

# Polycyclic Aromatic Hydrocarbons Degradation Techniques: A Review

Luke N. Ukiwe<sup>1</sup>, Ubazue U. Egereonu<sup>1</sup>, Pascal C. Njoku<sup>1</sup>, Christopher I. A. Nwoko<sup>1</sup> & Jude I. Allinor<sup>1</sup>

<sup>1</sup>Department of Chemistry, Federal University of Technology, Owerri, Nigeria

Correspondence: Luke N. Ukiwe, Department of Chemistry, Federal University of Technology, P.M.B. 1526, Owerri, Nigeria. Tel: 234-806-419-2946. E-mail: luggil2002@yahoo.com

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## Abstract

The demand for processed petroleum products and agricultural produce has exposed our environment to polycyclic aromatic hydrocarbons (PAHs) contamination. PAHs stick to solid sediments and are ubiquitous including soil, water and air. Their presence in these media creates problems because consuming products obtained from these sources could be deleterious to human health since several of these compounds (benz(a)anthracene, benzo(a)pyrene, chrysene etc) have been implicated in causing tumors in animals and cancer in humans. The present review describes several remediation techniques which are efficient and cost effective in removing PAHs from the environment. Some of these conventional clean-up methods are not only environmental friendly; they also present a novel approach in reducing the ability of PAHs to cause prospective risk to humans and the ecosystem.

**Keywords:** atmosphere, contaminants, environment, hydrophobic, pyrene, pollutants, organics

## 1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are potent environmental pollutants that comprise fused aromatic rings. They are found almost everywhere in the environment and are typically formed during incomplete burning of organic materials such as wood, coal, oil, gasoline etc. PAHs are also found in crude oil, coal tar and asphalt (Fetzer, 2000). The presence of PAHs in the environment is related to human activities within the environment. Large concentrations of PAHs are expected to be present in urban areas and in areas where bush burning for agricultural farming is commonly practiced as well as in petroleum exploration and refining operations (Fetzer, 2000). Naphthalene is the simplest polycyclic aromatic hydrocarbon (PAH). PAHs are of great concern to humans since as pollutant, some have been identified as carcinogenic, mutagenic and teratogenic (Larsson, Sahlberg, Eriksson, & Busk, 1993). In the environment, PAHs are primarily found in soil, sediment and oily substrates. Their concentration in water or air is relatively small compared to soil. Natural crude oil and coal deposits contain significant amount of PAHs arising from chemical conversion of natural products molecules such as steroids (Roy, 1995). PAHs are also formed by incomplete combustion of carbon containing fuels such as fat. Forest fires and agricultural bush burning account for the largest volume of PAHs from any natural source in the atmosphere. The actual amount of PAHs emitted from forest fires and agricultural bush burning vary with the type and nature of the fire as well as the intensity of the fire (Platt & Mackie, 1980). Once exposed to the atmosphere, most of the pollutant do not degrade quickly and may thus reside in the environment for extended periods of time (Platt & Mackie, 1980). During this period, winds may distribute the pollutant over a large area in a global manner (Platt & Mackie, 1980).

PAHs' presence in fossil fuels such as coal and crude oil deposits occur due to low temperature combustion of organic material over a significant period of time. Since most oil deposits are trapped deep beneath layers of rock, there is little chance of the oil deposits emitting PAHs to the surface environment. However, some petroleum bodies such as tar-sand exist near the soil surface and are capable of contributing PAHs to both atmospheric and aquatic systems. Incomplete combustion at high temperature appears to be one of the major anthropogenic sources of environmental PAHs contamination. The production of PAHs during pyrolysis involves many sources which include pyrosynthesis and catalytic break down of petroleum products. PAHs compounds contain two to seven membered (fused) benzene rings. They are hydrophobic (they mix more easily with oil than water) compounds with aqueous solubility decreasing almost linearly with increase in molecular mass (Parish, Banks, & Schwab,

2009). The compounds may be classified as low molecular weights (LMW) or high molecular weights (HMW). LMW PAHs are those containing two or three benzene rings, while those with four or more benzene rings are called HMW PAHs. LMW PAHs are relatively water soluble, but those containing four or more rings are quite hydrophobic and insoluble (Cerniglia & Heitkamp, 1989). However, the higher the molecular weight of a PAH, the more likely it is to adsorb to soil organic matter. This tendency to strongly adsorb on particulate matter renders the HMW PAHs less available and thus less susceptible to remediation (Cerniglia & Heitkamp, 1989). HMW PAHs have high resonance energies due to the dense clouds of pi-electrons surrounding the aromatic rings making them persistent in the environment and recalcitrant to degradation (Johnson, Wick, & Harms, 2005). Another reason for the compounds to exhibit recalcitrant nature is their low aqueous solubility and high soil sorption (Parish, Banks, & Schwab, 2009). PAHs are affected by several physical, chemical and biological processes which alter their fate and transport in the subsurface environment. The nature of the subsurface environment determines if the individual compound may remain as a non-aqueous phase liquid, metabolized by microorganisms, taken up by plants, be volatilized into the interstitial void spaces, or be sorbed onto soil organic matter (Cerniglia & Heitkamp, 1989). However, desorption from the organic matter is a critical step in the degradability of PAHs (Cerniglia & Heitkamp, 1989).

A critical over-view of several degradation techniques has been presented in this review. These techniques include; chemical degradation, biodegradation, phytodegradation as well as combined degradation methods. Other developing degradation methods that has gained wide public acceptance include; solar ultraviolet radiation, direct photolysis and ultrasound frequency degradation. However, sonochemical degradation, photocatalytic degradation as well as current density enhanced degradation are novel approaches that have been tested successfully for the compound's removal.

### *1.1 Determination of PAHs*

Many analytical techniques have been applied in the determination of PAHs and their metabolites in contaminated systems. Ter-Laak, Agbo, Barendregt, and Hermens (2006) examined the use of solid-phase extraction (SPE) in measuring freely dissolved concentrations of PAHs in soil pore water. Some researchers have suggested that solid-phase microextraction (SPME) with gas chromatographic/mass spectrometric (GC/MS) analysis can achieve detection limit as low as nanograms per litre of PAHs and alkyl PAHs in sediment pore water (Hawthorne, Grabanski, Miller, & Kreitinge, 2005). In soil samples, high resolution gas chromatography-mass spectrometry (HRGC-MS) and liquid chromatography-fluorescence detection (LC-FD) have been applied successfully in measuring the final concentrations of PAHs (Berset, Ejem, Holzer, & Lischer, 1999). It was revealed that HRGC-MS has a high linear range compared to LC-FD. Hence, under practical considerations, HRGC-MS was regarded as a superior analytical technique than LC-FD (Berset, Ejem, Holzer, & Lischer, 1999). A recent study had noted that laser-induced fluorescence (LIF) spectroscopy is a mature technique for PAHs determination in terrestrial sediments (Grundl, Aldstadt, & Harb, 2003). In a related study, SPME coupled with LIF was applied successfully in in-situ sampling in an effort to develop a simple field-portable method to determine total dissolved PAHs concentrations in sediment pore water (Hawthorne, St. Germain, & Azzolina, 2008). It was evident that PAHs undergo a variety of processes resulting from chemical, biological or photochemical reactions. Hence, environmental conditions usually affect intermediate products of PAHs formed during degradation processes. A notable study by Dabroska, Kot-Wasik, and Namiesnik (2005) has revealed that different degradation pathways of PAHs require specialized analytical tools in their degradation studies. Jiang et al. (2007) also used GC-MS in analyzing sediment samples in a study aimed at characterizing the distribution of PAHs in sediment samples.

## **2. PAHs Degradation Techniques**

### *2.1 Chemical Degradation*

Determination of PAHs degradation in the environment is quite an onerous task. The occurrence of PAHs in anaerobic conditions depends on certain factors which include substrate interaction, pH and redox conditions (Chang, Shiung, & Yuan, 2002). Stimulation of PAHs degradation rate under sulphate reducing conditions have been examined (Bach, Kim, Choi, & Oh, 2005). PAHs in soil could be degraded through biotic processes. Oxidation reactions are viewed as the most effective in this regard, although some authors have suggested that photochemical reactions may also aid oxidative reaction processes (Kochany & Maguire, 1994). It must be noted that most oxidation reactions in the environment are initiated by oxidants such as peroxides ( $H_2O_2$ ), ozone ( $O_3$ ) and hydroxyl radicals generated by photochemical processes. The degradation pathways are such that the oxidation reaction involving hydroxyl radicals or  $O_3$  react with aromatic compounds such as PAHs at near diffusion-controlled rates by abstracting hydrogen atoms or by addition to double bonds (Haag & Yao, 1992). Ozone may attack double bonds directly or it can form reactive hydroxyl radicals (which attack double bonds) by

decomposing water (Legrini, Oliveros, & Braun, 1993; Gurol & Singer, 1982; Yao, Huang, & Masten, 1998a, 1998b). The reaction proceeds with complex pathways producing numerous intermediates. However, the final reaction products include a mixture of ketones, quinones, aldehydes, phenols and carboxylic acids for both oxidants (Lee, Iso, & Hosomi, 2001; Rivas, Beltran, & Acedo, 2000; Reisen & Arey, 2002; Koeber, Bayona, & Niessner, 1997). Photochemical degradation of PAHs often involves the same oxidative species that are produced during the pure chemical oxidation of PAHs. Consequently, the reaction products include similar complex mixtures (Barbas, Sigman, & Dabestani, 1996; David & Boule, 1993; Mallakin, Dixon, & Greenberg, 2000).

When PAHs undergo chemical reactions, they are transformed into other polyaromatic hydrocarbons (they do not lose their aromatic character). Their aromaticity is conserved since considerable amounts of energy are required to change an aromatic compound into a non-aromatic compound.

The localization energy concept has proven very effective in determining the positions of reaction molecules within the PAH structure. These positions could be determined by considering electron distribution over the PAH molecule. The localization energy isolates a pi-electron at the centre of a PAH molecule from the remaining pi-electron system (Dewar, 1952). The attacking species may be an electrophile or a radical. This attack leads to a degradation process of complete mineralization of the PAH molecule resulting in carbon dioxide (CO<sub>2</sub>), water (H<sub>2</sub>O), and other inorganic and organic compounds (Barbas, Sigman, & Dabestani, 1996; David & Boule, 1993). If the chemical oxidant is added in insufficient quantity, the PAH could be metabolically transferred into dead-end products which are resistant to further degradation. This dead-end product could build-up in the environment and become a source for further contamination if no remedial process (especially the presence of microbe) is available for their further degradation (Freeman & Harris, 1995). Ambrosoli, Petruzzelli, Minati, and Minati (2005) suggested that under denitrifying conditions, PAHs could be degraded through fermentative metabolism, while some studies have demonstrated that PAHs degradation in anaerobic environment is considered much slower than in aerobic environment (McNally, Mihelcic, & Lucking, 1991). Fenton's reagent has been shown to have observed efficacy in degrading PAHs (Nam, Sweetman, & Jones, 2009). Other chemicals used effectively to degrade PAHs include electron donors such as acetate, lactate and pyruvate (Bach, Kim, Choi, & Oh, 2005). Under both aerobic and anaerobic conditions, degradation of PAHs has been observed to increase by physical/chemical pretreatment of contaminated soil using phosphorus (P) (Haritash & Kaushik, 2009). Effects of carbon (C), nitrogen (N), and phosphorus (P) on PAHs degradation have also been investigated by several authors including (Ley, Bastiaens, Verstraete, & Springael, 2005; Quan et al., 2009). Further studies have revealed that addition of N and P to soil can help to evaluate the response of phenanthrene degradation (Johnson & Scow, 1999). Nitrate reduction has been the focus of so many researches (Mihelcic & Luthy, 1988; Rockne & Strand, 1998). Another study by Leduc, Samson and Al-Bashir (1992) had noted that acenaphthrene, fluorene and anthracene were capable of being degraded in denitrifying environment. Lovley, Woodward, and Chapelle (1994) have reported that ferric oxide reduction process has a limiting factor when applied in PAHs degradation. This limiting factor stems from the fact that ferric oxide is sparingly soluble in water. However, the study went further to note that chelating agents are added to subsurface environment to enhance solubility of ferric oxides and hence increase its bioavailability.

As already noted, the efficiency of PAHs chemical degradation is limited by their low aqueous solubility and vapor pressure (Luning & Pritchard, 2002). Nonetheless, surfactants have been reported to contain properties that overcome problems related to PAHs low aqueous solubility (Boochan, Britz, & Stanley, 1998). Surfactants enhance the solubility of hydrophobic compounds (Boochan, Britz, & Stanley, 1998). Several studies have stressed the importance of surfactants to increase the solubility of PAHs by decreasing the interfacial surface tension between PAH and the soil/water interphase (Li & Chen, 2009). In one study, the efficiency of surfactants in enhancing desorption of PAHs from contaminated soils relative to water was evaluated (Zhou & Zhu, 2009). The study concluded that the efficiency of surfactant enhanced desorption for contaminated soils depended on the component characteristics of soil-surfactant-PAHs system and thus desorption efficiency show a strong dependence on the soil composition, surfactant structure, and PAH properties (Zhou & Zhu, 2009). Addition of non-ionic surfactant as additives to soil has positive effect on PAHs degradation (Grimberg, String-fellow, & Aitken, 1996; Volkering, Breure, Van Andel, & Rulkens, 1995). However, some researchers have reported negative or negligible effects of adding surfactants to soil substrate (Ghosh, Yeom, & Shi, 1995; Laha & Luthy, 1992). Possible reason for this negativity includes; the competition for substrate utilization and toxicity of the surfactants towards PAHs-degrading bacteria in the soil matrix (Liu, Zhu, & Shen, 2001). Hence, PAHs-degradation process involving surfactant utilization need to be optimized for each of the factors influencing degradation including, surfactant type and concentration, PAH specificity as well as presence of host

bacteria (Jin, Juang, Jing, & Ou, 2007).

## 2.2 Biodegradation

Biodegradation is one of the forms of bioremediation applied to treat soils, water or sediments contaminated with PAHs. It is the use of microorganisms to degrade or detoxify environmental pollutants (Bamforth & Singleton, 2005). Biodegradation is also a clean-up method that presents the possibility to eliminate organic contaminants with the aid of natural biological activity available in the substrate (Zeyaullah et al., 2009). The microorganisms used for biodegradation should be indigenous to the contaminated area or site (Das & Chandran, 2011). It is expected that the bacteria be able to degrade the contaminant by multiplying in population and then decline when the contaminant is finally degraded (Mougin, 2002). The products of complete mineralization of the pollutant by biodegradation process include; CO<sub>2</sub>, H<sub>2</sub>O and cell biomass (Gratia et al., 2006). The optimization of biodegradation process involves many factors among which are the existence of a microbial consortia capable of degrading the pollutant, the bioavailability of the contaminant to microbial attack and certain environmental factors (soil type, temperature, soil pH, oxygen level of soil, electron acceptor agents, nutrient content of soil) contributing to microbial growth (Gratia et al., 2006).

Many researchers are of the opinion that certain bacteria isolates are capable of degrading PAHs. Of particular note are the studies carried out by Punapayak, Prasongsuk, and Messner (2009) and Abd-Elsalam, Hafez, and Hussain (2009). Punapayak, Prasongsuk, and Messner (2009), investigated the use of laccase enzyme produced from an isolate of the white rot fungus *Genoderma lucidum*. It was revealed that *G. lucidum* degrade anthracene completely with or without the addition of a redox mediator. However, Abd-Elsalam, Hafez, and Hussain (2009), concluded that *Escherichia coli*, *Alcoligenes* sp., and *Thiobacter subterraneus* were efficient isolates for degrading anthracene and phenanthrene. A number of studies have reported extensively on a variety of other bacterial species that have been isolated and noted to possess the ability to utilize PAHs as energy source (Cerniglia, 1992; Kiyohara, Nagao, & Yana, 1982; Sahseverino, Applegate, King, & Saylor, 1993; Zhao, Wu, & Wang, 2009; Zhang et al., 2009; Ling et al., 2011; Zhao et al., 2008). Some microorganisms mainly from the genera *Pseudomonas* and *Mycobacterium* have been found capable of transforming and degrading PAHs under aerobic conditions (Mrozik, Piotrowska-Seget, & Labużek, 2008). It is also evident that anthracene could be completely mineralized by *Sphingomonas*, *Nocardia*, *Beijerinckia*, *Paracoccus*, and *Rhodococcus* with dihydriol as the initial oxygenated intermediate (Evans, Fernley, & Griffiths, 1965; Dean-Ross, Moody, & Freeman, 2001; Moody, Freeman, Doerge, & Cerniglia, 2001; Teng et al., 2010). The ultimate goal of any remediation process should not be limited to removing contaminants from polluted substrates but should also include restoring the ability of the soil to function according to its potential (Epelde, Mijangos, Becenil, & Garbisu, 2009). In this regard, the bioavailability of PAHs becomes a very important factor to consider. Bioavailability of PAHs in biodegradation is determined by certain complex interactions between biotic and abiotic factors. Biotic factors affecting bioavailability include; the metabolic ability of microorganisms to degrade PAHs as well as the ways in which the bacteria encourage PAHs accessibility. One way by which microbes encourage PAHs accessibility is by the production of biosurfactants. Biosurfactants are produced to increase the solubility of insoluble substrates or solubilized (emulsify) insoluble substrates in order to enhance their direct contact between microorganisms and contaminants (Mulligan, 2005). Evidence have been accumulating to suggest that certain microorganisms namely; *Bacillus subtilis*, *Pseudomonas*, *Aeruginosa* and *Torulopsis bombicola* could produce bioremediation surfactants such as surfactin, rhamolipid and sophorolipid capable of improving bioremediation by solubilizing PAHs into the aqueous medium and enhance their bioavailability for degradation (Cottin & Merlin, 2007; Kuyukina et al., 2005).

## 2.3 Phytodegradation

This is a process whereby plants are used in-situ as well as their associated microorganisms to extract, sequester or detoxify pollutants from contaminated systems (Epuri & Sorenson, 1997). Phytodegradation also referred to as phytotransformation is an important phytoremediation process which indicates the role of internal plant mechanisms and processes in removing contaminant from substrates (Newman & Reynolds, 2004). Research has indicated that various grasses and leguminous plants are potential candidates for phytodegradation of organics (Adam & Duncan, 1999). Some tropical plants have also been reported to show effective degradation tendency due to inherent properties such as deep fibrous root system and tolerance to high hydrocarbon and low nutrient availability (Dzantor, Chekol, & Vough, 2000). Recently published data have revealed that the tall fescue grass (*Festuca arundinacea*) and switch grass (*Panicum virgatum*) are capable of degrading about 38% of pyrene in 190 days (Chen, Banks, & Schwab, 2003). Other studies involving pyrene degradation include that of Chouychai et al. (2009) and Cheema et al. (2009) who documented evidence showing plant enhanced phenanthrene and pyrene degradation in acidic soil as well as degradation of phenanthrene and pyrene in spiked soils by single and

combined plants cultivation. These authors all agreed that the presence of vegetation such as corn (*Zea mays*), alfalfa (*Medicago sativa*) and rape seed (*Brassica napus*) significantly enhanced the adsorption of PAHs from contaminated soils. Moreover, *F. arundinacea* has been reported to show promising efficiency in promoting phytodegradation of PAHs in contaminated soils (Cheema et al., 2008). Meanwhile, it has been suggested that rice (*Oryza sativa*) is able to degrade PAHs successfully (Du et al., 2011). The effectiveness of phytodegradation has also been observed when the process was applied as a secondary treatment process for decontamination of PAHs composted soils (Parish, Banks, & Schwab, 2004). However, in contrast to the study of Parish, Banks, and Schwab (2004), some studies have documented phytodegradation as a primary remediation technology and a final polishing step for treatment of soil contaminated with PAHs (Pradham, Conrad, Paterek & Srivastava, 1998). Reduction of PAHs concentration was evident after six months of treatment with *P. virgatum* and little bluestem grass (*Schizachyrium scoparium*). In a related study, Campbell, Paquin, Awaya, and Li (2002) noted that using industrial hemp (*Cannabis sativa*) in treating PAHs contaminated soil, led to reduced concentrations of benzo(a)pyrene and chrysene. Recent advances in phytodegradation studies have come to light in the application of rye grass (*Lolium multiflorum*) and bermudagrass (*Cynodon dactylon*) in degrading alkylated two ring naphthalenes (White, Wolf, Thoma, & Reynolds, 2006). In their contribution on distribution of PAHs in sub-cellular root tissue, Kang, Chen, Gao, and Zhang (2010) and Ward, Singh, and Van Hamme (2003) had revealed that using *L. multiflorum*, pyrene was most adsorbed in the root of the plant than other PAHs. Previous studies from Simonich and Hites (1994), Bakker, Vorenhou, Sum, and Kollöffel (1999) and Gao and Zhu (2004) are of the opinion that the efficiency of plant uptake and metabolism of PAHs depended on the morphology of the plant system.

The efficiency of water hyacinth (*Eichhornia crassipes*) in degradation of organics has been investigated by Xia (2008). The plant is also reported to accumulate high levels of five and above rings PAHs as opposed to two and three rings compounds (Moustafa & Shara, 2009). Wolverson (1975), showed that *E. crassipes* was able to adsorb organics and rapidly metabolize these to other components, while in a follow-up study, Wolverson & McDonald (1976) had demonstrated that the plant can adsorb and metabolize phenols and other trace organics. According to Nesterenko, Kirzhner, Zimmels, and Armon (2012), *E. crassipes* devoid of rhizospheric bacteria reduced about 45% of naphthalene in waste water in 7 days. Some recognized studies have shown that *E. crassipes* could improve the quality of oil-refinery waste water by decreasing petroleum hydrocarbons by about 18% (Tang & Lu, 1993). Nor (1994), shared the opinion that the plant has tremendous capability to adsorb phenolic compounds as well as heavy metals simultaneously. Recent findings have suggested that adsorption of hydrocarbons by *E. crassipes* is dominated by Van Der Waals forces (Lin & Zheng, 2003). Hence, the plant has capability to adsorb other compounds such as inorganic nutrients and pesticides (Reddy, Agami, & Tucker, 1989; Xia & Ma, 2006; Rosas, Carbajal, & Gómez, 1984; Ebel, Evangelou, & Schaeffer, 2007; Ghabbour, Davies, Lam, & Vozzella, 2004).

#### 2.4 Combined Degradation

This is a novel degradation method whereby two or more degradation approaches are applied to remove PAHs from contaminated systems. It has the advantage over other degradation methods since it is regarded as efficient and cost effective, leaving behind no dead-end products capable of further contamination of the substrate after the clean-up exercise is over. Combined chemical pre-oxidation and bioremediation is a notable degradation approach investigated by Kulik, Goi, Trapido, and Tuhkanen (2005). Other studies in this regard include anaerobic digestion and ozonation (Bernal-Martínez, Carrière, Patureau, & Delgenè, 2005), biodegradation and modified Fenton reagent (Nam, Rodriguez, & Kukor, 2001), biological, chemical and electrochemical treatment (Zheng, Blais, & Mercier, 2007) as well as Fenton reagent versus ozonation (Goi & Trapido, 2004). A growing body of data have been reporting on the use of combined vegetation establishment with chemicals in degradation of PAHs (White, Wolf, Thoma, & Reynolds, 2006; Pan et al., 2009; White, Wolf, Thoma, & Reynolds, 2006) reported that a combination of *L. arundinacum* and *L. multiflorum* mixture with fertilizer successfully degraded two rings PAHs such as naphthalene. In a separate study, Pan et al. (2009) had observed that *B. napus* degraded PAHs in humic acid environment. Successes in combined degradation of PAHs have been documented using pressure assisted ozonation (Hong, Nakra, Jimmy, & Hayes, 2008) and integrated treatment using soil washing, ozonation, and biological treatment of substrate (Haapea & Tuhkanen, 2006). Oxidation using ozone in the presence of sand was examined by Choi et al. (2001), while combined treatment using sequence extraction with surfactant-electrochemical degradation was successfully employed by Alcántara, Gómez, Pazos, and Sanromán (2008). Recent developments in the study of combined degradation method have come to light following reports published by Bernal-Martínez, Patureau, Delgenè, and Carrière (2009) and Bernal-Martínez, Carrière, Patureau, and Delgenè (2007) in the use of anaerobic digestion with recirculation of ozonated digested sludge and

anaerobic digestion using ozone pre-treatment. Combined chemical and phytodegradation using inorganic nutrients such as  $\text{NaNO}_3$ ,  $\text{Na}_2\text{SO}_4$  and  $\text{Na}_3\text{PO}_4$  each with *E. crassipes* is an evolving innovative approach that is beginning to gain wide public approval. Ukiwe, Egereonu, Njoku, and Nwoko (2013) had documented evidence showing that a combination of each of the above mentioned inorganic nutrients together with *E. crassipes* is capable of degrading about 95% of PAHs in soil leachate, while the plant uses same nutrients as energy source leaving behind no by products.

### 2.5 Other Established Degradation Techniques

Solar ultraviolet radiation has been shown to degrade and alter the quantity of organic pollutants such as PAHs (Bertilsson & Widerfalk, 2002). Photochemical degradation of anthracene and phenanthrene was noted to be possible under the influence of humic acid (Bertilsson & Widerfalk, 2002). Direct photolysis of PAHs has also been observed under simulated solar radiation with pyrene degrading at a faster rate than phenanthrene and naphthalene (Jacobs, Weavers, & Chin, 2008). Similarly, ultra sound frequencies have been revealed to generate complete degradation of PAHs under operating conditions of 40 °C and applied current of 150 W (Psillakis, Goula, Kalogerakis, & Mantzavinos, 2004). Wheat and Tumeo (1997) reported on the effectiveness of using sonochemical method to degrade phenanthrene and biphenyls in aerated aqueous solutions in the presence of  $\text{Fe}^{3+}$  ions. Further studies by Wang, Chen, and Yao (2003) and Manariotis, Karapanagioti, and Chrysikopoulo (2011) investigated sonochemical degradation of PAHs using high frequency ultrasound. Published data by Wang, Chen, and Yao (2003) and Manariotis, Karapanagioti, and Chrysikopoulo (2011) noted that the presence of chlorinated solvent during sonication resulted in the formation of solvent radicals which react with PAHs leading to the build-up of chloro-PAHs by-products which are degraded forms of the PAHs compound. Gordon and Cain (2003) documented observations supporting the already held belief that titanium film annular photocatalytic reactors are able to degrade PAHs in dilute water streams. Nevertheless, in their separate contribution, Alshawabkeh and Sarahney (2005) examined the effect of current density on enhanced transformation of naphthalene and concluded that almost 88% of the compound was degraded after 8 h when the current density was increased from 13-18.2  $\text{mA L}^{-1}$ , making this degradation approach one of the ideal novel processes of PAHs decontamination.

### 3. Conclusion

Removing PAHs from the environment is a very difficult task. Hence it is important to have a thorough understanding of the mechanism of the various degradation processes. The present study thus note that in-as-much-as each of these protocols in their merit are effective in depolluting PAHs from contaminated waste streams, the combined chemical and phytodegradation approach appears to be the most efficient and cost effective environmental friendly method to decontaminate PAHs from substrates. Firstly, it is a green degradation method that is mindful of the environment and secondly, no dead-end products are produced to initiate further contamination of the environment.

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Polycyclic aromatic hydrocarbons (PAHs) and characteristics of their chemical structure. Polycyclic aromatic hydrocarbons (PAHs) are a large group of organic compounds with two or more single or condensed benzene rings. PAHs and their hybrid forms are part of the complex carbonaceous materials of the Earth's crust and landscape envelope in the form of dispersed bituminous substances, oils, bitumens, soil humus components, air aerosols, plant and animal tissue lipids [4]. These are high-molecular organic compounds containing in their structure several benzene rings connected together or sequentially. The degradation of PAHs by bacteria has been well examined, and the metabolic pathways have been elucidated [25, 26]. The degree of polycyclic aromatic hydrocarbon contamination of environmental matrices has increased over the last several years due to increase in industrial activities. Interest has surrounded the...  
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