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Biogeochemical Cycle, Occurrence and Biological Treatments of Polycyclic Aromatic Hydrocarbons (PAHs)

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Abstract

Polycyclic aromatic hydrocarbons are responsible for contaminating environmental compartments around the world, imposing risk associated with human health and ecosystem pollution. Emissions from anthropogenic activities predominate; nevertheless, open burning, volcanic activities, and natural losses of petroleum deposits are prominent natural sources. Different physical and chemical treatment technologies have been developed and tested for the removal of PAHs, but the use of biological entities was found most favourable for adaptation at industrial scale. This review can help to understand the mobility of PAHs in the environment. Focus of this review is on identifying processes through which PAHs are added to environment, their biogeochemical cycles, biodegradation, environmental and substrate-specific factors affecting biodegradation. Further studies related to different bioprocesses linked with remediation and removal methodologies along with factors affecting the treatment have also been brought into consideration. This review brings together inter-disciplinary aspects and understanding for PAHs, to which no previous review has focused.

Keywords Abiotic factors · Biodegradation · Biogeochemistry · Biotic factors · PAHs · Toxicity

1 Introduction

Combustion of different masses and incomplete pyrolysis of oil, petrol, diesel, wood and coal result in the formation of organic contaminates, among which polycyclic aromatic hydrocarbons (PAHs) are found in almost every environmental compartment (Halsall et al. 2001). Physico-chemical properties of PAHs predict their residence and behaviour in environment. More volatility and higher solubility were observed for 2 and 3 ring PAHs, when compared to PAHs having three or more rings. The first group is present more frequently in vapour phase, while the later bind more commonly with particulate matter. With about 30 PAHs and 100 of its derivatives being identified, out of which many have mutagenic and carcinogenic effects, PAHs represent leading class of chemical compounds capable of causing cancer (IARC 1987). Heavy quantities of PAHs occur near the vicinity of their emission source (Halsall et al. 2001). PAHs are rapidly transported from their primary source and cause severe human health impacts (Menzie et al. 1992). This review focuses on PAHs biogeochemical cycles, ways through which contamination occurs and associated toxicity. Further recent studies, related to different bioprocesses linked with remediation and removal methodologies along with factors affecting the treatment, have also been brought into consideration. This review brings together inter-disciplinary aspects and understanding for PAHs, to which no previous review has focused.

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2 Sources of PAHs

Ubiquitous distribution of PAHs in environment resulted in exposure of humans and other living beings by multiple routes (Jarvis et al. 2013). These routes include air, soil and sediments, water, and food (Alomirah et al. 2011). Natural processes and anthropogenic activities contribute to addition of these notorious contaminants into the environmental compartments. The proceeding section is related to different natural and anthropogenic sources of PAHs.

2.1 Natural Sources of PAHs

Among the notable natural source, forest and prairie fires, and volcanic eruptions are main sources that augment PAHs into the environmental matrices. Geochemical activities, notably sedimentary diagenesis, are also significant contributors of PAHs (Youngblood and Blumer 1975). However, the role of natural source in introduction of PAHs is insignificant and dramatically increased the quantity in the environment is linked with anthropogenic causes (Bamforth and Singleton 2005; Freeman and Cattell 1990).

2.2 Anthropogenic Sources of PAHs

The significant addition of PAHs into environment is due to anthropogenic activities. Sites, where fossil fuels and waste residuals are used or produced, were found to have heavily PAHs-contaminated soil, air, sediments, and water. Various consumer products and foods are also reported to contain these deleterious compounds (Menzie et al. 1992). Among the main anthropogenic activities, incomplete combustion of diesel, gasoline, coal, plants and other organic materials is the key foundation of PAHs contamination (Freeman and Cattell 1990). These activities lead to the formation of large quantities of airborne PAHs, which is the main and most important route of transport to very far parted areas.

Highlighted point sources of PAHs include diesel spills, coal liquefaction, and coke gasification (Bamforth and Singleton 2005). Such an example is creosote and coal tar, produced as a by-product of cooking, containing as much as 85% of PAHs in total weight (Mueller et al. 1989). Tobacco smoke and food burning are some of PAHs minor sources. The point sources are of highest concern when it comes to the production of PAHs. These sources though are contaminating comparatively smaller areas, but the concentration level is usually very high and the contaminated areas are also co-contaminated with other contaminants like heavy metals, benzene, toluene, ethylene and xylene (BTEX), and aliphatic hydrocarbons (Bamforth and

Singleton 2005). Air levels of PAHs due to incomplete combustion can be found between 0.06 and 3 mg m^{-3} (Freeman and Cattell 1990).

3 Environmental Fate and Biogeochemical Cycle of PAHs

Distributions of PAHs occur rapidly, in water, air and suspended particle, when hydrocarbons come in contact with any of these matrices. A layer of 0.01–3.0 mm in thickness, of insoluble fractions forms on the water surface (Lichtenthaler et al. 1989). Initially within few hours, evaporation of some part of this insoluble layer occurs, while remainders are adsorbed to soil, sediments, or suspended particulates in water bodies. Non-aqueous phase liquids (NAPLs) are formed, when concentrations of different insoluble hydrocarbon fractions occur at higher levels. The remaining hydrocarbons form aqueous layer or film on the water surface. Further evaporation of lighter fractions of hydrocarbons occurs within 24 h (Mukherji and Chavan 2012). Composition of oil plays a significant role in the evaporation. Alkanes, having up to 18 carbons in the carbon chain, contribute 0.1–17% of the total mass loss due to evaporation of heavier oils to lighter oils, respectively (Wang et al. 1998). Further, it facilitates the biodegradation processes, as the lighter fractions are more lethal to microorganisms (Delille et al. 1998). The portioning also proceeds toward degradation of these notorious pollutants in water, soil and sediment. Figure 1 illustrates the biogeochemical cycle of PAHs and other organics, while in the proceeding section the detail of distribution is discussed.

3.1 Atmospheric PAHs

PAHs occur ubiquitously in air and bulk of it is present in the environmental compartment. Incomplete combustion is the primary source of PAHs occurrence in atmosphere (Fig. 1). Once released PAHs are separated into two phases, vaporized or solidified (Bamforth and Singleton 2005). As PAHs have lower vapor pressures, compared to benzene, they frequently sorb onto atmospheric particulate matter. It is the variability in vapor pressures among different PAHs that contributes to differential distribution in vapor phase and with other sorbets (Kuo et al. 2013).

3.2 Water Dissolved PAHs and Other Hydrocarbons

The part that accumulates or comes in contact with organism is of concern in toxicological and biodegradation studies. Conversely, molecules adsorbed in the sediments
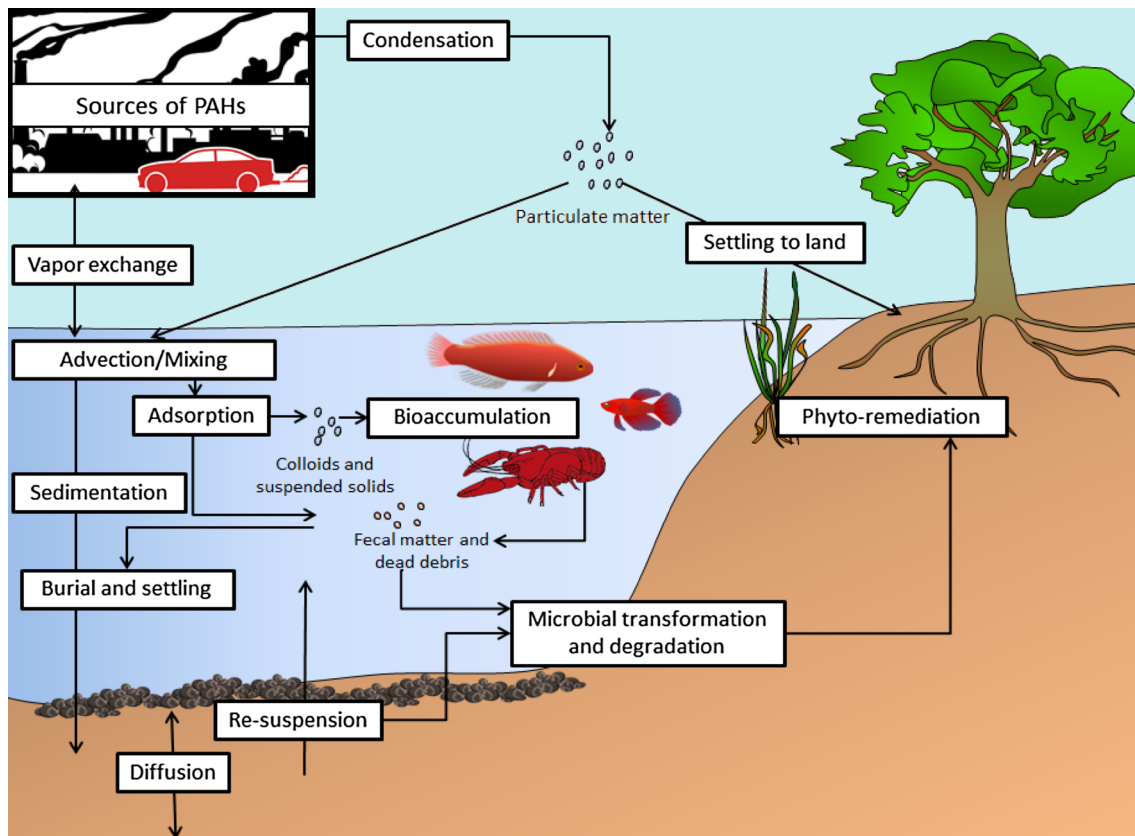
Fig. 1 Biogeochemical cycle of PAHs and other organic pollutants

remain longer in the environment as they are comparatively less available for degradation. These moieties often make oil–water emulsion in aquatic environments, because of the evaporation of volatile compounds, increasing the viscosity of NAPLs (Ortega-Calvo et al. 2013). This process is less favourable for biodegradation. Microorganisms mostly degrade hydrocarbon fraction that is dissolved in water; it is due to this reason that larger PAHs have long persistence (Fig. 1). Microorganisms produce biosurfactants to overcome and circumvent this problem (Pacwa-Płociniczak et al. 2011). Only, a maximum of 2% of total hydrocarbon wasted in water is available due to solvation (Nicodem et al. 1997). Remaining parts are absorbed in sediments, soil or suspended particulates. Solubility of light molecular weight (3 or 4 rings) PAHs is comparatively higher in water (31.7 mg L^{-1}), while higher molecular weight PAHs (five or more aromatic rings) are very insoluble in water (0.003 mg L^{-1}). It promotes binding of these heavy PAHs to suspended particles in water, making them more persistent (Shor et al. 2004).

The presence of organic matter is very important for solubility of PAHs (Ke et al. 2009). According to them, humic acid presence enhances the solubility of PAHs, which is insoluble in the absence of humic acids. In Fig. 2, lines are representing the increase in solubility with the

$$C_{PHE} = 4.00 C_{HA} + 0.39 \ (R^2 = 0.96)$$
$$C_{PYR} = 1.51 C_{HA} + 0.32 \ (R^2 = 0.96)$$
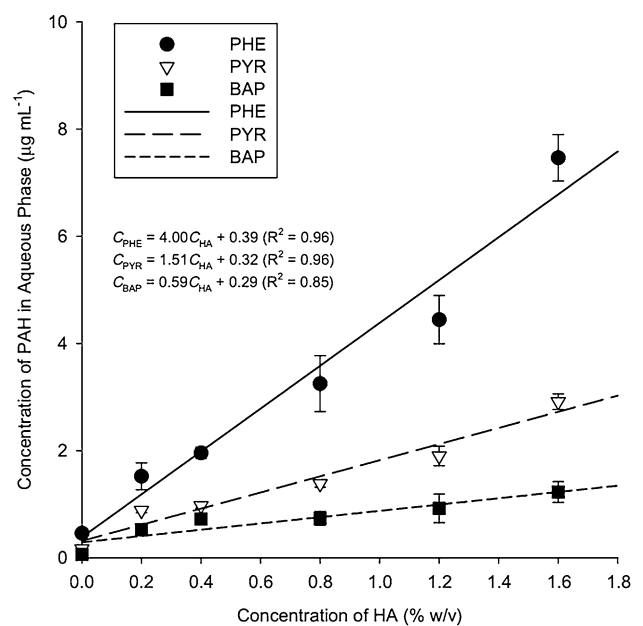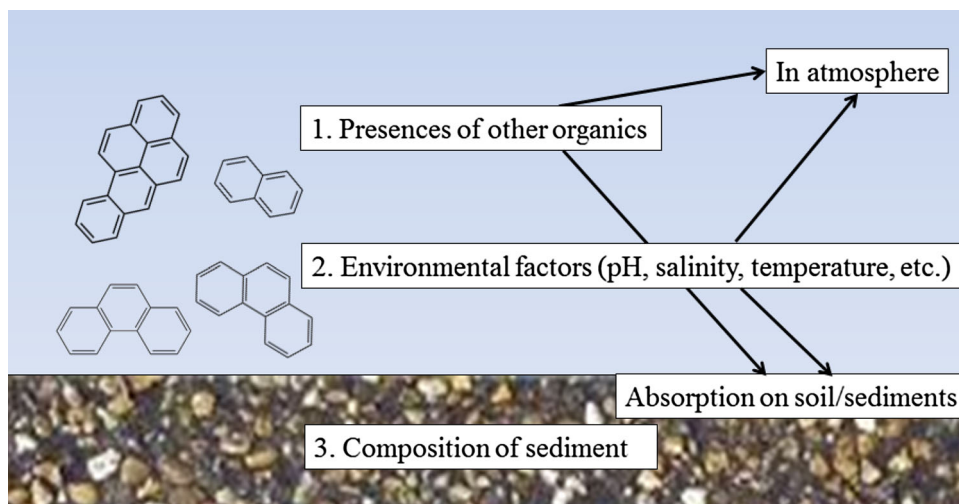$$C_{BAP} = 0.59 C_{HA} + 0.29 \ (R^2 = 0.85)$$

Fig. 2 Effect of humic acids on PAH solvability (Ke et al. 2009)

addition of humic acid, while different spots are showing the actual concentration added (Fig. 2, adopted from Ke et al. 2009). A positive effect of the presence of humic acid

Fig. 3 Factors affecting absorption of PAHs

on partition of PAHs in aqueous PAHs is clearly visible. In aquatic environment, emulsification contribute to the hydration of PAHs, which is important, as it leads to change in properties favourable for degradation. In general, emulsification spreads hydrocarbon on substances that are much polar for adsorption to sediments, increasing the time required for degradation. Asphaltic and aromatics fractions are generally associated with the formation of emulsion.

3.3 Bioaccumulation

PAHs are known for their bioaccumulation. They accumulate in the lipid-rich tissues of animals. This is especially seen in the liver of fish and in the pancreas of invertebrates (Vives et al. 2004). Aquatic organisms take up more hydrophilic PAHs from ventilated water, while more hydrophobic PAHs are taken via food, suspended small solid and sediments (Fig. 1). Accumulation of PAHs in the food chain is of interest in PAHs uptake via food, because humans are mostly the last part of the food chain. For animals, the uptake of PAHs shows a seasonal variation (Meador et al. 1995). Plants are also studied for the uptake of PAHs, and it was found that PAHs concentrations in plants are the result of a partitioning between the absorbed phase and the gas phase. Due to a large dependence of this partitioning on the temperature, seasonal variations are also seen (Simonich and Hites 1994).

3.4 Sorption to Sediments and Soil

Sediments adsorption of PAHs plays an imperative factor to forecast the fate of degradation, as it makes PAHs less available (Fig. 1). When in sediments, the uptake of concerned hydrocarbon by microorganism is shown to be very limited compared to hydrocarbon in dissolved state or in suspended form (Dong et al. 2016). Numerous factors

affect the absorption of organic compounds, specifically PAHs (Fig. 3). These include the composition of sediment, the presence of other organics, and lastly a list of environmental factors that include pH (affecting 6–9% decrease in adsorption upon an increase of one pH unit in range of 6.5–8.5), and salinity also affects adsorption of organics (Meyers and Quinn 1973). Rapid increase in adsorption occurs, when salinity is 1–4%, but any further increase results in the reduction of organics adsorption rate. Temperature was also studied to check the adsorption rate of organics (Cornelissen et al. 1997). In terms of entering into the sequestering process, PAHs having lighter weight are faster, while less soluble heavy molecular weight PAHs form colloidal dispersion that limits adsorption rates (Brion and Pelletier 2005). The sediment adsorption and temperature are inversely related to PAHs sorption.

Partition coefficient (K_p) determines the partitioning of different hydrocarbon fractions in sediments and water (Ghosh et al. 2003). Concentration of organic matter is the predicting element for K_p. The general formula is

$$K_p = K_{oc} \times F_{oc}$$

where K_{oc} is K_p corrected for sediment organic material fraction and F_{oc} is the organic material fraction of sediment. A specific K_{oc} is for each of organic substance in the sediment. Hence, it can be said that partitioning is independent from the concentration of PAHs but is reliant on the presence of organic matter in aquatic and terrestrial bodies, providing surface area for PAHs absorption (Hawthorne et al. 2002). Similarly, toxicity of hydrocarbons in sediments of harbour and soil factory is enormously dependent on the presence of coal and soot in these sites. Coal and soot, due to their high K_{oc}, even in very minute concentration, result in increasing K_p, bioavailability and toxicity. This pattern was found for different harmful organic toxicants, especially for PAHs (Lohmann

et al. 2005). The portioning of organic molecules with sediment, soil or other surfaces is a complex phenomenon to understand, due to the complexity of such matrices (Hawthorne et al. 2002).

Aging declines the availability of PAHs, when these compounds are adsorbed with sediments or soil. This effect can be studied by a simple extraction experiment (Xu et al. 2014). Diffusion of PAHs into soil organic matter, through intra-particular nanopores, causes aging (Wang et al. 2012). The aging is because of penetration of organic contaminant into inaccessible parts of soil matrix, limiting the degradation process. This process increases the time, from weeks to months and even years, required for the remediation of contaminated site. Increase in K_{ow} (octanol–water partition coefficient) and K_{oc} of the sediment and PAHs molecular weight improved aging affect (Northcott and Jones 2001).

3.5 Formation of Non-aqueous Phase Liquids (NALPs)

PAHs containing waste are generated by a number of industries including paint, varnish, lubricants, petroleum fractionation, and distillery producers. Industrial processes and activites influence the composition of waste generated, hence hetrogenocity in the compostion vary significantly with every batch of production (Shailubhai 1986). If the untreated waste is disposed into water streams, it could raise different issues. The absorption of these waste hydrocarbons, including aliphatics, cyclics and PAHs, with soil can lead to the formation of NALPs. This occurs when these organics concentrate and form insoluble phase in soil. The insoluble phase contains different types of hydrocarbons. Brown et al. (1999) found that NAPLs contain the highest concentration of harmful PAHs. The formation of NAPLs also affects the bioavailability of PAHs, just as it is seen with PAHs-sediment sorption and aging process, making it less available for biodegradation (Salanitro 2001).

3.6 Degradation of PAHs

PAHs-contaminated soil and sediment are treated by a number of methods. They are broadly classified as physico-chemical methods, utilizing certain physical or chemical treatments for remediation of contaminated soil, and biological methods of remediation, using microorganisms and plants for the treatment (Fig. 1). Physico-chemical methods adopted for the management of PAHs soil contamination include electrocoagulation, chemical oxidation, and physical separation (Lopez-Vizcaino et al. 2012). Despite various methods being available, most of them are either too expensive or require intensive labour, making them far

realistic for field application. Biological methods for remediation of PAHs tainted soils have a distinctive advantage over conventionally applied physico-chemical methods, as with the use of microorganism, oil fractions that contaminate soil can also be treated at the site (in situ), and these methods can be applied with little augmentation to indigenous microbial flora, already residing in the polluted environment (Maila and Cloete 2004; Xu et al. 2014). They can also be incorporated in combination with conventional methods making the approach more integrated (Huang et al. 2013). These techniques involve bio-piling, bio-stimulation, bioreactor, bioventing, land farming and phytoremediation (Van Hamme et al. 2003). Table 1 represents a small insight of these applied techniques. Good review in the domain of phytoremediation of PAHs by plant and terrestrial environment was already published by Edwards 1983 and Haritash and Kaushik 2009; hence, the details were not brought into discussion in this work. Despite some demerits related to time requirement for complete remediation of polluted site, bioremediation is gaining acceptability, due to its start-up low cost, ecological sustainability and less labour requirement. So, in the following section the focus of review shall be on bioremediation using microorganism for PAHs-contaminated soil and sediments.

4 Bioremediation of PAHs-Contaminated Soil with Microorganisms

Complex physico-chemical and microbiological processes are involved in the bioremediation of PAHs from each of the environmental compartments, which offer conditions feasible for natural bioremediation. Alcohols, aldehydes, esters, fatty acids, ketones, phenols and other intermediates are produced by these microorganisms through degradation of PAHs and other aromatics in these matrices. Apart from microbial-mediated PAHs degradation through assimilation to the environment, non-biological processes, like evaporation, photo-oxidation, chemical oxidation, and volatilization, play a key role for the management of waste containing aromatics (Khan et al. 2016a). The rate of effective treatment depends on environmental factor of given area, properties of petroleum hydrocarbon wastes and microbial population responsible for hydrocarbons degradation (Bento et al. 2005).

4.1 Environmental Factors Influencing PAHs Biodegradation

Environmental factors play a very critical role in squalidness reduction of different pollutants. These factors predict microbial population succession, as well as they also have

Table 1 Different types of biological treatment method adopted for treatment of PAHs

Type	Model, organisms or stimulating agent	Targeted contaminants	Objective and variables studied	References
Bio-piling	C/N/P ratio at 100:10:1, water content around 10–20% (wt%), and O_2 above 7% (vol%)	2,3, 4,5 and 6 ring PAHs	Effect of O_2 and CO_2 on microbe density and PAHs degradation	Lin et al. (2012)
	Bio-pile dimension (1.5 m high, 5.5 by 5.5 m^2, 1.5:1 slope)	TPHs, diesel fraction, BTEX, and PAHs	To check the competence of 27-m^3 bio-pile, for the removal of 40,000 mg/kg of TPH from contaminated soil	Iturbe et al. (2007)
Bioreactor	*Mycobacterium* PYR-1	Pyr and Phen	Nature of the interaction between *Mycobacterium* PYR-1, and the aqueous-organic interface in a two phase partitioning bioreactor system, fed on selected PAHs	MacLeod and Daugulis (2005)
	Staphylococcus warneri and *Bacillus pumilus*	Phen, Pyr, and BaA	Effect on PAHs removal rate by a bacterial consortium and influence of stirring of bioreactor on overall process	Moscoso et al. (2012)
Bio-stimulation	Mineral salt medium	Flu, Phen, and Pyr	Effect of natural attenuation, bio-augmentation and bio-stimulation, on PAHs degradation	Yu et al. (2005)
	Compost and rabbit food	Flu, Phen, Anth, Flt, Pyr, BaA, and Chr	Influence of *T. versicolor* bio-augmentation and compost and rabbit food bio-stimulation on contaminant biodegradation.	Sayara et al. (2011)
Bioventing	Oxygen	Phen	Identification of optimal humidity and C:N:P for bioventing	Frutos et al. (2010)
	Oxygen	TPHs, BTEX, TFHs, VOCs, total PHAs	Reduction in targeted contaminates	Lee and Swindoll (1993)
Land farming	Land application	2,3, 4,5 and 6 ring PAHs	Effect on different PAHs concentration, soil physiochemical properties and microorganism colonial structure	Picado et al. (2001)
	Sewage sludge consortia	Nap, Anth, Phen, Fluo, Pyr, Flt, Chr and BaP	Effects of bio-stimulation and bio-augmentation on land farming	Atagana (2004)
Phytoremediation	Ryegrass	Phen and Pyr	Consequence of microbes, vegetation roots, abiotic losses and root exudates on PAHs degradation	Sun et al. (2010)
	Ryegrass, White clover, and Celery	2,3, 4,5 and 6 ring PAHs	PAHs degradation under influence of monocultures or mixed culture of plant	Meng et al. (2011)

Anth anthracene, *BaA* benzo[a]anthracene, *BaP* benzo[a]pyrene, *Chr* chrysene, *Flt* fluoranthene, *Flu* fluorene, *Nap* naphthalene, *Phen* phenanthrene, *Pyr* pyrene, *TPHs* total petroleum hydrocarbons, *BTEX* benzene, toluene, ethyl benzene, and xylene, *TFHs* total fuel hydrocarbons, *VOCs* volatile organic compounds

their direct effect on pollutant. Each of these environmental factors, for microbial-mediated degradation, has an optimal range in which microorganisms are expected to perform as they have performed in lab or in different testing. In case of diversion from it, the model microorganism may show compromised potentiality. Similarly, the abiotic activity which changes the nature of pollutants within matrices can also affect bioremediation process positively as well as negatively, depending on the secondary nature of converted pollutant. The factors that are of most concern, when dealing bioremediation of petroleum hydrocarbon waste, include nutrients, oxygen, pH, soil texture of waste containing site, the presence of other pollutants, pressure, salinity, temperature, water activity and availability (Bento

et al. 2005; Khan et al. 2016b). Light is another environmental factor which can have important effects on microorganism (Briggs 2014). These factors are discussed in detail in the proceeding sections of this review.

4.1.1 Light

Light as an environmental factor is indispensable in the degradation of different petroleum hydrocarbons. Biodegradation and photo-oxidation together lead the central command in treatment and transformation of different petroleum hydrocarbon fractions (Dutta and Harayama 2000). Photo-oxidation promotes susceptibility of crude oil for biodegradation. Light causes the abiotic

degradation of hydrocarbons (Marquès et al. 2016) and also has the effect on biotic component of environmental compartments, including bacteria, fungi, and algae (Briggs 2014).

Photo-oxidative transformation of PAHs and aromatic hydrocarbons is achieved by the transfer to molecular oxygen through electronic excited state of aromatics and polar constituents generating singlet oxygen, capable of reacting with aromatic, addition of sulphur compound (Gorman 1992), auto-oxidation induced by free radical (Thominette and Verdu 1984), and oxygenation initiated by electronic transfer that can generate anionic and cationic free radicals (Lopez 1990).

Microbial degradation of crude oil (containing aliphatic and aromatic hydrocarbons) in combination with photo-oxidation was investigated by Dutta and Harayama (2000). They proposed that the mineralization of *n*-hexane and hexane:benzene fraction of crude oil was higher than 40% through biodegradation. Aromatics were transformed to polar fractions through photo-oxidation. Side by side, photo-oxidation enhanced biological mineralization through biodegradation from 28% without photo-oxidation to 36%.

Interestingly, light was also reported to affect the non-photosynthetic bacterial and fungal hydrocarbon biodegradations (Khan et al. 2016a, b). One of the possible links between light and microbial photo-physiology is the presence of photoreceptors and domains on bio-molecules, whose presence influences the microbial metabolism. Among many, one is light–oxygen–voltage (LOV) domain which is responsible for blue-light sensing in *Bacillus subtilis* (Losi et al. 2002). This concept of putative LOV domain is strengthened by other findings (Losi and Gärtner 2008). The LOV domain was identified in proteins of 10% of sequenced bacteria (Pathak et al. 2012). The same domains were also identified in many fungal proteins (Idnurm et al. 2010). Similarly, other functional photoreceptors, like blue-light sensing by photo yellow protein, and FAD BLUF (blue light sensing using FAD) domain proteins, have been reported in bacteria and fungi (Zoltowski et al. 2007).

These discoveries have changed the central dogma that chemotropic microorganism metabolism is not effected by visible light spectrum. In case of chemotropic microorganisms, who cannot utilize light for metabolism, these photo-sensory responses help us in understanding different activates. One of the possible reasons to respond to light stimulus is to avoid solar UV radiation damage by the production of different pigments that act as protective agents against the harmful effects of light (Gomelsky and Hoff 2011). The role of light in arbitrating the response of microorganism to biodegradation is yet to be identified in depth.

4.1.2 Nutrients

The level of hydrocarbon biodegradation by microorganism is affected with availability of different nutrients. Most important nutrients include carbon, nitrogen and phosphorus (Margesin et al. 2000). The addition of different nutrients has been studied extensively in many studies, to evaluate the effects on degradation of hydrocarbons by microorganism (Bento et al. 2005; Liebeg and Cutright 1999).

The most common used nutrient for bioremediation experiments is nitrogen. The basic importance of this nutrient is in cellular growth (as NH^{4+} or NO^{3-}); further, it also acts as an alternate electron acceptor (NO^{3-}). Most commonly, nitrogen was amended as urea, ammonium chloride and nitrate. An additional drawback for the amendment of ammonium ion is that it increases oxygen demand (Liebeg and Cutright 1999). Therefore, the ability of microorganism to utilize other forms of nitrogen source can add an advantage in terms of lowering the oxygen demands of bioremediation process, but it depletes the pool of nitrogen available for any plant, which can have considerably negative effects when dealing with phytoremediation. The activity of using different nitrogen sources can be observed using assays like urease, nitrate and nitrite reductase or even nitrogen fixation (Margesin et al. 2000).

The second most commonly added nutrient is phosphorus that enhances the microbial growth in different bioremediation experiments. Orthophosphates, potassium phosphates, polyphosphate salt and others are used for nutrient supplementation. The availability of phosphates for biological activity is low in soil and sediments, as phosphates have higher affinity for different constituents of these matrices. The immobilized phosphates in soil and sediment are not available to plant or microbial population. Hence, any microbial strain that can improve the pool of available phosphates in soil and sediments would be advantageous when selected for biodegradation. Phosphatase test, utilizing $CaPO_4$ as a sole source of phosphate in agar plates, can be used to check phosphate solubilisation activity (Nautiyal 1999). Many field and lab studies showed that enhanced oil degradation cannot be achieved only by addition of different microbial strains, but a proper addition of nutrients is also required to achieve desired results (Bento et al. 2005; Liebeg and Cutright 1999). The optimal C:N:P mole ratio reported best for bioremediation processes was 100:10:1 (Cookson 1995).

4.1.3 Oxygen

Oxygen is a fundamental component in terms of aerobic degradation (Vonwedel et al. 1988). Bacterial- and fungal-mediated degradation of aliphatic, cyclic and aromatic

hydrocarbons require molecular oxygen, for substrate's oxidation by different monooxygenases (Morgan and Watkinson 1994; Van Hamme et al. 2003). Under aerobic conditions, oxygenase enzyme attacks terminal methyl group, resulting in the formation of primary alcohol, during initial step of aliphatic, saturated *n*-alkane degradation. The formed alcohol is centred to TCA (tricarboxylic acid) cycle through oxidation and conversion to aldehyde and fatty acid. Acetyl CoA is formed by cytoplasmic β-oxidation of fatty acid, and enters into TCA cycle (Van Hamme et al. 2003).

Degradation of cycloalkanes, including condensed cycloalkanes, takes place by co-oxidation, and as a result cyclic alcohol and ketones are formed. The cyclic ring cleavage starts with the introduction of oxygen into cyclic ketone. This substitution of cycloalkane enhances the degradation process compared to cycloalkane not having substituents, making them more difficult to degrade (Morgan and Watkinson 1994).

Naphthalene, biphenyl and phenanthrene degrade readily under aerobic conditions. Initiation by dihydroxylation of any of the polycyclic rings is generally the initial step of degradation for such simpler polycyclic aromatic hydrocarbons (PAHs). Dioxygenases catalyse ring hydroxylation reaction. The sequential cleavage of carbon skeleton occurs through dismantling, due to ring cleavage reaction, prior to the cleavage of second ring of aromatic hydrocarbon (Saito et al. 2000). The biochemical mechanism of different fractions of petroleum hydrocarbon degradation is well understood with bacterial models, while there are some studies with fungal model for degradation of these different fractions (Mollea et al. 2005); the biochemical processes involved in biodegradation of PAHs by fungi are yet to be investigated in detail.

Microbial consumption rates of oxygen, soil and sediment type, and utilizable substrate availability are important for predicting availability of oxygen in environmental matrices (Bossert and Bartha 1984). To apply aerobic biodegradation for treatment of PAHs, microbial strain must exhibit growth in the presence of oxygen. In the presence of oxygen, different processes produce elemental oxygen. This stress can be lethal to microorganism. To survive in such stressful conditions, microorganism must contain system to overcome problem of free radical generation. Catalase activity is a good indicator for monitoring potential of a microorganism resistance to stress associated with free radical and reactive oxygen species attack. This activity is present in the most aerobic and some facultative anaerobic bacteria (Brioukhanov et al. 2006), and found in all types of fungi (Isobe et al. 2006).

4.1.4 pH

The pH of contaminated compartment can show a wide variability ranging from 2.5 in mine spoils to a level of 11 in alkaline desert (Bossert and Bartha 1984). Microorganisms, including bacteria and fungi, prefer near neutral pH, while fungi have capacity to tolerate acidic conditions as well (Leahy and Colwell 1990). Extreme pH can hinder the bioremediation process, as its negative effects are expected on microbial activity to perform degradation. The variability of pH does not only affect the biological processes for the treatment of PAHs, but was also reported to affect electrokinetic removal of phenanthrene (Saichek and Reddy 2003).

To obtain good results for the treatment applied for PAHs remediation, proper pH control cannot be neglected. In a study, increase in soil pH from 4.5 to 7.4 increased the rates of bioremediation of gasoline two times. However, a significant drop was observed when pH reached 8.5. Mineralization of oily waste was found optimal at pH 7.8 with a range of 5.0 to 7.8 (Dibble and Bartha 1979). It also influences the mobility of different heavy metals. The change in pH can disturb microorganisms as well as plants growing on the contaminated site. It is well documented that at acidic pH leaching of metals increases in soil and sediments (Peng et al. 2009). Siderophore production, which is solubilisation and sequestering iron, by microorganism including bacteria and fungi, is reported to promote plant growth (Milagres et al. 1999). Hence using microorganisms that can perform bioremediation along with promotion of plant growth is an added beneficial feature, for a selected microorganism.

4.1.5 Presence of Other Pollutants

Oily waste generated by different petroleum industries varies in the composition. Similarly, site or any substance contaminated with PAHs is also co-contaminated with any other contaminant. Apart from the major constituents of such waste, which are largely hydrocarbons, it also contains different metallic contaminants. Metallic contaminants like chromium, copper, lead, nickel, vanadium and zinc are frequently available on contaminated site, as these pollutants are added in a number of processes of product developmental cycles, and released or produced synergistically as a by-product (Shailubhai 1986).

One of the reasons of failure of effective strategy to implement bioremediation is due to the ignorance of the fact that contaminated site can be co-contaminated with other organic pollutants. The use of biosurfactants can facilitate the recovery of oil from such contaminated site (Dua et al. 2002). It is important to design an integrated approach utilizing phytoremediation with bacterial, fungal

or both microorganisms along with some chemical treatment in order to achieve desired goals. These containments themselves are not only hazardous to human and other animals and plants but also have devastating effects on microbial populations (Asatiani et al. 2004).

Intercellular chromium, in the form of chromate, acts as reducing factor for vitamins like C and B12, activity of cytochrome P-450, and cellular respiration (Junaid et al. 2016). Cytochrome P-450 enzyme plays a critical role in performing biotransformation reaction; in case of its reduction, there shall be significant decrease in microbial activity. Similarly, different metals are also responsible for oxidative damage to DNA. Hence, it is important to keep in mind that heavy metals can hinder PAHs bioremediation process.

4.1.6 Salinity

Alkaline soil or sediments along with salinity can behave as an extreme environment for microbial growth (Vega-Jarquin et al. 2003). Inhibition of microbial processes of nitrification and cellulose degradation was reported, due to alkaline saline soil (Betancur-Galvis et al. 2006). Effect on mineralization of oil was also reported, because of artificial salinity. It is evident that high electrical conductivity (EC) and pH produce inhibitory effects on microbial activity (Luna-Guido et al. 2003). In such a condition, along with the contamination of PAHs and other petroleum hydrocarbons, severity of stress on microbial species, degrading hydrocarbons, increases. Inorganic nutrients addition results in the increase of decomposition of organic matter (Conde et al. 2005). Similarly, addition of bio-solids, biochar and other nutrients can stimulate biodegradation of PAHs (Betancur-Galvis et al. 2006; Conde et al. 2005). At salinity above 24% w v^{-1} NaCl, inhibitory effect for bioremediation of aromatic and polar fraction was greater as compared to saturated petroleum hydrocarbon fraction (Mille et al. 1991). Use of biochar is beneficial, as it decreases pH and manage salinity in soil (Siddique et al. 2013).

The role of bacteria and fungi has been investigated in different laboratory and field studies to overcome issues of salinity on biodegradation of petroleum waste or for individual PAHs (Valentin et al. 2006). One of such studies includes field study by Zhanga et al. (2008). The Na$^+$ concentration decreased from 1597 ± 394 to 543 ± 217 mg kg^{-1}, similarly 1520 ± 922 to 421 ± 253 mg kg^{-1} for soil Cl$^-$, with an increase of 170 fold in bacterial biomass and 11 fold in fungal biomass, when wheat straws were added in soil, compared to soil with no addition of wheat straws. Decrease in total petroleum hydrocarbons to 2260 ± 420 mg kg^{-1} from 6320 ± 1180 after 45 days was also observed. Remediated soil was used to grow wheat and 72% grain yield was achieved

(Zhanga et al. 2008). These results support the use of bio-solids like wheat straws to promote treatment of saline petroleum-contaminated mediums through bio-augmentation.

4.1.7 Temperature

Temperature, among other environmental factors, is crucial for biodegradation of PAHs and other hydrocarbons. Temperature is not only responsible to affect the pollutant chemistry, but is also known to affect microbial physiology and diversity (Venosa and Zhu 2003). At low temperatures the viscosity of different hydrocarbons, which are toxic and are of low molecular weight, increases that delay the process of biodegradation (Mohn and Stewart 2000). Solubility of hydrocarbons increases at low temperature (Miller et al. 1998). The rate of biodegradation tends to decrease with lowering temperature; this is called Q_{IO} effect which is due to the decreased enzymatic activity (Atlas 1991).

In environment, the highest degradation of PAHs and other hydrocarbons was observed in temperature range of 30–40 °C (Das and Chandran 2010). Climate of a given site, where bioremediation is to be practised, can directly affect the selection of different microbial population to grow. Many studies for bioremediation at mesophilic range of temperature are available but other extreme ranges have also been investigated (Pelletier et al. 2004).

Research on endophytic microorganism can help in combating odd temperature through symbiotic relationships. One of such studies was conducted on plant fungal symbiosis. Tropical panic grass (*Dichanthelium lanugionisum*) and fungus (*Curvularia protuberata*) were reported to be growing in mutualistic manner at Yellowstone national park at high temperature (Redman et al. 2002). *Curvularia protuberata* itself do not possess any thermal tolerance, but when the fungus was infected with *Curvularia thermal tolerance virus* (CThTV), the fungus acquired the potential of thermal tolerance DNA sequence (Márquez et al. 2007). When the CThTV-infected fungus associated itself in endophytic symbiosis with tropical panic grass, both fungus and plant showed tolerance to high temperature, tolerating temperature up to 65 °C. At the same condition, non-symbiotic plants underwent chlorosis and died, while symbiotic plants were able to tolerate temperature regime. The symbiosis of plant and fungus resulted in enhanced capacity to tolerate elevated temperature which was incapable of tolerating temperature higher than 38 °C, individually. Further, in the absence of temperature-stressed conditions improved growth rate and drought resistance were also reported for symbiotic plants, compared to non-symbiotic plants (Rodriguez et al. 2010). Based on this, it can be inferred that the interaction between plant, microorganism and even virus can lift the resistance against harsh and extreme environment. This

advantage can be introduced into PAHs-tolerant plant to achieve higher effectivity of phytoremediation.

4.1.8 Water Activity and Availability

The ratio of vapour pressure of water in environment (p) to vapour pressure of pure water at same temperature is known as water activity. The maximum value of water activity of 1 is for pure water, while least is 0 for absolutely dry soils. In soil and sediments, the range of water activity or water potential is highly variable ranging from 0.0 to 0.99, compared to aquatic environment, where it is stable at 0.98 (Bossert and Bartha 1984). At water activity below 0.91 and 0.4, the most bacterial and fungal growth is inhibited, respectively (Rockland and Beuchat 1987). Due to the low availability of water for microbial growth and metabolism in terrestrial ecosystems, hydrocarbon bioremediation in such conditions can be limited. Hydrocarbon itself reduces water holding capacity of contaminated matrices, which also is attributed to slowing and inhibition of degradation process. Water saturation of 30–90% was reported optimal for bioremediation rates (Dibble and Bartha 1979). Water is needed for a number of biochemical processes; a scheduled watering and mixing of petroleum hydrocarbon containing waste can, therefore, positively affect the biodegradation process.

4.2 Problems Associated with the Properties of Hydrocarbon Contaminated Site

Petroleum waste treatment offers a challenging environment to microbial flora. These challenges are due to composition, concentration and physical states of PAHs and other hydrocarbons in waste. Problems associated with these are discussed individually in preceding section in this review.

4.2.1 Composition

There are four major classes of petroleum hydrocarbons including, saturated aliphatic, aromatic (PAHs), asphaltene (ester, fatty acids, ketones and others), and resins (amide, carbazole, quinolines and others) (Colwell et al. 1977). Among these, the most commonly seen pattern for susceptibility to microbial degradation is in the following descending hierarchy: aliphatic > branched alkane > aromatics with low molecular weight > cyclic alkanes (Perry 1984). The overall treatment process of petroleum waste is dependent on the complexities in the composition of different constituents, present at the contaminated site. The evidence supporting above given hierarchy for susceptibility of microbial degradation was also reported in another study. Bacterial-mediated biodegradation of n-paraffin was

noted to be the first among different fractions of hydrocarbons present in the crude oil. It was followed by the metabolism of isoprenoids, pristane and phytane which are branched alkanes. Lower ring aromatics were biodegraded at the same time along with paraffins, earlier than aromatics. Asphaltenes were produced due to the biodegradation of hydrocarbons, while cyclic hydrocarbons remain unaffected. Similar results were seen with *Acinetobacter calcoaceticus* and *Alcaligenes odorans*-mediated biodegradation of crude oil (Lal and Khanna 1996).

One of these few studies showed that fungi prefer to assimilate paraffin base crude oil compared to asphalt base crude oil (Cerniglia and Perry 1973). In another study fungus, notably *Penicillium* species were identified to degrade *n*-alkanes. While isoprenoids, pristane and phytane remained persistent to fungal attack. Same is the case with polycyclic aromatic hydrocarbons that were unable to be degraded by fungal strains used (Fedorak et al. 1984). Hence, treatment of oil waste, containing PAHs, in situ is a complex activity, and depends on the different types of hydrocarbons present on the contaminated waste site. Despite these studies, in which results suggested that fungal strains do not perform well when dealing with the bioremediation in complex composition condition, fungi were reported to possess potential to co-metabolise Benzo [a] pyrene, a known carcinogen, completely, in the presence of a proper co-substrate (Kanaly et al. 1997). This is due to the fact that fungi have substrate non-specific enzymes and cytochrome series of bio-transforming enzymes (Harms et al. 2011).

4.2.2 Concentration and Physical State of Petroleum Hydrocarbons

Soil environment is a non-homogeneous and unpredictable in terms of its nature; this can also hinder the processes for treatment of PAHs. For reliability of results related to microbial population in contaminated environment, proper sampling and analytical activates are required to be done in three-dimensional grid (Van Hamme et al. 2003). Availability of nutrients and oxygen to support microbial growth is negativity affected at higher concentration of contamination with petroleum hydrocarbon and PAHs, limiting the applicability of bioremediation process (Leahy and Colwell 1990). The maximum concentration or threshold concentration for soil microbial population can be helpful to identify the limit of tolerance by any microbial strain or consortium. Decrease in the activity of soil microbial population in biodegradation of petroleum waste is also because of toxic components.

Aging of soil and sediments also contributes negatively to biodegradation of PAHs, as aging results in lowering the bioavailability of different hydrocarbons. It is well

established that a slow and incomplete degradation is generally taking place in aged soil (Huesemann et al. 2003). Due to aging, with the passage of time, the hydrophobic organic containments of soil become hard to extract and also bioavailable fraction is reduced. This phenomenon is also known as contaminant sequestering hypothesis (Luthy et al. 1997). It can be perceived that the toxicity to environmental receptors is reduced as the organics are partitioning into different soil or sediments components including organic matter and other portions. The degree of removal or desorption of these organic hydrophobic contaminates is a two-phase process, starting from initial release, and followed by slower sequestered fraction desorption (Cornelissen et al. 1997). Although it was well known about contaminant sequestering hypothesis, limited work was done where biodegradation and desorption rate are directly compared to determine whether slow or incomplete biodegradation of organic contaminant of aged soil is either caused because of mass transfer rate or due to less bioavailability (Huesemann et al. 2003). The desorption of PAHs from freshly spiked soil was faster compared to its degradation, while biodegradation was as fast as desorption occurred in aged soil (Carmichael et al. 1996). This indicated that in aged soil or sediments, a mass transfer rate is limiting in determining rate of biodegradation kinetics. In another study, higher molecular weight PAHs (5 or 6 rings), despite their availability after bioremediation treatment, were not degraded (Cornelissen et al. 1998). This clearly tells that with higher molecular weight PAHs, degradation is affected because of microbial potential rather than low bioavailability.

Slurry of bio-treated six different soils was used, in a study, to determine whether the rate of desorption and bioavailability has any effect on biodegradation of *n*-alkane and PAHs. It was concluded that biodegradation of *n*-alkane did not require change in phase for degradation by microorganism. For low-molecular weight PAHs (2 and 3 rings) the rate of biodegradation was equivalent to the rate of desorption, indicating that in such a case desorption was a limiting factor for bioremediation. While in case of higher molecular weight (four rings or more) PAHs, biodegradation kinetics in initial phase was at higher rate of desorption, when compared to biodegradation rate. In second phase of high molecular weight PAHs, the desorption rate kept increasing, while due to desorption the toxicity of environment became more lethal to microorganism; hence, the degradation rate due to biotic factor was limited (Huesemann et al. 2003). It can be concluded that the toxicity of the end product by treatment can possess serious health impacts. The physical characteristics of PAHs-contaminated medium and contaminating PAHs are important in determining that fate of treatment kinetics.

4.2.3 Texture of PAHs-Contaminated Soil and Sediments

As discussed earlier, the process of PAHs treatment is dependent on the addition of nutrients, availability of appropriate moisture, and specific texture. Higher levels of coarse textured fraction of soils, after getting contaminated with PAHs and other hydrocarbons, showed inhibited biodegradation processes. This was due to lower water activity (Aislabie et al. 2006). This lowering of water availability was due to decrease in osmotic and matric forces, limiting the microbial growth. The oily layer on soil particles increases the soil hydrophobicity. Due to its grain size, coarse textured soils have lower water holding capacity and granules after being coated with petroleum hydrocarbon cause more reduction in water holding capacity (Dibble and Bartha 1979).

Similarly, the addition of optimal level of different nutrients is dependent on soil type. Sensitivity for over fertilization of sand and loamy sand with inorganic nitrogen, due to low water holding capacity, is more often than that of silt loam (Aislabie et al. 2006). Apart from water availability, texture also plays a very significant role in extraction of soil bound PAHs and hydrocarbons. Chemical extraction from soil containing higher clay fractions was reported to be significantly lower than soil containing higher coarser and silt fractions (Schwab et al. 1999).

Aging of soil affects the bioavailability of targeted PAHs, due to degradation, incorporation, and volatilization in matrix. For efficient bioremediation, bioavailability is an important aspect. Use of suitable non-ionic surfactant influences PAHs and hydrocarbon degradation (Rahman et al. 2003). Unfortunately, chemical surfactants can cause ecological hazards (Anastas and Eghbali 2010); on the other hand, microbial biosurfactants have low toxicity and are also partially biodegradable (Cameotra and Makkar 2004).

A number of different synthetic surfactants were used, along with bacterial and fungal biosurfactants in different remediation studies of soil contaminated with petroleum hydrocarbons (Kumari et al. 2012, Luna et al. 2013). Despite the very diverse work in bacterial model, fungi as a microbial model for biosurfactant production are not frequently utilized. A very wide room for investigations related to biosurfactant production, identification and characterization by fungi is still open.

To screen a microbial strain for biosurfactant production, a number of different methods are available ranging from qualitative to quantitative. Qualitative methods include drop collapse assay, microplate assay, penetration assay, oil spreading assay, emulsification capacity assay, CTAB agar plate assay and haemolysis assay. While qualitative methods rely on the presence or absence of biosurfactant produced, quantitative methods measure the

decrease in surface tension. Such quantitative methods include hydrophobic interaction chromatography (HIC), bacterial adhesion to hydrocarbons assay (BATH), stalagmometric method, Du-Nouy ring method, direct surface or interfacial tension measurements (Walter et al. 2010). A microbial strain capable of biosurfactant production can be beneficial to fructify biodegradation process, hence adding a merit to concerned microbial strain.

4.3 Biological Degradation of Aliphatics (Linear Chain), and Aromatics (BTEX and PAHs)

Bioremediation, compared to physico-chemical methods, is effective for removal of oily pollution due to the fact that a number of different crude oil fraction and also refined products are biodegradable, while degrading population is ubiquitous. Compared to physico-chemical methods, bioremediation offers an effective technology for the treatment of PAHs. Fungi and bacteria are distributed everywhere in the environment even which is contaminated with PAHs and hydrocarbons, provided that growth promoting factors are available. Total heterotrophic microbial population of hydrocarbon utilizers is highly variable among each contaminated site. Use of any hydrocarbon as a substrate by individual microorganism is limited to range of some fraction of petroleum hydrocarbons (Hadibarata and Kristanti 2012). This is due to the fact that many microorganisms do not have inherited genetic capacity for induction of catabolic enzymes against these notorious contaminants, and require adaptation to the given stress. In general, overall microbial populations produce diverse and broad spectrum enzymes, which are required to degrade complex mixtures of PAHs and other hydrocarbons through coupling biodegradation, via microorganisms and plants, where the end product produced by one microorganism is utilized by other (Xu et al. 2014). It is important to establish the details of other hydrocarbons present as co-contaminants at the bioremediation site; hence, a small insight on the properties and biodegradation of different petroleum fraction is discussed in terms of aliphatic, cycloalkanes and aromatics.

4.3.1 Aliphatics

Alipahtic hydrocarbons, ranging from C14 to C20, are ubiquitously present in petroleum contaminated sites. It includes saturated alkanes (paraffins), as well as unsaturated alkene (olefins). At higher concentrations, aliphatics can cause carcinogenicity and impose deleterious effects on biological receptors, due to the formation of carcinogenic metabolites. Microbial indigenous communities play a vital role in aliphatic degradation by the specialized uptake mechanism enabling soil or surface sorbed

hydrocarbon degradation. Due to the hydrophobicity of aliphatics, a significant concentration of it remains in soil persistently. For effective removal, bio-stimulation of microbial community and increment in bioavailability is very important (Stroud et al. 2007).

Paraffins or n-alkane are readily degradable in aerobic conditions by a number of different pathways. In *Pseudomonas putida* containing the OCT plasmid, the degradation of medium length alkanes is initiated through enzyme mediated by alkane hydroxylase (Harayama et al. 1999). Upon oxidation n-alkanols are formed, due to alkane hydroxylase-mediated attack at methyl ends of n-alkane. The n-alkanols are further oxidized to from n-alkanals via alcohol dehydrogenase, a membrane bound enzyme. The n-alkanals are converted into fatty acid; further, it is then transformed via aldehyde dehydrogenase and acyl-CoA synthetase into acyl-CoA (Van Beilen et al. 1994). Secondary alcohols are also formed through alkane degradation. In this pathway, n-alkane oxidation occurs via monooxygenases yielding secondary alcohol, further to ketone and ultimately fatty acid (Harayama et al. 1999).

The importance of bacteria was investigated in different studies for aliphatics degradation. Koma et al. (2001) identified the role of *Acinetobacter* sp. in degradation of n-paraffins as a sole source of carbon. After 96 h, isolated strain mineralized n-paraffins (0.1 w v^{-1}). Further, it was also reported that 20% of waste oil weight was reduced after 72 h, without biosurfactant. Through gas chromatography/mass spectrometry (GC/MS), intermediates including 1-hexadecanol and 1-hexadecanoic acid were detected, when fed substrate n-hexadecane was added. This finding supported that terminal oxidation pathway of n-alkane was used by *Acinetobacter* sp., for metabolism of n-paraffins. The formation of alcohol and saturated fatty acid as metabolic intermediates was also suggested in *Micrococcus ceripcans* assisted degradation of n-Nonacosane, plant wax paraffin (Hankin and Kolattukudy 1968).

Yeast species including *Candida maltose, Candida apicola,* and *Candida tropicalis* were used for investigation linked to n-alkane degradation. Long chain n-alkane's terminal hydroxylation and fatty acids' omega (Ω) hydroxylation catalysed by P450 monooxygenase are the first stages of alkane degradation. Fatty alcohol oxidase and aldehyde dehydrogenase vulcanized the formed alcohols (Harayama et al. 1999). Scheller et al. (1998) reported that enzyme P450 also catalyses reaction that yields α, Ω-dioic acids and fatty acids.

Similarly, fungal-mediated biodegradation of aliphatics was also reported in different studies. Colombo et al. (1996) studied the role of seven fungal strains including imperfect and higher level lignolitic fungal species in a 90-day experiment, on unfertilized soil contaminated with 10% crude oil. Degradation of 26–35% was observed by

pure fungi cultures. Degradation of alkanes was achieved in first 15 days. *Aspergillus terreus, Fusarium solani, Pleurotus ostreatus, Trametes villosus* and *Coriolopsis rigida* were identified to degrade aliphatic components, very effectively. In another study, *Trichoderma asperellum* strains (SA4, SA5, and SA6), *Penicillium* species (P1), and *Aspergillus* species (P9) used for their hydrocarbon biodegradation potential. *Penicillium* species (P1) among all these studied strains, showed significant degree of degrading *n*-alkane (C15–C23), almost degrading completely which were present in motor oil (Husaini et al. 2008). In general, the most frequently obtained strains among all fungi include *Penicillium* sp., *Trichoderma* sp. and *Aspergillus* sp. (Husaini et al. 2008). While filamentous fungi *Aspergillus* and *Penicillium* sp. are most commonly reported (Colombo et al. 1996). Despite the fact that fungi have been used for the biodegradation experimentation, very little to no knowledge of the degradation mechanism is known.

The available literature related to oxidation of alkene (olefins) focuses on terminal alkene (1-alkene) degradation and a little emphasis on internal alkene oxidation was reported (Morgan and Watkinson 1994). The biodegradability of alkene is affected by position of double bond, the more at the terminal end bond is present, the more will be the biodegradability. Four products are recognized upon aerobic oxidation, as a result of initial attack at double bond or saturated ends. Oxidation of saturated end (methyl groups) either forms an alkenol or fatty acid and a primary or secondary methyl ketone or alcohol, while oxidation of the double bond results in production of either a diol or an epoxide (Morgan and Watkinson 1994; Stroud et al. 2007).

4.3.2 Cycloalkanes

Cycloalkanes are saturated hydrocarbon molecules, forming a ring of carbon linked with single bond. The degradation of unsubstituted cycloalkane is more arduous than that of substituted cycloalkane (Morgan and Watkinson 1994). Degradation by co-oxidation occurs for cycloalkane. A cyclic alcohol and a ketone are formed, upon co-oxidation. The introduction of oxygen into cyclic ketone results in ring cleavage. This reaction is mediated by monooxygenases (Stroud et al. 2007).

4.3.3 Aromatics

Aromatics include one or more cyclic hydrocarbon rings, with or without any substitution of alkyl group. Generally, aromatics are considered more toxic than aliphatics. The simplest aromatic compound is benzene, but in crude oil alkyl-substituted is high in concentration compared to non-substituted, while more complex are PAHs, having 2 or more aromatic rings. Bacteria utilize different catabolic pathways for degradation of aromatics. Toluene, for example, is degraded by five different catabolic pathways (Harayama et al. 1999). TOL plasmid encodes one of such degradation pathways, in which intermediates are centred to TCA intermediate formation, via formation to benzyl alcohol, benzalehyde and benzonate. In case of *Pseudomonas putida*, two hydroxyl groups are introduced into toluene, resulting cis-toluene dihydrodiol. Cis-toluene dihydrodiol is transformed into 3-methylcatechol. *Pseudomonas mendocina* KR1 utilizes toluene 4-monoxygenase and covert toluene into p-cresol. Later, *p*-hydroxybenzoate is formed by the methyl side chain oxidation of p-cresol. *Pseudomonas pickettii* PKO1 oxidizes toluene to m-cresol by utilizing toluene 3-monoxygenase, which is later transformed, via monooxygenases, into 3-methylcatechol. *Bukholderia cepacia* G4 employs toluene 2-monoxygenase forming o-cresol, which further converted into 3-methyl-catechol (Harayama et al. 1999).

Fungi can also degrade toluene. *Mortierella isabellina* transformed toluene to benzyl alcohol (Holland et al. 1988). *Phanerochaete chrysosporium*, a white rot fungus, also mineralized toluene, but the pathway is not reported (Yadav and Reddy 1993). The degradation of toluene in these cases was due to co-metabolism (Prenafeta-Boldú et al. 2001). *Cladosporium sphaerospermum* was able to utilize toluene as a sole source of carbon (Weber et al. 1995). It was suggested for toluene that the initial oxidation occurred at methyl group, not at aromatic ring (Prenafeta-Boldú et al. 2001). However, a detailed pathway of degradation needs to be investigated.

Naphthalene, phenanthrene and other simpler PAHs are frequently degradable in aerobic conditions. In bacteria, dihydroxylation initiates degradation process at any one ring, resulting in dihydroxylated ring cleavage. The reaction occurs via multicomponent dioxygenases. Before the breaking of second aromatic ring, dismantling of carbon skeleton is produced by the ring cleavage (Saito et al. 1999). Lower solubility in water and absorptivity to solids are known features of PAHs containing four or more aromatic rings, which contribute negatively in biodegradation of such compounds. *Mycobacteria, Sphingomonas, Pseudomonas, Bacillus* and other bacterial strain are reported to degrade these higher molecular mass PAHs (Harayama 1997).

Degradation of PAHs has been investigated using fungi. Lignin peroxidase, phenoloxidase, and manganese-dependent peroxidase are important enzymes in lignolytic system, having low substrate specificity. These enzymes are responsible for one electron radical oxidation, which causes production of cationic radicals from contaminant, leading to formation of quinines (Vyas et al. 1994). Soil fungi were also reported to produce these lignolytic

enzymes under very low oxygen or microaerobic conditions (Silva et al. 2009). *Aspergillus* sp., *Trichocladium canadense* and *Fusarium oxysporum* are known to degrade low-molecular weight PAHs (2–3 rings). While *Verticullium* sp., *T. canadense*, *Achremonium* sp., and *Aspergillus* sp. were reported capable of degrading PAHs of high molecular weight (4–7 ring) (Haritash and Kaushik 2009).

Epoxides formation through cytochrome P-450 monooxygenases is also involved in degradation of aromatics, in general. The formed epoxides can be converted into hydroxyl derivatives or can be hydrolysed forming vicinal dihyrodiols. *Irpex lacteus,* a lignolitic fungus, degrade anthracene and phenanthrene. Major products after degradation include phenantherene-9, 10-dihydrodiol and anthraquinione. Cajthaml et al. (2002) proposed degradation pathway of anthracene and phenanthrene. Phenanthrene is converted into 9-Methoxyphenenthrene or phenenthrene-9, 10-dihydrodiol in presence of enzyme cytochrome P-450. Phenenthrene-9, 10-dihydrodiol is converted into 2-Hydroxy-2-carboxy biphenyl. *Phanerochaete chrysosporium, Bjerkandera adusta,* and *Pleurotus ostreatus* were among those white rot fungi which are extensively studied for the degradation of PAHs. Quinones, hydroxyl and dihydroxy-PAH were among most frequently isolated intermediates in PAHs degradation studies. There is no clear evidence whether these intermediates accumulate as dead end products or are further metabolized and mineralized (Cajthaml et al. 2002).

Yeast is the most frequently isolated fungi in petroleum-contaminated environment (Berdicevsky et al. 1993; Leahy and Colwell 1990). Yeast can co-metabolize PAHs with other carbon sources, as well as can also utilize PAHs as a sole source of carbon. Phenanthrene degradation rate of *Rhodotorula glutinis*, yeast was found to be equivalent to the degradation rate by *Pseudomonas aeruginosa* (Romero et al. 1998). It can be extrapolated that potential of each microbial phylum is diverse and have an unexploited potential that is needed to be investigated, especially fungi and algae which were not utilized to a good and comparable extent.

5 Conclusion

This review was an effort to harmonize and link previously reported studies that focused on the release, distribution, pollution and treatment of PAHs. It can help to identify the area of concern in terms of PAHs pollution of different environmental matrices, especially the biogeochemistry of the PAHs. A number of studies have proven that PAHs can cause problematic complications. The associated problems with PAHs treatment were also brought into discussion. In the light of these given fact based arguments, a proper

disposal methodology and treatment processes are of utmost importance, for the future proceedings in this domain. Not just the proper disposal and treatment methodology, but also understanding biogeochemical cycle with focus on the sources and methods through which PAHs are introduced into the environment can be beneficial for managing these tricky substances to a level where they are of least concern.

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