidise the recalcitrant PAHs. By changing the $Fe^{2+}:Fe^{3+}$ ratio in the Fenton process to approach unity, the formation of feryl or perterryl iron ($Fe^{3+}O^{2-}$) and mixed metal- O_2 -complexes ($Fe^{2+}-O_2-Fe^{3+}$) will occur, and further promote the lipid peroxidation [104]. Nevertheless, excess Fe^{2+} oxidation or Fe^{3+} reduction can inhibit lipid peroxidation by changing the $Fe^{2+}:Fe^{3+}$ ratio [104].

Bogan et al. [99] are the only ones who studied the application of corn oil and palm kernel oil in Fenton treatment for PAH removal

from highly contaminated aged soils with up to 7700 mg/kg concentration. The degradation of PAHs was significantly enhanced by an estimated 15–45% with 5% (per dry wt. of soil) oil addition, and the effect was most significant in the cases of HMW PAHs. In contrast, Fenton treatment alone was only able to remove a few LMW PAHs. The overall PAH removal was low for the integrated treatment, approximately 35–60% for 2–3 h soil/oil contact time and 5–14 days of Fenton treatment. These results might have been due to the extremely high contamination levels in the soil. To enhance Fenton treatment, the oil addition should be enough to facilitate the mass transfer of contaminants into lipid aggregates. Excess lipids, above 5% (per dry wt. of soil), may negatively impact the removal performance as a higher percentage of lipid aggregates would unproductively consume the initial oxidants. The authors also showed that PAH removal using polyunsaturated oil (corn oil) was not greatly different from that of highly saturated oil (palm kernel oil) and monounsaturated oil (olive oil). Here, the effects of competition between lipids and PAHs for the OH^\bullet radicals may be offset by the degradation of PAHs by lipid derived radicals. Further details on the optimisation of oil addition are necessary in order to improve the efficiency of PAH removal. Since this is the only reported case on the use of vegetable oil to enhance Fenton oxidation of PAHs in soil, more comprehensive studies are necessary in order to suitably comment on the feasibility of this remedial technique.

5. Vegetable oil regeneration

The regeneration of vegetable oil is vital especially when high amounts of oil are used in the treatment of PAH-contaminated soils. Destruction methods using biodegradation, ozonation and catalytic oxidation are only efficient for oils containing less than 10 mg/l PAHs as these methods are mainly for aqueous, gas or solid phases [105]. Gong et al. [105] and Pannu et al. [29] demonstrated that activated carbon is a powerful adsorbent for all types of PAHs in oil, with 90% and 68.1–93.5% removal efficiencies using batch and column systems respectively. Activated carbon can adsorb both HMW and LMW PAHs equally effectively. The adsorption capacity depends on the internal surface area, the distribution of pore sizes and shapes, and the surface chemistry of the activated carbon [106]. The potential capacity ranges from 20 mg/g [29] to 50 mg/g [105]. The contaminated activated carbon needs to be further recycled, either by conventional thermal treatment or by bioregeneration [107]. Activated carbon is to be destructed via incineration or disposal in the landfill when its efficiency decreases; in which case recycling is no longer a cost-effective option.

The physical separation of PAHs from rapeseed oil using polystyrene column has been demonstrated by Berg and Mattiasson [14]. Vegetable oil was recovered in the first 6 ml of the mobile phase and the first PAHs left the column after 8 ml of eluted chloroform. The results suggested that PAHs were easily removed by this solid phase separation. However, further destruction of the PAHs on solid phase and the costs of polystyrene columns need to be considered in this regeneration method.

6. Environmental impacts of vegetable oil residues in soil

Vegetable oil in soil can be rapidly degraded if optimal microbial conditions are well maintained, since the enzymes required for degradation such as lipases, esterase, cellulases and hemicellulases are common in microorganisms [108]. The degradation rate is dependent on the soil matrices, environmental factors and ecosystem. However, unsaturated oils are subject to chemical oxidation which potentially leads to polymerisation through cross-linking and inhibition of biodegradation. Rapid mineralisation requires an

adequate supply of oxygen and nutrients. In systems lacking in oxygen, anaerobic degradation of vegetable oil may result in a higher transient increase of toxicity [109].

Basically, the risk assessment of vegetable oil residues in soil is based on the level of contamination: (a) low (10s of mg/kg): biodegradation less likely to be limited by nitrogen and phosphorus, natural attenuation may be feasible, (b) medium (1–80 g/kg): biodegradation likely to be limited by nitrogen and phosphorus, may or may not need nutrient treatment, (c) high (>80 g/kg): the oil level may be inhibitory or toxic to biomass [110].

Among the remediation treatments, the sole oil extraction system resulted in the highest oil residues retained in soil, approximately 4–5% of the quantity used [29] and due to the high ratio of oil addition (up to 4:1 oil: soil ratio), the treated soil contained 5–10% (50–100 g/kg) of oil. Gong et al. [111] stated that soil respiration was reactivated after soil microorganisms acclimatised to the residual oil. With proper nutrient amendment and sufficient air exchange, soil respiration took as long as 170 days and with longer incubation, it was expected that more vegetable oil could be degraded. Scherr et al. [39] reported that residues of 1% (w/dry wt.) and 5% (w/dry wt.) canola oil addition to the contaminated soil were 50–3500 mg/kg after 98 and 105 days treatment in the bioslurry system. In a field study, Haigh [112] reported that although the vegetable oil (1 l/m²) biodegraded rapidly, it took more than 1 year for the extractable residues to decrease to levels comparable to the naturally occurring lipids (<0.3 mg/g) present in soil.

In soil toxicity tests, vegetable oil residues as low as 1% (10 g/kg) were shown to have inhibitory effects on plant growth [113] with the degree of inhibition varying with plant type. The direct effects of vegetable oil residues in soil on plant growth include: (a) possible growth inhibition by root suffocation or by oxygen depletion of the soil by the oil biodegradation process, (b) possible poor growth due to reduced water uptake by the plants and/or immobilisation of nitrogen and phosphorus in the soil [112]. It has been suggested that the reactive oxygen species including superoxide, hydrogen peroxide, and hydroxyl free radicals are produced in excess under such environmental stress, causing lipid peroxidation and damaged plant cells and seriously disrupting normal metabolism [114]. Both the accumulation of metabolites from the oil degradation and nutrient amendment during treatment can alter soil pH and affect plant growth. On the other hand, one study demonstrated that in certain plant species, proper combination of oil residues concentration (1%) and nutrient amendment could counteract the adverse effects of pH variation and stimulate oil degradation simultaneously [113]. Scherr et al. [39] reported that the oil residues within the range of 50–3500 mg/kg in soil did not change the pH of the bioslurry system. This indicated that there was sufficient capacity in the soil system to buffer the possible acidic oil metabolites produced.

Germination of some plants would also be inhibited if their propagules are relatively small in size and are completely covered by oil [115]. Some researchers showed that vegetable oil retention can aggravate the high salinity problem and reduce salt-stress tolerance of seedlings [116], and indirectly affect the germination of plant seeds [117]. However, the effects of vegetable oils on growth rates of various crops vary from small reduction to complete inhibition [112].

Soil texture may also affect the movement and the retention of oil in soil and mixing pattern with water [118]. Sandy soil allows deeper and faster penetration of the oil which leads to damages at the root zone; however, due to large pore spaces available for the growth of the microbes, the microbial breakdown of the oil is relatively fast. Dinel et al. [119] claimed that the direct addition of lipid compounds to the soil encouraged the formation of polycationic bridges that bind the lipids to soil particles that enhance soil aggregation. Sonnleitner et al. [120], meanwhile, reported that less than 0.5% of lipid was sufficient for the formation of unwettable

aggregates in sandy soils. Soil permeability was reduced in these cases hence affecting its future use in agriculture.

The toxicity of the oil residues in soil can be expected to decrease over time as the oil degrades [109], although it is not related to its persistency in the soil [112]. This means that it is important to monitor both biodegradation and toxicity of the oil in its application in soil remediation.

7. Comparison with other PAH soil remediation techniques

Table 2 presents the comparison of PAH soil remediation techniques utilising vegetable oil with other commonly employed remediation techniques. Physical extraction at ambient conditions typically involves mixtures of water either with chemical solvents, surfactants or cyclodextrins. Although the extraction or washing process is simple, but post-treatment of extraction fluids requires either distillation at high temperatures or other phase separation followed by destructive treatment of PAHs. Unlike the typical solvents used, vegetable oil is water immiscible which allows for easier separation if used in an oil/water/soil extraction system. Likewise to cyclodextrins, vegetable oil is non-toxic and biodegradable as compared to chemical solvents. However, in contrast to cyclodextrins, vegetable oil is less costly. The optimised extraction efficiency of vegetable oil (>90%) [25] is comparable to conventional co-solvent (95%) [121] and exceeds that of cyclodextrins (31–43%) [122]. Using surfactant, on the other hand, results in inconsistent removal efficiencies. It has been recently postulated that it is possible for surfactants to be adsorbed by the soil matrix which immobilise the PAHs that partitioned onto them [123].

Extraction using vegetable oil has been demonstrated to have comparable removal efficiency as supercritical fluid extraction (88–90%) [124]. However, the obtainable extraction efficiency with vegetable oil is slightly less when compared to subcritical fluid extraction and in situ thermal desorption techniques (>99%) [125,126]. However, the use of subcritical and supercritical fluids requires the use of high pressure and/or temperature equipment which entails greater costs. In situ thermal desorption requires no excavation but its efficiency is subjected to the heat transfer resistances due to in situ soil heterogeneity and consideration needs to be given to the treatment for the gases produced.

Bioremediation offers the advantage over physical extraction as it is a destructive technique that requires no secondary treatment. However, the duration of treatment is long and the obtainable removal efficiency tends to be low. The addition of chemical solvent [127] can enhance biodegradation rate but this is more toxic than vegetable oil [127] whereas surfactants addition may result in positive, negative, or no discernible effects on the degradation of PAHs [128].

Unlike bioremediation, the chemical oxidation is a fast destructive remediation technique. Of three typically used oxidants, ozone, potassium permanganate (KMnO₄) and Fenton's reagent, ozone is more effective for LMW PAHs [129], KMnO₄ selectively degrades PAHs depending on the aromatic structures [130] whereas Fenton's reagent is relatively less selective [129]. Nonetheless, the efficiency of these chemical oxidations decreases when applied to aged soil especially for HMW PAHs. Ethanol addition has been shown to improve the efficiency of Fenton treatment, but the high dosage involved (>30%) entails greater environmental risks [131]. Likewise to bioremediation, surfactant addition results in positive, negative, or no discernible effects on Fenton oxidation [132]. Both cyclodextrins [133] and vegetable oil additions [99] are able to enhance Fenton oxidation especially for HMW PAHs but the former is more costly. Other integrated technologies such as biological–chemical and physical–chemical–biological treatments which combine separation and destruction of PAHs offer better removal efficiencies

Table 2

Comparison of PAH soil remediation techniques utilising vegetable oil with other remediation techniques.

Treatment technique	Advantages	Disadvantages	Reference
<i>Physical extraction</i>			
Solvent extraction (chemical solvent, surfactant or cyclodextrins)	Ambient conditions, portable	Extraction efficiency dependent on type of solvent, difficult solute separation, further treatment of extracts, residual pollution	[121–123]
Supercritical or subcritical fluid extraction	Rapid PAH removal, high selectivity for PAHs versus bulk organic matter, high extraction efficiency, no secondary pollution, soil structure is left intact	Post-treatment of extracts, high-pressure equipment, soil excavation required	[124,125]
In situ thermal desorption	No excavation required, applicable to heterogeneous soil, broad applicability	Further treatment of extracts, high temperature, slow process, extraction efficiency dependent on in situ soil conditions	[126]
Vegetable oil extraction	High extraction efficiency, environmentally friendly, ambient conditions, portable	Further treatment of extracts, residual pollution	[25,29]
<i>Bioremediation</i>			
Conventional bioremediation	No second hand pollution, broad land applications, ambient conditions	Low destruction efficiency, very slow process	[134]
Vegetable oil-biological treatment	Ambient conditions, environmentally friendly, moderate to high efficiency.	Removal rate dependent on the technique used	[14,48,78,92]
<i>Chemical remediation</i>			
Ozonation	Rapid removal, no secondary pollution, insensitive to external disturbance	Efficiency decreases for HMW aged PAHs, high equipment cost	[129]
KMnO ₄ oxidation	Rapid removal, flexible, portable, insensitive to external disturbance	Selective destruction	[130]
Vegetable oil-Fenton treatment	Rapid removal of full range of PAHs, flexible, portable, insensitive to external disturbance	Unproductive consumption of chemicals by oil	[99]

than techniques utilising vegetable oils but these inherently involve higher costs [7].

8. Conclusions

The use of vegetable oil as extraction solvent for soil washing and as soil amendment has been shown through several studies to be a viable approach for the treatment of PAH-contaminated soils. In this context, vegetable oil usage is targeted towards the removal of HMW PAHs, which has long been the major challenge in other conventional remediation methods. Nevertheless, the demonstrated technologies have not proceeded beyond bench-scale testing and there is scope for further exploration within this interesting development in PAH soil remediation.

For physical extraction with oil, the PAH removal efficiencies have been shown to be comparable to common solvents and surfactants used in soil washing. Here, vegetable oil can be considered to be more superior in the sense that it is biodegradable and less toxic than typical solvents used. However, due to the high quantity of oil used especially for highly contaminated soils, the negative impacts on the environment are a concern. Before this technology can be applied on a full-scale, site study should be carried out to assess contamination factors such as type of PAHs, level of contamination, ageing period and soil properties. Both the oil usage in the treatment and oil residues in the treated soil should be kept to the minimum possible level to avoid subsequent pollution. Thorough assessment of transportation and treatment of soil, costs, ecological risks, and treatment/disposal of contaminated oils is necessary prior to field implementation.

For integrated oil-biological soil treatments, various techniques have been reported in the specialised literature. Since biological processes are complicated by many microbial and environmental factors, further intensive and thorough studies are necessary to better understand the processes behind the effects of oil inclusion and to optimise the methodologies. In this respect, the areas requiring more focus include the verification of complete PAH mineralisation, the transformation of metabolites and their environmental impacts, the metabolic capacity for PAH degradation, the shift in microbial community under xenobiotic conditions and the resultant effects on PAH degradation. Finally, integrated oil-Fenton soil

treatment is a new concept which offers the potential for further exploration and development, especially for the removal of recalcitrant HMW PAHs.

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