# Advances in water treatment technologies for removal of polycyclic aromatic hydrocarbons: Existing concepts, emerging trends, and future prospects

Adedapo O. Adeola [1] and Patricia B.C. Forbes [1*]

[1] *Department of Chemistry, Faculty of Natural and Agricultural Sciences, University of Pretoria, Lynnwood Road, Hatfield, Pretoria 0002, South Africa.*

## Abstract

In the last two decades, environmental experts have focused on the development of several biological, chemical, physical and thermal methods/technologies for remediation of PAH polluted water. Some of the findings have been applied to field-scale treatment, while others have remained as prototypes and semi-pilot studies. Existing treatment options include extraction, chemical oxidation, bioremediation, photocatalytic degradation, and adsorption (employing adsorbents such as biomass derivatives, geosorbents, zeolites, mesoporous silica, polymers, nanocomposites and graphene-based materials). Electrokinetic remediation, advanced phytoremediation, green nanoremediation, enhanced remediation using biocatalysts, and integrated approaches are still at the developmental stage and hold great potential. Water is an essential component of the ecosystem and highly susceptible to PAH contamination due to crude oil exploration and spillage, and improper municipal and industrial waste management, yet comprehensive reviews on PAH remediation are only available for contaminated soils, despite the several treatment methods developed for the remediation of PAH polluted water. This review seeks to provide a comprehensive overview of existing and emerging methods/technologies, in order to bridge information gaps towards ensuring a green and sustainable remedial approach for PAH contaminated aqueous systems.\

**Keywords:** *environment; pollution; polycyclic aromatic hydrocarbons; remediation; water treatment.*

## 1. Introduction

PAHs are hydrocarbons containing two or more benzene rings fused together with C-C bonds, which have unique physicochemical characteristics (Mohan et al., 2006; Okere, 2011). They are hazardous organic micropollutants, which are ubiquitous and recalcitrant to degradation (Duan *et al.,* 2015; Ghosal *et al.,* 2016). They are commonly found in water bodies with proximity to crude oil exploration, gas production, and wood/coal processing industries, for example. (Abdel-Shafy and Mansour, 2016; Sun *et al.*, 2009; Zhao *et al.*, 2011a). Some PAHs possess carcinogenic toxicities even at very low concentrations and humans are hazardously exposed through several routes – air (atmospheric deposition, inhalation etc.), water (domestic, recreational use etc.), food, and occupational exposures. However, one of the core routes of human exposure is through polluted water (Wang *et al.*, 2009; Wu *et al.*, 2011a). For simplicity, PAHs can be classified into two groups which are the lower molecular weight (LMW), structurally 2-3 ringed PAHs which are less toxic than the second class, the higher molecular weight (HMW), 4-7 ring PAHs which are more resistant to degradation and have higher carcinogenicity (Kuppusamy *et al.,* 2016).

In water bodies, the concentrations of PAHs range widely from 0.03 ng/L {Southeastern Sea, Japan} (Hayakawa et al., 2016) to 753 ng/L {Yellow River Delta, China} (Yuan *et al.*, 2014) to as high as 16.59 mg/L {Limpopo Province, South Africa} (Edokpayi *et al*., 2016). Furthermore, the bioconcentration of ∑16 PAHs in aquatic animals (fish) ranges from 11.2 ng/g (*Cynoscion guatucupa*, South America) to as high as 4,207.5 ng/g (*Saurida undosquamis*, Egypt) (Mojiri *et al.*, 2019). Hundreds of different PAHs and derivatives exist, however, the United States Environmental Protection Agency (US EPA) named 16 PAHs as priority pollutants (USEPA, 2000).

Water is pivotal to the sustenance of life and creation of energy, however, potable water suitable for domestic use including drinking, was estimated to be around 0.01 % of the total (Ritchie and Roser, 2020). Moreover, water is unevenly distributed around the world, as a result, there are regions faced with water shortage, particularly in low latitudes and millions of people globally are suffering due to a shortfall of clean and safe portable water (WHO/UNICEF, 2012). Rapid growth in industrialization, population, and urbanization have significantly spurred severe water pollution. Remediation of PAH contaminated water systems is important due to the ability of PAHs to bioaccumulate and the risk they pose to human health (Figure 1) (García-Suástegui *et al.*, 2010; Lawal, 2017; Olsson *et al.*, 2010). The United Nations Sustainable Development Goals (SDGs) prioritized the need to address the mitigation of numerous challenges associated with water, which include flooding, drought and water pollution. Although some successes have been recorded, there is still a need for the development of efficient, ecofriendly, affordable and sustainable means to achieve the SGDs by 2030 (United Nations Information Center, 2017).

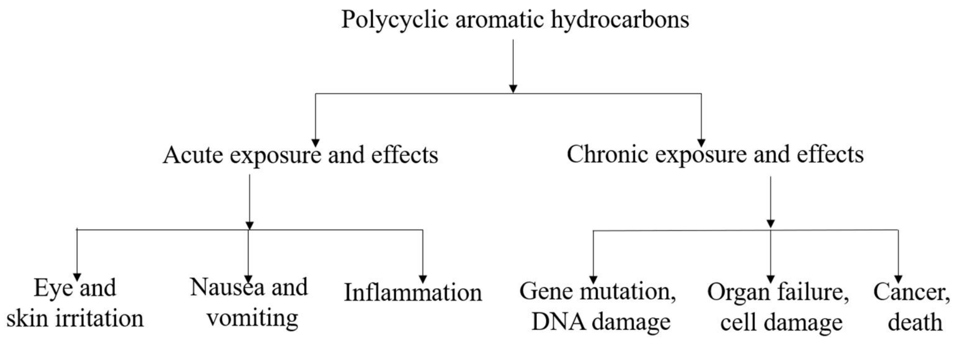

***Figure 1:*** *Flow chart showing the effect of acute (short-term) and chronic (long-term) exposure to PAHs.*

Polycyclic aromatic hydrocarbons are hydrophobic organic compounds, therefore they are often deposited on sediments and adhere to solid particles in aquatic environments (Rockne *et al.*, 2002;

Maletic *et al.*, 2019). Contaminated soil and sediment could potentially contaminate ground and surface water via leaching, runoff and re-suspension. Therefore, many reviews have been published on the treatment methods and strategies which can be employed for PAH contaminated soils as well as sediments (de Boer and Wagelmans, 2016; Gan *et al.*, 2009; Kuppusamy *et al.*, 2017; Maletic *et al.*, 2019; Mohan *et al.*, 2006; Samanta *et al.*, 2002; Wise, 2000). However, there is no comprehensive literature review which focuses solely on the treatment technologies for PAH polluted water. This review therefore focuses on target-specific existing and emerging technologies in this regard, and highlights successes, limitations, areas of improvement, and the potential field application of the methods. Prospects for the development of innovative approaches to enhance the efficiency of PAH remediation are also explored. This review thus provides holistic insights and a fundamental basis to inform decision making with respect to the development of suitable, ecofriendly and cost-effective technique(s) that can be adopted for the treatment of PAH contaminated water.

## 2.0. Extraction and membrane technologies

Solid-phase extraction (SE/SPE) is a clean-up technique used for LMW and HMW PAHs based on the preferential solubility of PAHs in organic solvents. The use of basic apparatus such as a separatory funnel and rotary evaporator, along with a suitable nonpolar solvent such as hexane, dichloromethane or mixture of both, have been used to isolate PAHs from water (Gong *et al.*, 2006). This technique often involves SPE or gel permeation chromatography (GPC) with different adsorbent phases, while others include membrane-based extractions such as liquid-phase micro-extractions and membrane-assisted extraction (Egli *et al.*, 2015; Hussain *et al.*, 2018; Martinez *et al.*, 2004). The selective removal of PAHs from water has been optimized and over 90 % extraction efficiency has been recorded, as well as the capacity of SPE to isolate target PAHs in trace amounts

(Egli *et al.*, 2015). Graphitic carbon nitride derivatives have been reported as sorbents for solid-phase microextraction of PAHs, with recoveries in the range of 83.3 to 103.0 % (Nian *et al.*, 2019; Feng *et al.*, 2020). However, SPE and other forms of extraction have only been applied for analytical determination and monitoring of PAHs in water. This is due to its lack of robustness and capacity to deal with a large volume of water; also, the cost of solvents and their environmental impact makes it uneconomical to adopt solid-phase extraction principles for wastewater treatment plants.

Several membrane technologies have been reported in the literature for the treatment of PAH polluted water, including microfiltration (Klejnowski *et al.*, 2010), ultrafiltration (Dudziak *et al.*, 2003; Smol and Wlodarczyk-Makula, 2012), nanofiltration and reverse osmosis (Smol *et al.*, 2014a). PAHs have a molecular size smaller than the pore radius of microfiltration and ultrafiltration membranes, but studies have shown that they retain PAHs to a large extent, via hydrophobic effects and adsorption onto the membrane surface (Smol and Wlodarczyk-Makula, 2012). Unlike micro- and ultra-filtration processes, the mechanism of nanofiltration is mainly size exclusion, which indicates that its efficiency is independent of process variables such as discharge or influent pressure, concentration, pH etc. (Smol *et al.*, 2014b). Reverse osmosis has been employed for the treatment of water and landfill leachates, and improved efficiencies are found with higher molecular weight PAHs, because the process is controlled by sieving and diffusion mechanisms. Overall, reports show that PAH removal efficiency increases in the order: microfiltration < ultrafiltration < reverse osmosis < nanofiltration (Dudziak *et al.*, 2003; Smol *et al.*, 2014a), although integrated systems such as coagulation-membrane separation provide the best results (> 98 %) (Smol *et al.*, 2014b). Membrane fouling and operational costs are drawbacks of these processes, although back-washing assists with fouling, membrane performance often diminishes over time.

### 3.0. Chemical oxidation processes

The treatment of PAH contamination in soil and municipal/industrial landfill leachates has been reported using basic and advanced chemical oxidation techniques, and they proved successful with over 90 % degradation (Li *et al.*, 2016; Wu *et al.*, 2011c; Yap *et al.*, 2012).

Chemical oxidation techniques involve the use of oxidants such as hydrogen peroxide (Flotron *et al.*, 2005), activated persulfate (Huling and Pivetz, 2006), ozone (Lian *et al.*, 2017; Rivas *et al.*, 2009) and Fenton's reagent (Zhang *et al.*, 2019). These techniques involve the generation of very reactive radicals (e.g. $^{\bullet}OH$, $SO_4^{\bullet -}$, $O_3^{\bullet}$ radicals) and other reactive species (e.g., persulfate anion, peroxides), which are responsible for the breakdown of the aromatic rings of PAHs (Figure 2). Merits of chemical oxidation over conventional remediation methods include relatively shorter treatment time, effectiveness for remediation of a broad range of PAHs due to high radical reactivity, and *in situ* degradation of contaminants. However, the application of very reactive oxidizing agents is complicated due to oxidation of non-target constituents such as dissolved/particulate organic matter, the volume of water to be decontaminated, and corrosiveness makes it unsuitable for treatment of portable water. Furthermore, $H_2O_2$ requires careful pH control (i.e. 2.5-4.0), and is quite expensive (Flotron *et al.*, 2005). $Cl^-$ inhibits the destruction of organic contaminants by persulfate based advanced oxidation processes (AOPs) (Deng and Zhao, 2015). These factors provide constraints to the use of $H_2O_2$ and persulfate for PAH degradation, thus making these oxidants inappropriate or uneconomical for large-scale water remediation (Huang *et al.*, 2003). Advanced methods involving the combination of Fenton oxidative-coagulation and ultraviolet photo-Fenton processes also recorded significant success in the removal of PAHs in solid waste and leachates (Li *et al.*, 2016). However, there are limited reports on the use of chemical oxidation techniques for the remediation of PAHs in water.

## 4.0. Bioremediation

Bioremediation is regarded as an efficient means of degrading organic compounds, including PAHs, in environmental media. The technique involves the use of microorganisms, plants, and enzymatic reactions in the detoxification and degradation of environmental contaminants in water and other environmental compartments (Ghosal *et al.*, 2016; Gouma *et al.*, 2014). Fungi such as *Peniophora gigantea, Phanerochaete chrysosporium, Pycnosporus coccineus, Trametes versicolor*, and others have been reported to efficiently degrade many organic pollutants, especially PAHs (Silva *et al.*, 2009). Bacterial species (*Aspergillus sp*., *Trichocladium sp*., *Fusarium sp., and Pseudomonas sp.)* are also capable of degrading PAHs (Quinn *et al.*, 2009; Soleimani, 2012; Sun *et al.*, 2014; Wu *et al.*, 2013).

A recent study revealed that degradation of PAHs by *Aeromonas hydrophila*, *Bacillus megaterium, Raoultella ornithinolytica* and *Serratia marcescens* recorded over 90 % degradation efficiency for fluorene and acenaphthene (Alegbeleye *et al.*, 2017). However, certain environmental variables such as temperature and pH, were reported to have a considerable influence on the efficiency of the bioremediation processes. Specifically, temperatures above room temperature between 30 ºC and 38 ºC were optimum for degradation of PAHs, due to enhanced microbial growth (Abdou, 2003; Antizar-Ladislao *et al.*, 2008; Moscoso *et al.*, 2013). However, bioremediation is not a rigid and robust technique, as was evident in a study carried out at slightly higher temperature between 40 ºC and 45 ºC, which recorded a significant decline in PAH degradation from 92 % (37 ºC) to 73 % (45 ºC). Increase in temperature reduces the solubility of oxygen, which leads to a decrease in dissolved oxygen available for microbial growth in the bioreactor (Alegbeleye *et al.*, 2017; Viñas *et al.*, 2005).

## 5.0. Photocatalytic degradation

The synergistic role of photocatalysis and chemical catalysts on PAH degradation has been investigated, with the aid of UV irradiation and titanium oxide ($TiO_2$) catalyst (Zhang *et al.*, 2008). The photocatalytic degradation of phenanthrene, pyrene, and benzo(a)pyrene under UV irradiation followed the pseudo-first-order kinetics pathway and was accelerated by the addition of $TiO_2$, due its established catalytic activity (Garg *et al.*, 2019; Wu *et al.*, 2004; Zertal *et al.*, 2004). Different PAHs degrade to various extents under varying UV radiation intensities whilst an increase in $TiO_2$ dosage from 0.5 to 3 wt% had an insignificant effect on PAH photodegradation which was highest under acidic pH conditions (Zhang *et al.*, 2008).

Composites with photocatalytic properties have been synthesized and applied to PAH degradation (e.g. $Pt/TiO_2$-$SiO_2$) (Luo *et al.*, 2015). The correlation between molecular structure and photocatalytic degradability of PAHs was also investigated. Naphthalene, fluorene, phenanthrene, pyrene, benzo[a]pyrene, and dibenzo[a,h]anthracene degraded using a $Pt/TiO_2$-$SiO_2$ suspension under UV irradiation. Results revealed improved efficiency of the process for biorefractory HMW PAHs with the inclusion of $Pt/TiO_2$-$SiO_2$, while that of LMW PAHs were reduced under the same conditions. A pseudo-first-order equation fit both the photolysis and photocatalysis of fluorene which displayed a different trend, by fitting best to first-order kinetics**.**

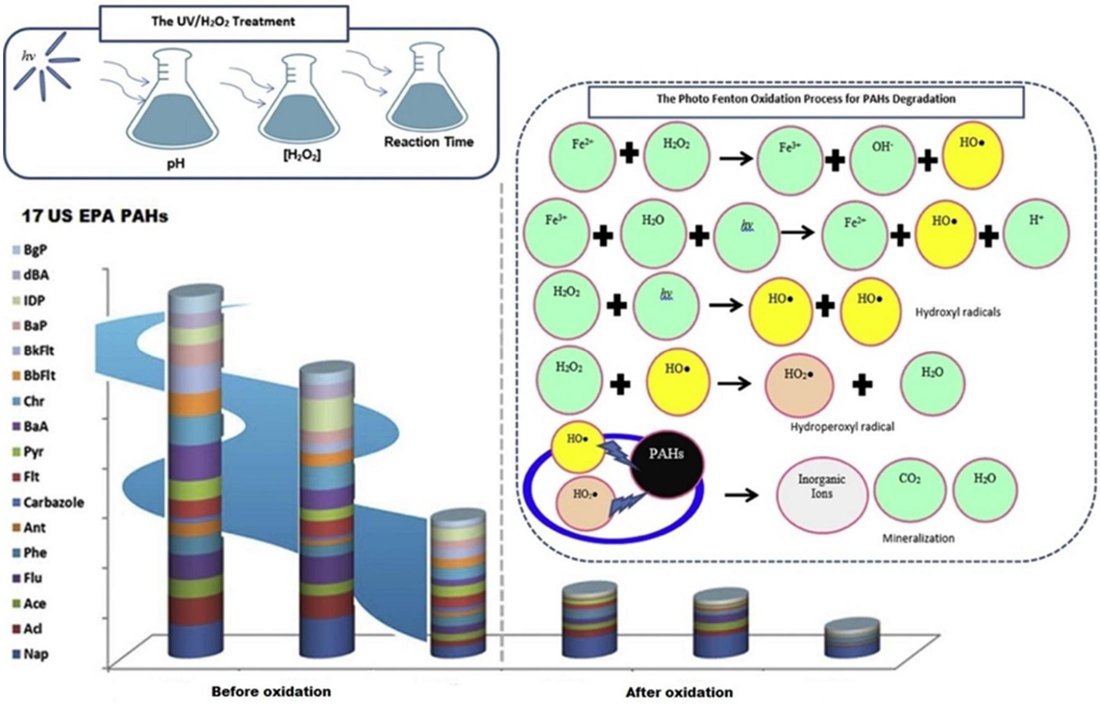

***Figure 2:** Ultraviolet light-assisted chemical oxidation process for PAH degradation. (Adapted with slight modification from Abd Manan, T. S. B., Beddu, S., Khan, T., Wan Mohtar, W. H. M., Sarwono, A., Jusoh, H., Mohd Kamal, N. L., Sivapalan, S. & Ghanim, A. A. J. (2019). MethodX. 6, 1701-1705. Copyright 2019 Elsevier.)*

A model involving the use of molecular descriptors was established using the difference between highest occupied molecular orbital ($E_{\text{homo}}$) and lowest unoccupied molecular orbital ($E_{\text{lumo}}$), which equates to GAP (GAP = $E_{\text{lumo}} - E_{\text{homo}}$). This was compared with the maximum GAP (7.4529 eV) of PAHs (for dibenzo[a,h]anthracene) and the minimum GAP (8.2086 eV) of PAHs (for pyrene) which was degraded. This was further used to predict the photocatalytic degradation of 67 PAHs (Luo *et al.*, 2015). A $TiO_2$-graphene composite has also been used for photocatalytic treatment of PAHs in water and 80 % efficiency was achieved in 2 hours (Bai *et al.*, 2017).

## 6.0. Adsorption processes

Contaminated water can be treated in several ways based on the target pollutant (Cohen-Tanugi and Grossman, 2012; Kemp *et al.*, 2013; Shannon *et al.*, 2008), however, adsorption processes have been widely used and possess several advantages over other techniques (Kemp *et al.*, 2013). The adsorption process is a surface phenomenon that involves the adherence of pollutants onto the surface of an adsorbent via physical, chemical and/or electrostatic attraction. Adsorption of organic compounds can be influenced by many process variables such as temperature, pH, concentration of sorbate, contact time, particle and pore size, temperature, and other physicochemical properties of the adsorbate and adsorbent (Adeola and Forbes, 2019). Several materials have been developed over the last two decades for the sorption of PAHs from aqueous system, many of which are discussed in this section.

## 6.1. Agricultural waste and biomass

Various absorbents for the remediation of PAHs have been derived from agricultural waste such as coconut shells, rice husks, sugar cane bagasse, peat, sawdust etc. (Amstaetter *et al.*, 2012; Crisafully *et al.*, 2008; Olivella *et al.*, 2011). The decision to explore these materials was driven by the concept of green and sustainable chemistry, which promotes the conversion of ‘waste to wealth ‘as an economical path to waste management and ecofriendly material science (Xu *et al.*, 2019). Low-cost adsorbents with high porosity and efficiency have been generated from these materials via simple thermal and/or chemical reaction processes, which has led to improved morphology of the biomass-derived sorbents for water treatment applications (Bhatnagar and Sillanpää, 2010; Pérez-Gregorio *et al.*, 2010).

The remediation performance of activated carbon derived from wheat straw on PAH contaminated water was reported (Xu *et al.*, 2019). Results revealed that the PAH adsorption capacity of the adsorbent increased with increase in the number of aromatic rings and the surface area of adsorbent had the greatest influence on removal of both HMW and LMW PAHs with the pseudo-second order model giving the best fit to kinetic experiments. Adsorption of naphthalene (NAP), phenanthrene (PHEN), and pyrene (PYR) from water were evaluated using activated rice husk (RH) (Yakout and Daifullah, 2013). The Freundlich, generalized and BET isotherms best fit adsorption data for naphthalene, phenanthrene and pyrene. The results suggest that a significant amount of heat was dissipated, as the thermodynamic system was exothermic and spontaneous (Yakout and Daifullah, 2013).

The cross-linkages of starch molecules with epichlorohydrin, 1,6-hexamethylene diisocyanate, 4,4-methylene diphenyl diisocyanate, for the synthesis of a functionalized starch polymer adsorbent for PAHs were reported (Delval *et al.*, 2005; Okoli *et al.*, 2015). The cross-linking process enhanced the morphology, hydrophobicity and incorporated specific functional groups into the starch polymer. Adsorption occurred in multilayers, and diffusion controlled the adsorption kinetics. Thermodynamic variables suggest that the sorption mechanism was endothermic and spontaneous and physisorption occurred via hydrophobic, van der Waals and $\pi$–$\pi$ interactions between sorbent and adsorbate (Okoli *et al.*, 2015).

Plant materials have been used as adsorbent and an indirect form of phytoremediation of PAH contaminated water (Figure 3). Plant residues, brown seaweed (*Sargassum hemiphyllum*), wood fibers, wood char, fruit cuticles, potato periderm, modified pine bark, tea leaf powders, corn cob etc., have all been reported for the removal of PAHs from aquatic media via adsorption routes (Boving and Zhang, 2004; Chen *et al.*, 2011; Chung *et al.*, 2007; Crini, 2005; Huang *et al.*, 2006;

Ye *et al.*, 2019a). A biochar-based nanocomposite has been synthesized from rice straw and the material exhibited both adsorptive and photodegradation activity, making it suitable for the remediation of water contaminated with organic compounds (Ye *et al.*, 2019b).

However, the use of biomass in powdered form as column packing material has several limitations, such as difficulty in biomass recovery after sorption, complicated regeneration, low mechanical strength and density, and small particle size. An attempt to address these shortcomings through immobilization of biomass within a polymeric matrix was carried out and an improvement in biomass efficiency, sorption capacity, robustness, ruggedness and recovery of biomass from the pollutant containing solution was reported (Aksu, 2005). This class of adsorbents proved efficient in treatment of simulated and field water samples, and thus was regarded as a promising cost-effective alternative for remediation of aqueous PAH pollution (Cabal *et al.*, 2009, Zhang *et al.*, 2017). Possible negative environmental impacts of using biomass, such as deforestation and food scarcity, must be considered. Improved biomass recovery through advanced waste management systems is therefore important.

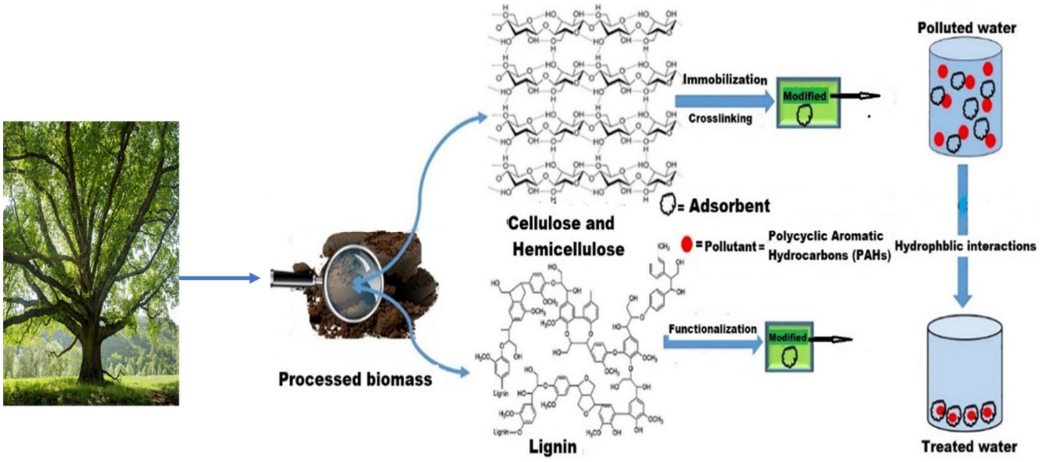

***Figure 3:*** *Treatment of PAH contaminated water using plant derivatives (biomass)*

### 6.2. Geosorbents

Geosorbent is generic term for soils, sediments and natural solid minerals, with different compositions depending on the parent rocks, anthropogenic activities, depth of sample aggregate, particle size, extent of maturation and ageing process (Luthy *et al.*, 1997). Combustion residue in particulate form (e.g., char, soot, and ash), clay minerals, silica (sand) and several forms of amorphous and condensed carbon such as kerogen, black carbon, aged carbon etc., are chemically and structurally different in different soils and sediments (Figure 4) (Cornelissen, 2005; Heijden, 2009; Rockne, 2002).

Porous carbon derived from petroleum coke (specific surface area (SSA): 562 - 1904 $m^2$/g) was reported for the adsorption of five LMW PAHs (fluoranthene, fluorene, phenanthrene, pyrene and naphthalene) from aqueous solution (Yuan *et al.*, 2014). It was found that the PAH uptake by the sorbent can be described by three successive and complimentary steps: (1) diffusion of molecules of PAHs from contaminated water to the outer walls of porous carbon particles through solid-liquid interphase, also known as film diffusion; (2) intraparticle diffusion of the PAHs within the pores of the carbon, and (3) PAH adsorption onto active sites on the interior surface. Adsorption kinetics is controlled by (1) and (2), while adsorption capacity and binding strength is controlled by step (3) to a very large extent. Furthermore, the petroleum coke derivative provided a removal efficiency of 99 % at 1 g/L dosage of the adsorbent and adsorption capacities for the PAHs were > 5 mg/g (Yuan *et al.*, 2014).

Leonardite, also known as immature coal, composed of 55 % carbon and mainly humic substances, has been studied for the removal of selected PAHs from water (Zeledón-Toruño *et al.*, 2007). Leonardite adsorbed over 90 % of fluorene, pyrene, benzo(k)fluoranthene, benzo(a)pyrene, and benzo(g,h,i)perylene present in solution, after 24 hours of contact at a dosage of 1 g/L, which is quite unique for a material with a relatively low surface area (19.1 $m^2$/g). The high removal efficiency and adsorption capacity can be attributed to the vast number of hydrophobic functionalities (carboxyl, carbonyl and hydroxyl groups) associated with humic acids and humic-containing geosorbents, which are readily available for chemical bonding (Lao *et al.*, 2005; Solé *et al.*, 2003).

Sepiolite is a fibrous clay mineral with a highly porous structure and silanol-surface-active sorption sites. Its molecular sieving and adsorptive abilities have been reported (Sabah and Ouki, 2017). Sepiolite has a relatively high surface area (358 $m^2$/g,), mean pore diameter (47.3 Å) and total pore volume (0.559 $cm^3$/g), which makes it a unique material/mineral for PAH remediation of contaminated water (Cobas *et al.*, 2014). It has a three-dimensional micro-crystalline structure, which makes it rigid, rugged and robust, with no significant change in morphology after adsorption of PAHs (Álvarez *et al.*, 2011). The adsorption of pyrene and naphthalene onto sepiolite and organo-sepiolite occurred via *H*-type sorption and chemisorption and reached a maximum capacity of 8 mg/g. The process was entirely endothermic with an activation energy between 26.3 – 31.2 kJ/mol and Gibbs free energy ($\Delta G$) of -29.35 kJ/mol, indicating that the process was diffusion controlled and involved weak chemical bonds (Gök *et al.*, 2008).

One major shortcoming of natural geosorbents is the problem attributed to designing a physicochemical sequestration model for the extremely heterogeneous systems found in various geological materials. The practicality of fractionating geosorbents into sorption domains and the establishment of dominant mechanisms of adsorption, is questionable given that there is typically insufficient microscopic data. However, it was suggested that predictions can be approached mechanistically by gaining knowledge of simpler systems via study of the components (Ololade *et al*., 2018; Ran *et al*., 2002; Ran *et al*., 2003; Wu and Zhu, 2012), thereby establishing an in-depth knowledge base for prediction of complex, heterogeneous geosorbents in their bulk state.

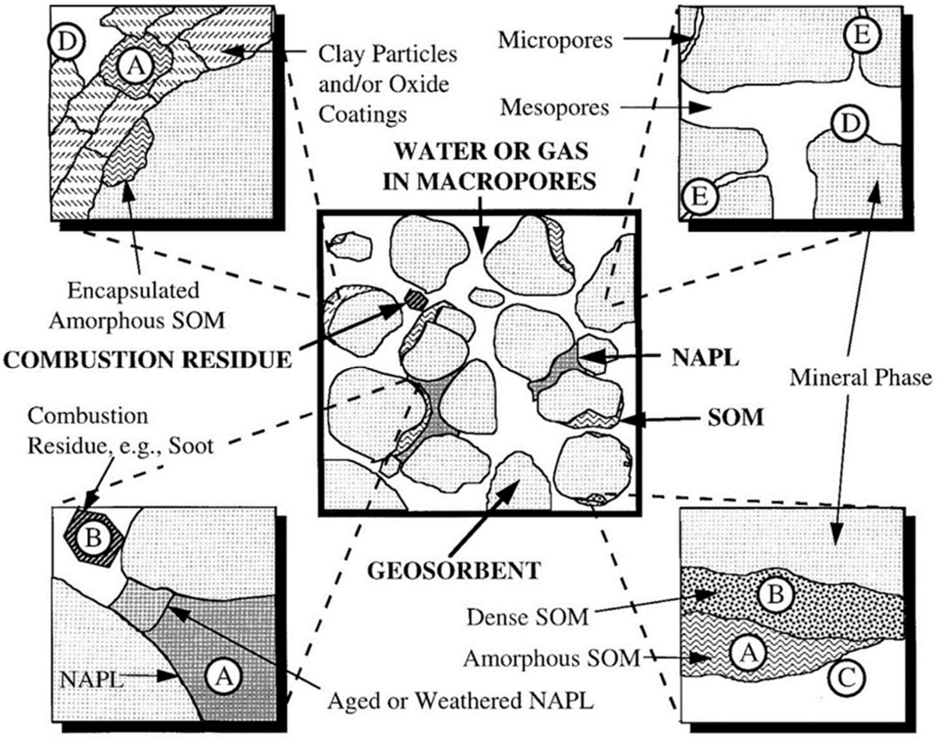

***Figure 4:*** *Geosorbent domains which include a mineral and organic matter component (SOM), as well as combustion residues and nonaqueous liquids (NAPL). (A) Absorption to soft natural organic matter or NAPL (B) Adsorption onto hard organic condensed matter (C) Adsorption onto wet-water organic surfaces i.e. soot. (D) Adsorption onto mineral phases e.g. quartz. (Reprinted with permission from Luthy, R. G., Aiken, G. R., Brusseau, M. L., Cunningham, S. D., Gschwend, P. M., Pignatello, J. J., Reinhard, M., Traina, S. J., Weber, W. J. & Westall, J. C. (1997). Environmental Science & Technology, 31 (12), 3341-3347. Copyright 1997 American Chemical Society.)*

### 6.3. Zeolites

Zeolites are aluminosilicates with different ratios of Si/Al. They exist naturally and can be synthesized and are important due to their essential physicochemical properties such as specific surface area, mechanical and thermal stability, high ion exchange capacity, adsorption, and sieving properties (Chao and Chen, 2012; Fletcher *et al.*, 2017). Zeolites have been used as adsorbents, membranes, ion exchangers, molecular sieves, and for water and soil remediation. This essential modified clay mineral has been identified as viable, low-cost, and readily available sorbent (Lee and Tiwari, 2012; Lee *et al.*, 2004; Li and Bowman, 2001).

Zeolite and its modified forms were applied to remove phenanthrene, pyrene and benzo(a)pyrene from water via a sorption process (Müller *et al.*, 2007; Torabian *et al.*, 2010; Zhang *et al.*, 2011). Using organo-zeolite as adsorbent recorded an average of 98% removal of fluorene, fluoranthene, pyrene, phenanthrene, benzo(a)anthracene from water (Lemić *et al.*, 2007). The particle size of zeolites is round 1 mm or greater, and they are not susceptible to contraction and expansion ("shrink-swell") behaviour, thus making them suitable for filtration systems as well as adsorption (Vidal *et al.*, 2011; Xi and Chen, 2014).

Polycyclic aromatic hydrocarbons were adsorbed by both zeolites and surfactant-modified zeolites, and the removal efficiency for both sorbents were in the order dibenz[a,h]anthracene > benzo[a]pyrene > anthracene > naphthalene (Wołowiec *et al.*, 2017). The adsorption capacity was highest with higher molecular weight PAHs (HMW), for example dibenz[a,h]anthracene had an adsorption capacity of 0.65 mg/g and was lowest for naphthalene (LMW) (0.058 mg/g). At a concentration of 20 μg/L, the adsorption efficiency for benz[*a*]anthracene by modified zeolite was 100% (Lemić *et al.*, 2007). The removal efficiency depends on the chemical properties of the PAHs (molar weight, molecule structure and dipole interactions) and the properties and morphology of the zeolites (i.e. Si/Al ratio, surface area, particle size, and cation exchange capacity). It was suggested that the sorption mechanism was dominated by penetration/diffusion of PAH molecules into the mesopores of the adsorbent (Wołowiec *et al.*, 2017).

### 6.4. Functionalized mesoporous silica

Topuz et al. (2017) reported the synthesis of β-cyclodextrin-functionalized periodic mesoporous organo-silica (PMO), which was used to adsorb five PAHs from water (Figure 5). The adsorption capacities were in the range of 0.3 to 1.65 mg/g (Topuz and Uyar, 2017). Pentynyl β-cyclodextrin as an organic moiety for mesoporous silica was used for remediation of phenanthrene was reported to have an efficiency above 95 % (Choi *et al.*, 2017). Several organic reagents prior to β-cyclodextrin have previously been reported, such as macrocyclic tetraazacalix[2]arene[2]triazine which recorded 94-102% removal efficiencies for five PAHs in water samples (Zhao *et al.*, 2016).

Functionalized silica with phenyl groups for removal of five PAHs in aqueous solutions were also investigated and adsorption efficiencies and capacities were within the range of 40–70 % and 0.72–1.69 mg/g, respectively (Vidal *et al.*, 2011). Haemoglobin-coated mesoporous silica yielded a PAH removal efficiency of 82 % for 11 different PAH compounds in water. Macrocyclic polyamine functionalized with 1,3-dibutylimidazolium bis[(trifluoromethyl)sulfonyl]imide (ionic liquid) achieved an estimated efficiency ranging from 81–120 % for the removal of five PAHs from aqueous solution (Liu *et al.*, 2014).

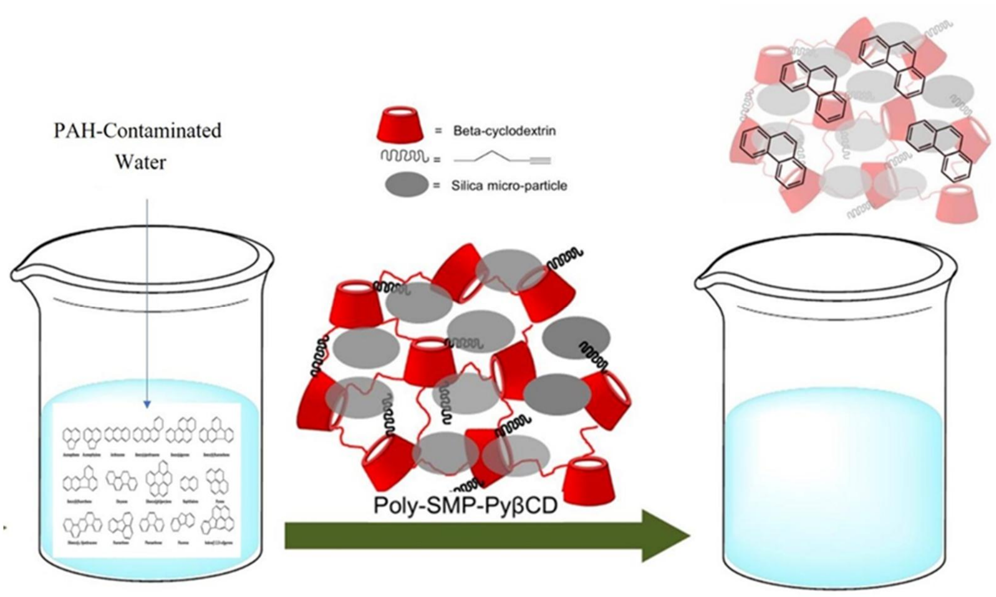

***Figure 5:** β-cyclodextrin based PMO for PAH decontamination. (Adapted with slight modification from Choi, J. M., Jeong, D., Cho, E., Yu, J.-H., Tahir, M. N. & Jung, S. (2017). Polymers, 9(1), 1-11.)*

### 6.5. Synthetic polymers

Polymeric adsorbents and supports have presented a useful alternative to the widely used granular/powdered activated carbon (GAC) for polycyclic aromatic hydrocarbon removal from water using permeable/porous reactive barriers (PRB) (Anbia and Moradi, 2009; Schad, 2005; Valderrama *et al.*, 2007). The quest to discover appropriate and efficient polymeric adsorbents for PAH removal from aqueous solution have spurred the synthesis of innovative resins, with new functionalities and/or modified polymeric frameworks (cross-links), in order to solve existing problems and shortcomings. A functionalized adsorbent called Macronet Hypersol, made up of a macroporous hyper-reticulated network of styrene–divinylbenzene has been evaluated and reported (Valderrama *et al.*, 2007). Due to its adsorptive properties, it has been considered as an economical reactive sorbent for water remediation (Streat and Sweetland, 1997). Batch experiments were carried out to determine the kinetics of adsorption of naphthalene, fluorene, anthracene, acenaphthene, pyrene, and fluoranthene from water. The study showed that sorption systems followed a pseudo-first-order reaction pathway (chemisorption). It was recommended that sorption media thickness of 0.1 – 1 m will be sufficient to treat PAH-polluted water and the medium would withstand a high-water flux of 0.1–2 $m^3/m^2$/day (Valderrama *et al.*, 2007).

The molecular imprinting technique has been used to synthesize nanoporous polymers for PAH remediation of polluted water (Augusto *et al.*, 2010; Hassan *et al.*, 2016). Specific molecular materials were synthesized via copolymerization of a monomeric cross linker with the complex derived from template (PAH) and functional monomers. The resultant molecular material possesses specific affinity for the PAH used as precursor, because its binding sites were of similar shape and size to the target PAH (Figure 6) (Dickert *et al.*, 1999; Montaseri and Forbes, 2018; Zimmerman *et al.*, 2002). A study reported the synthesis of a molecular imprinted polymer (MIP) in acetonitrile using a four PAH mix as template, and methacrylic acid and ethylene glycol dimethacrylate as functional monomer and cross-linking monomer (Krupadam, 2012). The microspheric size of the molecularly imprinted polymers (MIPs) generated ranged from 10 to 20 μm and the sorption affinity of the nanoporous polymeric material (NPM) for benzo[a]anthracene, benzo[a]pyrene, benzo[k]fluoranthene, and chrysene were studied via batch sorption experiments. A partition mechanism controlled the sorption interaction between the MIPs and the PAHs (benzo[a]anthracene, benzo[a]pyrene, benzo[k]fluoranthene, and chrysene), with an adsorption capacity of 3.12 μg/g, which was over five times higher than conventional activated carbon (Krupadam, 2012). Regeneration of MIPs was possible with methanol/acetic acid rinsing, with no significant loss in PAH removal efficiency (Baggiani *et al.*, 2007; Krupadam *et al.*, 2007; Krupadam, 2012).

Currently, various adsorbent materials have been studied as remediation materials for PAH decontamination of water. However, it has been difficult to clean-up ultra-trace levels of PAHs, which is achievable via molecular imprinting technology, with high selectivity and specificity. Although costs of chemicals such as monomers and solvents are also factors to consider.

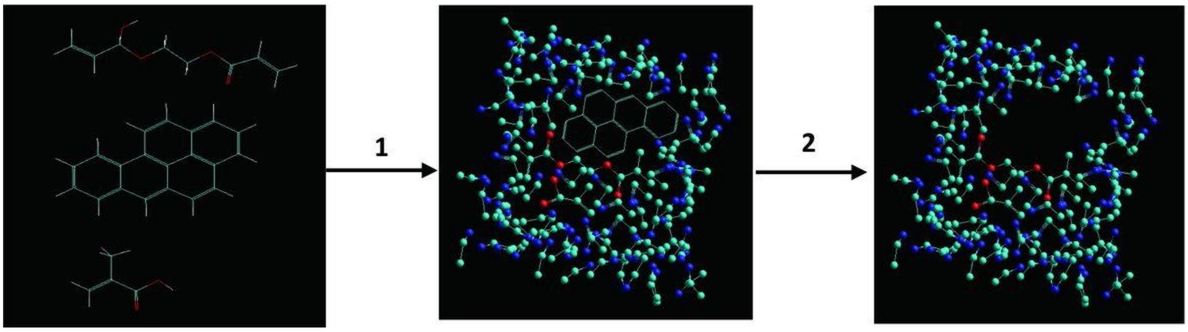

***Figure 6:*** *Molecular imprinting of benzo[a]pyrene using methacrylic acid as monomer to generate binding sites. Step (1) involves the polymerization and step (2) involves the removal of the PAHs and creation of binding cites complementary to the specific PAHs. (Reprinted from Polycyclic aromatic hydrocarbons, Volume 32, Krupadam, R. J. Nanoporous polymeric material for remediation of PAHs polluted water. 313-333, 2012, with permission from Elsevier.)*

## 6.6. Nanoparticles and composites

Nanotechnology has gained immense scientific relevance as a branch of science in the 21st century. It has the capability of generating nano-sized materials with unique properties, which have found application in drug delivery, biosensors as well as in the remediation of different environmental compartments; such as air, water and soil; via clean-up of environmental pollutants (Adeola *et al*., 2019, Nsibande *et al*., 2019). The adsorption of three PAHs, naphthalene (NAP), acenaphthylene (ACN), and phenanthrene (PHEN), from wastewater using a silica-based organic–inorganic nanohybrid material ($NH_2$-SBA-15) was reported (Balati *et al*., 2015). Adsorption kinetics of PAHs by the hybrid followed the pseudo-second-order pathway, providing evidence of chemisorption and pore mass transfer. The adsorption capacity of $NH_2$-SBA-15 for PAHs studied were 1.67, 1.06, and 0.24 mg/g for NAPH, ACN and PHEN, respectively; and the material was highly reusable for five sequential applications (Balati *et al.*, 2015).

Hydrophobic $C_{18}$-functionalized iron (III) oxide magnetic nanoparticles ($Fe_3O_4@C_{18}$) were trapped in a hydrophilic barium alginate ($Ba^{2+}$-ALG) polymer to generate an adsorbent suitable for solid-phase extraction and treatment of PAH contamination. The sorbents proved very efficient and the magnetic property thereof aided easy recovery and re-use. It was reported that a water-friendly $Ba^{2+-}$ALG polymer caged $Fe_3O_4@C_{18}$ nanomaterial can be used for extraction or possible remediation of organic pollutants in water on an industrial scale (Zhang *et al.*, 2010).

Additionally, tetraethyl orthosilicate magnetized with maghemite ($Fe_2O_3$) nanoparticles with an adsorption capacity of 0.39 mg/g has been applied for the removal of acenaphthene (ACN) from water with a removal efficiency of 85 % (Huang *et al.*, 2016). Hassan *et al.* (2018) reported an ecofriendly method for the synthesis of iron nanoparticles (IONPs) for the removal of benzo(a)pyrene and pyrene from contaminated water (Wang *et al.*, 2014b). Factors such as IONPs dosage, pH, temperature, and initial concentration of PAHs were evaluated. The maximum sorption capacities of IONPs towards pyrene and benzo(a)pyrene were 2.8 and 0.029 mg/g, and removal efficiencies were 98.5 and 99 %, respectively. The sorption process was exothermic, well defined by a monolayer adsorption mechanism (Langmuir model) and followed the pseudo-second order kinetic reaction pathway. The study revealed that IONPs are regenerable up to 5 cycles and possess anti-microbial properties (Hassan *et al.*, 2018).

However, there are major drawbacks in the field-based application of nanoparticles for PAH remediation. The fine powdered form of nanomaterials has a very high sorption affinity for PAHs, however, to achieve a reasonable treatment time, a large amount of the nanomaterial is required to treat a large volume of polluted water. In addition, the resulting nanomaterial residue dispersed or suspended in the treated water may cause toxicity if it is not properly recovered, due to the composition of the nanomaterial (metal poisoning) and/or the small particle size thereof, which aids mobility into tissues when ingested. Membrane separation protocols have been developed to separate fine suspended or dispersed solids from water, however, this increases operational costs. Nanomaterials may also have limited re-use potential, as they tend to lose activity with time as a result of aggregation, fouling, or side reactions.

### 6.7. Graphene and its composites

Graphene as a term was first proposed in 1986 and introduced to the International Union of Pure and Applied Chemistry (IUPAC) in 1995 (Boehm *et al.*, 1994; Fitzer *et al.*, 1995; Katsnelson, 2007; Peng *et al.*, 2017). Graphene is two-dimensional (2D), with $sp^2$ hybridized carbon atoms arranged hexagonally with a closed packed crystal lattice structure containing sigma- and $\pi$-bonds (Ali *et al.*, 2019). Graphene is presented in different forms such as pristine graphene, graphene oxide (GO), reduced graphene oxide (RGO), graphene nanoshell (GNS), graphene quantum dots, graphene wool, graphene-based composites and functionalized graphene (Adegoke *et al.*, 2017; Apul *et al.*, 2013; Nsibande and Forbes, 2020; Oyedotun *et al.*, 2019; Schoonraad *et al;* 2020; Sun *et al.*, 2013; Wang *et al.*, 2017). The large specific surface area, thermal stability, thermal conductivity, high tensile strength, chemical robustness, charge mobility, flexibility, thin-film thickness; provide the basis for the vast applications of graphene and its composites in many fields of science (Dreyer *et al.*, 2010; Geim, 2009; Novoselov *et al.*, 2012). Graphene has been utilized as an efficient sorbent for water remediation purposes, such as removal of contamination involving toxic organic and inorganic species (Ali *et al.*, 2019; Ersan *et al.*, 2017; Wang *et al.*, 2014a; Zhao *et al.*, 2011b).

The mechanism of interaction between PAHs and different forms of graphene in water is described mainly by partitioning and adsorption, and generally follows second order reaction kinetics. From the studies presented in Table 1, it is evident that the efficiency of different forms of graphene is largely dependent on the dosage and concentration of PAHs and also influenced by temperature of the reaction and ionic strength of the solution (Lamichhane *et al.*, 2016). The effect of pH is typically negligible due to the lack of specific functional groups in PAHs (Su *et al.*, 2006; Adeola and Forbes, 2019), if they are not derivatized as in the case of 1-napthalenesulfonic acid (Wu *et al.*, 2011b).

Several factors influence the choice of adsorbent for water treatment applications, such as efficiency of the material, non-toxicity, availability of the material, flexibility, robustness, reusability, to mention a few. Graphene wool holds a competitive advantage over other forms of graphene tested for water treatment applications, due to its high PAH removal efficiency > 98%, wool-associated flexibility and reusability. GW has a very high volume to mass ratio and porosity which makes it a suitable packing material for membrane separations/filters, as well as a good polishing tool for water remediation (Adeola and Forbes, 2019).

**Table 1:** Comparison of different forms of graphene used for remediation of PAH-contaminated water

| **Adsorbent** | **Dosage ($g L^{-1}$)** | **Contact time (hours)** | **Removal efficiency (%)** | **Adsorption capacity** | **Reference** |
|---|---|---|---|---|---|
| Graphene | 1 | 96 | - | 1.46 g/g (1-napthalenesulfonic acid) | (Wu *et al.*, 2011b) |
| Graphene nanosheets | | 168 | - | 150.2 mg/g (PHEN) | (Apul *et al.*, 2013) |
| Reduced graphene oxide (RGO) | 0.4 | 168 | - | 5.912 g/g (NAPH), 0.183 g/g (ANT) and 0.979 g/g (PYR) | (Sun *et al.*, 2013) |
| RGO/FeO.$Fe_3O_4$ composite | 1 | 48 | - | 2.63 mg/g *(NAPH)* | (Yang *et al.*, 2013) |
| Graphene oxide/ brilliant blue (BBGO) | 0.025 | 264 | 72.7 - 93.2 | 1.676 mmol/g (ANTM), 2.212 mmol/g (FLR) | (Zhang *et al.*, 2013) |
| Graphene nanosheets | 0.5 | 90 | - | 116 mg/g (PHEN), 123 mg/g (PYR) | (Wang *et al.*, 2014a) |
| Graphene oxide (GO) | 0.5 | 90 | - | 5.9 mg/g (PHEN), 6.12 mg/g (PYR) | (Wang *et al.*, 2014a) |
| Exfoliated graphene | 1 | 48 | - | 24.1 mg/g (PHEN) | (Zhao *et al.*, 2014) |
| Graphene coated materials (GCMs) | 0.5 | 36 | 80 | 1.74 mg/g (PHEN) | (Yang *et al.*, 2015) |
| Graphene wool | 0.67 | 24 | 98.5 - 99.9 | 5 mg/g (PHEN),<br>20 mg/g (PYR) | (Adeola and Forbes, 2019) |

*ANT: anthracene; ANTM: anthracenemethanol; FLR: fluoranthene; NAPH: naphthalene; PHEN: Phenanthrene; PYR: pyrene*

## 7.0. Emerging trends and prospects

It is evident that adsorption using various efficient and cost-effective materials as well as bioremediation are the most widely used remedial approaches, however, bioremediation still has limitations such as accumulation of metabolites or degradation products which could be more harmful; as in the case of dichlorodiphenyltrichloroethane (DDT) and its metabolite dichlorodiphenyldichloroethylene (DDE) (ATSDR, 1994); longer duration requirements for treatment procedures and cost. Therefore, to address these challenges or limitations, hyphenated methods or integrated systems have been suggested (Kuppusamy *et al.*, 2017). These may involve chemical-physical (such as chemical oxidation and solvent extraction), biological-physical (e.g. bioremediation and solvent extraction), biological-chemical (such as bioremediation and chemical oxidation) processes. The bioaugmentation technique is an integrated system which can potentially be used for PAH remediation of polluted water, if the bacteria employed are not harmful to humans, or are easily recovered or removed by a simple chlorination step during the treatment of potable water. Commercial materials developed in line with bioaugmentation include SediMite and AquaGate+GAC. The bio-amendment of granular activated carbon (GAC) with anaerobic and aerobic bacteria as degradants, has been reported for the *in-situ* treatment of organic contamination, where the porewater concentration of polychlorinated biphenyls (PCBs) reduced by 94 – 97 % (Payne *et al.*, 2017).

Phytoremediation, which is plant aided bioremediation, is a remedial approach that can potentially address PAH contamination on a large scale (Jeelani *et al.*, 2017; Petruzzelli *et al.*, 2016). Plant degradation of PAHs in water is worthy of investigation, because plants possess the ability to sequester, accumulate and chemically transform chemical pollutants. They can secrete enzymes that can play the role of surfactants and enhance the bioavailability of the pollutant in solution. In addition, rhizospheric microbes have xenobiotic-degrading capabilities (Gan *et al.*, 2009). The application of specific plants (such as lichens) for bioaccumulation and phytoremediation of metals, metalloids and PAHs from the surrounding environment have been reported (Kroukamp *et al.,* 2016; Van der Wat and Forbes, 2019). Phytoremediation of a PAH and heavy metal contaminated brownfield site was also reported by Roy *et al.* (2005). These are case studies with proven hypotheses towards successful plant-based remediation, and with the existence of aquatic plants, phytoremediation of PAH polluted water is worth exploring. Plants with long roots and large surface area are highly adaptable to unfriendly environmental conditions (i.e. drought) and are preferred for *in situ* treatment of contaminated water (Alagić *et al.*, 2016). Intercropping of different plants infuses desired physiological attributes and vast microbial groups in the rhizosphere of plants with a commensurate impact on PAH remediation (Meng *et al.*, 2011; Sun *et al.*, 2011; Sun and Zhou, 2016). Enhanced phytoremediation can be obtained with the aid of plant growth promoting rhizobacteria (PGPR) such as *Azospirillum brasilense, Enterobacter cloacae* and *Pseudomona putida*, for stimulating physiological development, accelerated plant growth, and survival of remediating plant species (de Boer and Wagelmans, 2016; Huang *et al.*, 2004a, b; Jeelani *et al.*, 2017). Although phytoremediation may offer an added advantage of absorbing excess atmospheric $CO_2$ and reducing air pollution, it may require several years to achieve PAH treatment objectives.

Electrokinetic remediation is an electrochemical technique involving the application of direct current (DC) through appropriate electrodes for the purpose of remediation. Basically, the concept of electrolysis comes into play as ionic pollutants in solution migrate to their oppositely charged electrodes and electroosmotic movement provides the force for transportation of soluble pollutants (Pazos *et al.*, 2010; Reddy *et al.*, 2006). Electrokinetic remediation is an established tool for decontamination of soils, although its application in PAH remediation of water has not been investigated on a pilot-, field-, or industrial-scale. Application of this method would potentially have its own challenges due to the hydrophobicity/insolubility of PAHs and the fact that they do not readily ionize in water. Therefore, it has been suggested that surfactants designed to minimize the tension between the pollutant molecule and water molecules, co-solvents and cyclodextrins should be considered as additives in order to improve the efficiency of PAH remediation in field-water samples using the electrokinetic method (Pourfadakari *et al.*, 2019; Saichek and Reddy, 2005). An integrated system comprising an electrochemical test cell enhanced by a persulfate oxidizing agent has been used for treatment of PAH-contaminated clay with 35 % PAH removal efficiency as compared to 12 to 20 % efficiency recorded for either of the methods alone. This integrated system could potentially be used for remediation of PAH polluted water. It is noted that the efficiency of the integrated approach depends on the applied voltage, ratio of AC-DC voltage, nature of the electrode, process duration and reagent (oxidizing agent) dosage (Isosaari *et al.*, 2007; Pourfadakari *et al.*, 2019; Wang *et al.*, 2013).

Green nanoremediation is a promising and notable approach to remediation of contaminated aqueous systems, based on the concept of green/ecofriendly and sustainable chemistry. In the last decade, nanoscience and technology has received immense attention with respect to research and development, and it holds great potential for remediation of polluted water/wastewater and environmental protection (Huang *et al.*, 2016; Kuppusamy *et al.*, 2015). The intrinsic properties of nanoparticles such as their small size (1-100 nm size), good surface-coating ability and large surface area, in comparison with macroscopic materials, make nanoparticles preferable for *in situ* applications. Thus green nanoremediation should be investigated and functionally integrated with established remedial methods such as the chemical oxidation or Fenton process via synthesis of nano-oxidizers (to allow for PAH oxidation), and most importantly adsorption processes by novel, green, efficient and sustainable nano-adsorbents should be further explored (Basheer, 2018; Guerra *et al.*, 2018). Efficient integration of established remediation approaches with green nanoremediation and membrane filtration will potentially improve efficiency and allow for rapid PAH degradation or removal during field or industrial applications.

A few examples of treatment technologies readily available on a commercial scale and those still in the prototype/developmental phase are presented in Table 2. The absence of methods such as advanced oxidation, catalytic degradation and bioremediation, indicates that although these methods have been shown to be promising and efficient on a laboratory-scale, they have not been commercialized for field/industrial scale water treatment as yet, unlike membrane technologies, due to high operational cost. This is likely due to the fact that these methods are not easily incorporated into existing water treatment plants or due to possible difficulties in their scale up to treat large volumes of water. Furthermore, some of the treatment methods are not robust enough to deal with heavily polluted water. Future research should be directed towards the development of materials/methods that are more economical, durable, efficient and adaptable with simple designs for the removal of PAHs and other environmental contaminants from wastewater.

## 8.0. Field application

The treatment of a PAH-contaminated water system essentially involves three phases: (1) site inspection and risk assessment, (2) choice of treatment method, and (3) treatment and post-treatment assessment/monitoring. Phase 1 simply requires that the level/extent of pollution is determined with respect to permissible levels or thresholds (WHO, 1984).

Phase 2 requires evaluation of existing remediation technologies and choosing the most feasible method, considering the site of pollution and its environment, as well as cost considerations. Laboratory scale experiments may prove useful in determining the most effective method for successful remediation of field contamination. Several factors that affect field-scale remediation of PAH contaminated water include but are not limited to; (1) physicochemical conditions of the water and sediment (organic matter content, temperature, turbidity, pH, nutrients/mineral content, redox potential, ionic strength/salinity etc.); (2) microbial/biotic community (diversity, population, resistance, activity, symbiosis etc.); (3) target contaminants and co-existing contaminants (concentration, toxicity, bioavailable fraction, solubility, volatility, mass transfer etc.); (4) cost (pre-treatment and post-treatment); and other factors which are non-technical such as government and standard regulations, research funding, human resources, infrastructure etc.

In Phase 3, the chosen remediation strategies are implemented, and treatment efficiency is determined on site. If the pollution persists, the treatment protocol is repeated or another approach may need to be adopted (Duan *et al.*, 2015).

**Table 2:** Examples of commercially available water treatment technologies which are applicable to PAH removal, including materials, scale of application and brand names.

| **Treatment material** | **Treatment process** | **Scale of application** | **Commercial/brand name** | **Source** |
|---|---|---|---|---|
| Granular activated carbon (GAC) and aeration | Adsorption and filtration | Drinking water and industrial wastewater | Evoqua water technologies<br>CECO Mefiag filters | www.evoqua.com/en/brands/IPS/Pages/Organic-Chemicals-Removal-from-Groundwater<br>https://www.environmental-expert.com/products/ceco-mefiag-activated-carbon-filter-tubes-638430 |
| Polyethersulfone (PES) | Direct nanofiltration | Potable water, surface water and industrial wastewater | Nxfiltration (dNf membrane) | https://nxfiltration.com/technology |
| Zeolite, activated alumina | Filtration, adsorption | Domestic and industrial wastewater | Zhulin | https://www.zhulincarbon.com/products/filter-media/ |
| Copper & zinc alloy/GAC | Reverse osmosis | Potable water, industrial and surface water | KDF-GAC Filtration | https://www.ampac1.com/emergency-portable-reverse-osmosis-20000-gpd |
| Silver impregnated coconut activated carbon (Ag/GAC) | Adsorption | Portable water | Zhulin carbon | https://www.zhulincarbon.com/products/special-activated-carbon/25.html |
| Powdered activated carbon (PAC) from wood and coal | Adsorption | Industrial wastewater | Zhulin carbon | https://www.zhulincarbon.com/products/powdered-activated-carbon/ |
| PAC + PAH degrading microbes | Bioaugmentation | Navigable water and wetland treatments | Bio-amended sediMite | http://www.sedimite.com/sedimite |
| PAC, bentonite (clay), cellulose-based polymer | Adsorption and capping | Aquatic environments | AquaGate+PAC™ | https://www.environmental-expert.com/products/aquagate-pac-activated-carbon-for-active-capping-or-in-situ-treatment-169605 |
| Wetlands and gravel filter | Geo-sorption, sedimentation | Domestic wastewater | Prototype | Fountoulakis *et al.* (2009) |
| Graphene membrane | Advanced reverse osmosis | Portable water | Prototype | Homaeigohar and Elbahri, (2017). |
| $H_2O_2$:$FeSO_4$/UV irradiation | Advanced oxidation process | Potable water | Prototype | Abd Manan *et al.* (2019b) |

## 9.0. Conclusion

A number of the technologies discussed in this review are still at the prototype stage, awaiting field trials, while others have been used on an industrial-scale and have been found to be effective, although some have limitations including high operational cost, fouling, non-regenerable materials, non-ecofriendly processes, long treatment time, generation of a large amount of sludge or secondary pollutants, etc. Therefore, emerging technologies must seek to surmount these challenges and consider all these factors, in order to arrive at a sustainable remediation approach for hazardous pollutants such as PAHs. Adsorption, nanofiltration and integrated systems are very promising technologies, with further development potential towards commercialization. Frankly, it is almost impossible or impracticable to restore heavily PAH polluted water to its pristine state rapidly, with its full natural functions restored. Therefore, a purpose-directed, risk-based sustainable remediation approach may prove to be most appropriate for the management of long-term and/or severely PAH polluted water.

## Acknowledgements

Authors acknowledge the University of Pretoria Commonwealth Doctoral Scholarship funding (AA), and Departments of Chemistry and Physics at the University of Pretoria, South Africa for their support.

## Conflict of interest

The authors declare that there is no conflict of interest regarding the publication of this article.

## References

Abd Manan, T. S. B., Beddu, S., Khan, T., Wan Mohtar, W. H. M., Sarwono, A., Jusoh, H., Mohd Kamal, N. L., Sivapalan, S. & Ghanim, A. A. J. (2019a). Step by step procedures: Degradation of polycyclic aromatic hydrocarbons in potable water using photo-Fenton oxidation process. *MethodsX*, 6, 1701-1705. https://doi.org/10.1016/j.mex.2019.07.011

Abd Manan, T. S. B., Khan, T., Sivapalan, S., Jusoh, H., Sapari, N., Sarwono, A., . . . Malakahmad, A. (2019b). Application of response surface methodology for the optimization of polycyclic aromatic hydrocarbons degradation from potable water using photo-Fenton oxidation process. *Science of The Total Environment*, 665, 196-212. doi:https://doi.org/10.1016/j.scitotenv.2019.02.060

Abdel-Shafy, H. I.; Mansour, M. S. M. (2016) A review on polycyclic aromatic hydrocarbons: Source, environmental impact, effect on human health and remediation. Egyptian Journal of Petroleum, 25, 107-123. https://doi.org/10.1016/j.ejpe.2015.03.011

Abdou, A. M. (2003). Purification and partial characterization of psychrotrophic *Serratia marcescen*s lipase. *Journal of Dairy Science*, 86, 127-132. https://doi.org/10.3168/jds.S0022-0302(03)73591-7

Adegoke, O., Montaseri, H., Nsibande, S. A. & Forbes, P. B. C. (2017). Alloyed quaternary/binary core/shell quantum dot-graphene oxide nanocomposite: Preparation, characterization and application as a fluorescence “switch ON” probe for environmental pollutants. *Journal of Alloys and Compounds*, 720, 70-78. https://doi.org/10.1016/j.jallcom.2017.05.242

Adeola, A. O., Fapohunda, O., Jimoh, A. T., Toluwaloju, T. I., Ige, A. O. & Ogunyele, A. C. (2019). Scientific application and prospect of nanomaterials: a multidisciplinary review. *African Journal of Biotechnology*, 18, 946-961. https://doi.org/10.5897/AJB2019.16812

Adeola, A. O. & Forbes, P. B. C. (2019). Optimisation of the sorption of selected polycyclic aromatic hydrocarbons by regenerable graphene wool. *Water Science and Technology*. 80 (10), 1931-1943. https://doi.org/10.2166/wst.2020.011

Aksu, Z. (2005). Application of biosorption for the removal of organic pollutants: a review. *Process Biochemistry*, 40, 997-1026. https://doi.org/10.1016/j.procbio.2004.04.008

Alagić, S. Č., Jovanović, V. P. S., Mitić, V. D., Cvetković, J. S., Petrović, G. M. & Stojanović, G. S. (2016). Bioaccumulation of HMW PAHs in the roots of wild blackberry from the Bor region (Serbia): Phytoremediation and biomonitoring aspects. *Science of The Total Environment*, 562, 561-570. https://doi.org/10.1016/j.scitotenv.2016.04.063

Alegbeleye, O. O., Opeolu, B. O. & Jackson, V. (2017). Bioremediation of polycyclic aromatic hydrocarbon (PAH) compounds: (acenaphthene and fluorene) in water using indigenous bacterial species isolated from the Diep and Plankenburg rivers, Western Cape, South Africa. *Brazilian Journal of Microbiology*, 48, 314-325. https://doi.org/10.1016/j.bjm.2016.07.027

Ali, I., Basheer, A. A., Mbianda, X. Y., Burakov, A., Galunin, E., Burakova, I., Mkrtchyan, E., Tkachev, A. & Grachev, V. (2019). Graphene based adsorbents for remediation of noxious pollutants from wastewater. *Environment International*, 127, 160-180. https://doi.org/10.1016/j.envint.2019.03.029

Álvarez, A., Santarén, J., Esteban-Cubillo, A. & Aparicio, P. (2011). Chapter 12 - Current industrial applications of palygorskite and sepiolite, in: Galàn, E.; Singer, A. (Eds.), *Developments in Clay Science*. Elsevier, pp. 281-298.

Amstaetter, K., Eek, E. & Cornelissen, G. (2012). Sorption of PAHs and PCBs to activated carbon: Coal versus biomass-based quality. *Chemosphere*, 87, 573-578. https://doi.org/10.1016/j.chemosphere.2012.01.007

Anbia, M. & Moradi, S. E. (2009). Removal of naphthalene from petrochemical wastewater streams using carbon nanoporous adsorbent. *Applied Surface Science*, 255(9), 5041-5047. https://doi.org/10.1016/j.apsusc.2008.12.065

Antizar-Ladislao, B., Spanova, K., Beck, A. J. & Russell, N. J. (2008). Microbial community structure changes during bioremediation of PAHs in an aged coal-tar contaminated soil by in-vessel composting. *International Biodeterioration & Biodegradation*, 61, 357-364. https://doi.org/10.1016/j.ibiod.2007.10.002

Apul, O. G., Wang, Q., Zhou, Y. & Karanfil, T. (2013). Adsorption of aromatic organic contaminants by graphene nanosheets: comparison with carbon nanotubes and activated carbon. *Water Research*, 47, 1648-1654. http://doi.org/10.1016/j.watres.2012.12.031

ATSDR, Agency for Toxic Substances and Disease Registry (1994). Toxicological Profile for 4,4-DDT, 4,4-DDE, and 4,4-DDD. Public Health Service, U.S. Department of Health and Human Services, Atlanta, GA.

Augusto, F., Carasek, E., Silva, R. G. C., Rivellino, S. R., Batista, A. D. & Martendal, E. (2010). New sorbents for extraction and microextraction techniques. *Journal of Chromatography A*, 1217, 2533-2542. http://doi.org/10.1016/j.chroma.2009.12.033

Balati, A., Shahbazi, A., Amini, M. M. & Hashemi, S. H. (2014). Adsorption of polycyclic aromatic hydrocarbons from wastewater by using silica-based organic–inorganic nanohybrid material. *Journal of Water Reuse and Desalination*, 5, 50-63. https://doi.org/10.2166/wrd.2014.013

Baggiani, C., Anfossi, L., Baravalle, P., Giovannoli, C. & Giraudi, G. (2007). Molecular recognition of polycyclic aromatic hydrocarbons by pyrene-imprinted microspheres. *Analytical and Bioanalytical Chemistry*, 389, 413-422. https://doi.org/10.1007/s00216-007-1318-8

Bai, H., Zhou, J., Zhang, H. & Tang, G. (2017). Enhanced adsorbability and photocatalytic activity of TiO2-graphene composite for polycyclic aromatic hydrocarbons removal in aqueous phase.

*Colloids and Surfaces B: Biointerfaces*, 150, 68-77. https://doi.org/10.1016/j.colsurfb.2016.11.017

Balati, A., Shahbazi, A., Amini, M. M. & Hashemi, S. H. (2014). Adsorption of polycyclic aromatic hydrocarbons from wastewater by using silica-based organic–inorganic nanohybrid material. *Journal of Water Reuse and Desalination*, 5(1), 50-63. https://doi.org/10.2166/wrd.2014.013

Basheer, A. A. (2018). New generation nano-adsorbents for the removal of emerging contaminants in water. *Journal of Molecular Liquids*, 261, 583-593. https://doi.org/10.1016/j.molliq.2018.04.021

Bhatnagar, A. & Sillanpää, M. (2010). Utilization of agro-industrial and municipal waste materials as potential adsorbents for water treatment—A review. *Chemical Engineering Journal*, 157, 277-296. https://doi.org/10.1016/j.cej.2010.01.007

Boehm, H. P. Setton, R. & Stumpp, E. (1994). Nomenclature and terminology of graphite intercalation compounds (IUPAC nomenclature 1994). *Pure and Applied Chemistry*, 66(9), 1893-1901. https://doi.org/10.1351/pac199466091893

Boving, T. B. & Zhang, W. (2004). Removal of aqueous-phase polynuclear aromatic hydrocarbons using aspen wood fibers. *Chemosphere*, 54, 831-839. https://doi.org/10.1016/j.chemosphere.2003.07.007

Cabal, B., Ania, C. O., Parra, J. B. and Pis, J. J. (2009). Kinetics of naphthalene adsorption on an activated carbon: Comparison between aqueous and organic media. *Chemosphere*, 76, 433-438. http://doi.org/10.1016/j.chemosphere.2009.04.002

Chao, H.-P. & Chen, S.-H. (2012). Adsorption characteristics of both cationic and oxyanionic metal ions on hexadecyltrimethylammonium bromide-modified NaY zeolite. *Chemical Engineering Journal*, 193-194, 283-289. https://doi.org/10.1016/j.cej.2012.04.059

Chen, B., Yuan, M. & Liu, H. (2011). Removal of polycyclic aromatic hydrocarbons from aqueous solution using plant residue materials as a biosorbent. *Journal of Hazardous Materials*, 188, 436-442. http://doi.org/10.1016/j.jhazmat.2011.01.114

Choi, J. M., Jeong, D., Cho, E., Yu, J.-H., Tahir, M. N. & Jung, S. (2017). Pentynyl ether of β-Cyclodextrin polymer and silica micro-particles: A new hybrid material for adsorption of phenanthrene from water. *Polymers*, 9(1), 1-11. https://dx.doi.org/10.3390%2Fpolym9010010

Chung, M. K., Tsui, M. T. K., Cheung, K. C., Tam, N. F. Y. & Wong, M. H. (2007). Removal of aqueous phenanthrene by brown seaweed *Sargassum hemiphyllum*: Sorption-kinetic and equilibrium studies. *Separation and Purification Technology*, 54, 355-362. https://doi.org/10.1016/j.seppur.2006.10.008

Cobas, M., Ferreira, L., Sanromán, M. A. & Pazos, M. (2014). Assessment of sepiolite as a low-cost adsorbent for phenanthrene and pyrene removal: Kinetic and equilibrium studies. *Ecological Engineering*, 70, 287-294. https://doi.org/10.1016/j.ecoleng.2014.06.014

Cohen-Tanugi, D. & Grossman, J. C. (2012). Water Desalination across nanoporous graphene. *Nano Letters*, 12, 3602-3608. https://doi.org/10.1021/nl3012853

Cornelissen, G. & Gustafsson, O. (2005). Importance of unburned coal carbon, black carbon, and amorphous organic carbon to phenanthrene sorption in sediments. *Environmental Science and Technology*, 39(3), 764-769. https://doi.org/10.1021/es049320z

Crini, G. (2005). Recent developments in polysaccharide-based materials used as adsorbents in wastewater treatment. *Progress in Polymer Science*, 30, 38-70. http://dx.doi.org/10.1016/j.progpolymsci.2004.11.002

Crisafully, R., Milhome, M. A., Cavalcante, R. M., Silveira, E. R., De Keukeleire, D. & Nascimento, R. F. (2008). Removal of some polycyclic aromatic hydrocarbons from petrochemical wastewater using low-cost adsorbents of natural origin. *Bioresources Technology*, 99, 4515-4519. https://doi.org/10.1016/j.biortech.2007.08.041

de Boer, J. & Wagelmans, M. (2016). Polycyclic aromatic hydrocarbons in soil – practical options for remediation. *CLEAN - Soil, Air, Water*, 44, 648-653. https://doi.org/10.1002/clen.201500199

Deng, Y. & Zhao, R. (2015). Advanced oxidation processes (AOPs) in wastewater treatment. *Current Pollution Reports*, 1, 167–176. https://doi.org/10.1007/s40726-015-0015-z

Delval, F., Crini, G., Bertini, S., Filiatre, C. & Torri, G. (2005). Preparation, characterization and sorption properties of crosslinked starch-based exchangers. *Carbohydrate Polymers*, 60, 67-75. http://dx.doi.org/10.1016/j.carbpol.2004.11.025

Dickert, F. L., Tortschanoff, M., Bulst, W. E. & Fischerauer, G. (1999). Molecularly imprinted sensor layers for the detection of polycyclic aromatic hydrocarbons in water. *Analytical Chemistry*, 71(20), 4559-4563. https://doi.org/10.1021/ac990513s

Dreyer, D. R., Ruoff, R. S. & Bielawski, C. W. (2010). From conception to realization: An historial account of graphene and some perspectives for its future. *Angewandte Chemie International Edition*, 49, 9336-9344. https://doi.org/10.1002/anie.201003024

Duan, L., Naidu, R., Thavamani, P., Meaklim, J. & Megharaj, M. (2015). Managing long-term polycyclic aromatic hydrocarbon contaminated soils: a risk-based approach. *Environmental Science and Pollution Research*, 22, 8927-8941. https://doi.org/10.1007/s11356-013-2270-0

Dudziak, M., Luks – Betlej, K. & Bodzek, M. (2003). Removal of PAHs from water using membrane processes. *Engineering and Protection of Environment*. 3–4, 299–311.

Edokpayi, J.N., Odiyo, J.O. Popoola, E. O. & Msagati, A.M.T. (2016). Determination and distribution of polycyclic aromatic hydrocarbons in rivers, sediments and wastewater effluents in Vhembe District, South Africa. *International Journal of Environmental Research and Public Health*, 13, 387-398. https://doi.org/10.3390/ijerph13040387

Egli, S. N., Butler, E. D. & Bottaro, C. S. (2015). Selective extraction of light polycyclic aromatic hydrocarbons in environmental water samples with pseudo-template thin-film molecularly imprinted polymers. *Analytical Methods*, 7, 2028-2035. https://doi.org/10.1039/C4AY02849J

Ersan, G., Apul, O. G., Perreault, F. & Karanfil, T. (2017). Adsorption of organic contaminants by graphene nanosheets: A review. *Water Research*, 126, 385-398. https://doi.org/10.1016/j.watres.2017.08.010

Feng, Z., Huang, C., Guo, Y., Liu, W., & Zhang, L. (2020). Graphitic carbon nitride derivative with large mesopores as sorbent for solid-phase microextraction of polycyclic aromatic hydrocarbons. *Talanta*, 209, 120541. https://doi.org/10.1016/j.talanta.2019.120541

Fitzer, E., Kochling, K. H., Boehm, H. P. & Marsh, H. (1995). Recommended terminology for the description of carbon as a solid (IUPAC Recommendations 1995), *Pure and Applied Chemistry*, 67(3). 473-506. http://dx.doi.org/10.1351/pac199567030473

Fletcher, R. E., Ling, S. & Slater, B. (2017). Violations of Löwenstein's rule in zeolites. *Chemical Science*, 8, 7483-7491. https://doi.org/10.1039/C7SC02531A

Flotron, V., Delteil, C., Bermond, A. & Camel, V. (2005). Degradation of polycyclic aromatic hydrocarbons in sewage sludges by Fenton's reagent, in: Lichtfouse, E.; Schwarzbauer, J.; Robert, D. (Eds.), Environmental Chemistry: Green Chemistry and Pollutants in Ecosystems. Springer Berlin Heidelberg, Berlin, Heidelberg, pp. 449-459

Fountoulakis, M. S., Terzakis, S., Kalogerakis, N. & Manios, T. (2009). Removal of polycyclic aromatic hydrocarbons and linear alkylbenzene sulfonates from domestic wastewater in pilot constructed wetlands and a gravel filter. *Ecological Engineering*, 35(12), 1702-1709. https://doi.org/10.1016/j.ecoleng.2009.06.011

Gan, S., Lau, E. V. & Ng, H. K. (2009). Remediation of soils contaminated with polycyclic aromatic hydrocarbons (PAHs). *Journal of Hazardous Materials*, 172, 532-549. https://doi.org/10.1016/j.jhazmat.2009.07.118

García-Suástegui, W. A., Huerta-Chagoya, A., Carrasco-Colín, K. L., Pratt, M. M., John, K., Petrosyan, P., Rubio, J., Poirier, M. C. & Gonsebatt, M. E. (2010). Seasonal variations in the levels of PAH–DNA adducts in young adults living in Mexico City. *Mutagenesis*, 26, 385-391. https://doi.org/10.1093/mutage/geq104

Garg, A., Singhania, T., Singh, A., Sharma, S., Rani, S., Neogy, A., Yadav, S. R., Sangal, V. K. & Garg, N. (2019). Photocatalytic degradation of bisphenol-A using N, Co codoped $TiO_2$ catalyst under solar light. *Scientific Reports*, 9, 765, 1-13. https://dx.doi.org/10.1038%2Fs41598-018-38358-w

Geim, A. K. (2009). Graphene: status and prospects. *Science*, 324, 1530-1534. https://doi.org/10.1126/science.1158877

Ghosal, D., Ghosh, S., Dutta, T. K. & Ahn, Y. (2016). Current state of knowledge in microbial degradation of polycyclic aromatic hydrocarbons (PAHs): A review. *Frontiers in Microbiology*, 7, 1369, 1-27. https://doi.org/10.3389/fmicb.2016.01369

Gök, Ö., Özcan, A. S. & Özcan, A. (2008). Adsorption kinetics of naphthalene onto organo-sepiolite from aqueous solutions. *Desalination*, 220, 96-107. https://doi.org/10.1016/j.desal.2007.01.025

Gong, Z., Wilke, B. M., Alef, K., Li, P. & Zhou, Q. (2006). Removal of polycyclic aromatic hydrocarbons from manufactured gas plant-contaminated soils using sunflower oil: Laboratory column experiments. *Chemosphere,* 62, 780-787. https://doi.org/10.1016/j.chemosphere.2005.04.078

Gouma, S., Fragoeiro, S., Bastos, A. C. & Magan, N. (2014). 13 - Bacterial and fungal bioremediation strategies, in: Das, S. (Ed.), Microbial biodegradation and bioremediation. Elsevier, Oxford, pp. 301-323.

Guerra, F. D., Attia, M. F., Whitehead, D. C. & Alexis, F. (2018). Nanotechnology for environmental remediation: materials and applications. *Molecules*, 23(7), 1760-1783. https://doi.org/10.3390/molecules23071760

Hassan, S., Sayour, H., El Azab, W. & Mansour, M. (2016). Synthesis and characterization of molecularly imprinted nanoparticle polymers for selective separation of anthracene. *Journal of Dispersion Science and Technology*, 37, 1241-1251. https://doi.org/10.1080/01932691.2015.1089514

Hassan, S. S. M., Abdel-Shafy, H. I. & Mansour, M. S. M. (2018). Removal of pyrene and benzo(a)pyrene micropollutant from water via adsorption by green synthesized iron oxide nanoparticles. *Advances in Natural Sciences: Nanoscience and Nanotechnology*, 9, 015006, 1-15. https://doi.org/10.1088/2043-6254/aaa6f0

Hayakawa, K., Makino, F., Yasuma, M., Yoshida, S., Chondo, Y., Toriba, A., Kameda, T., Tang, N., Kunugi, M., Nakase, H., Kinoshita, C., Kawanishi, T., Zhou, Z., Qing, W., Mishukov, V., Tishchenko, P., Lobanov, V. B., Chizhova, T. & Koudryashova, Y. (2016). Polycyclic aromatic hydrocarbons in surface water of the southeastern Japan sea. *Chemical and Pharmaceutical Bulletin*, 64, 625-631. https://doi.org/10.1248/cpb.c16-00063

Heijden, S. A. v. d. & Jonker, M. T. O (2009). PAH bioavailability in field sediments: comparing different methods for predicting in situ bioaccumulation. *Environmental Science and Technology*, 43(10), 3757-3763. https://doi.org/10.1021/es803329p

Homaeigohar, S. & Elbahri, M. (2017). Graphene membranes for water desalination. *NPG Asia Materials*, 9(8), e427-e427. https://doi.org/10.1038/am.2017.135

Huang, H.-H., Lu, M.-C., Chen, J.-N. & Lee, C.-T. (2003). Catalytic decomposition of hydrogen peroxide and 4-chlorophenol in the presence of modified activated carbons. *Chemosphere*, 51(9), 935-943. https://doi.org/10.1016/S0045-6535(03)00042-0

Huang, L., Boving, T. B. & Xing, B. (2006). Sorption of PAHs by aspen wood fibers as affected by chemical alterations. *Environmental Science & Technology*, 40(10), 3279-3284. https://doi.org/10.1021/es0524651

Huang, X.-D., El-Alawi, Y., Penrose, D. M., Glick, B. R. & Greenberg, B. M. (2004a). A multi-process phytoremediation system for removal of polycyclic aromatic hydrocarbons from contaminated soils. *Environmental Pollution*, 130, 465-476. https://doi.org/10.1016/j.envpol.2003.09.031

Huang, X.-D., El-Alawi, Y., Penrose, D. M., Glick, B. R. & Greenberg, B. M. (2004b). Responses of three grass species to creosote during phytoremediation. *Environmental Pollution*, 130(3), 453-463. https://doi.org/10.1016/j.envpol.2003.12.018

Huang, Y.. Fulton, A. N. & Keller, A. A. (2016). Simultaneous removal of PAHs and metal contaminants from water using magnetic nanoparticle adsorbents. *Science of The Total Environment*, 571, 1029-1036. http://dx.doi.org/10.1016/j.scitotenv.2016.07.093

Huling, S. G. & Pivetz, B. E. (2006). In-situ chemical oxidation In-situ chemical oxidation. EPA/600/R-06/072. Cincinnati, Ohio: United States Environmental Protection Agency.

Hussain, K., Hoque, R. R., Balachandran, S., Medhi, S., Idris, M. G., Rahman, M. & Hussain, F. L. (2018). Monitoring and risk analysis of PAHs in the environment, in: Hussain, C. M. (Ed.), Handbook of environmental materials management. Springer International Publishing, pp. 1-35.

Isosaari, P., Piskonen, R., Ojala, P., Voipio, S., Eilola, K., Lehmus, E. & Itävaara, M. (2007). Integration of electrokinetics and chemical oxidation for the remediation of creosote-contaminated clay. *Journal of Hazardous Materials*, 144, 538-548. https://doi.org/10.1016/j.jhazmat.2006.10.068

Jeelani, N., Yang, W., Xu, L., Qiao, Y., An, S. & Leng, X. (2017). Phytoremediation potential of Acorus calamus in soils co-contaminated with cadmium and polycyclic aromatic hydrocarbons. *Scientific Reports*, 7(1), 1-9. https://doi.org/10.1038/s41598-017-07831-3

Katsnelson, M. I. (2007). Graphene: carbon in two dimensions. *Materials Today*, 10(1-2), 20-27. https://doi.org/10.1016/S1369-7021(06)71788-6

Kemp, K. C., Seema, H., Saleh, M., Le, N. H., Mahesh, K., Chandra, V. & Kim, K. S. (2013). Environmental applications using graphene composites: water remediation and gas adsorption. *Nanoscale*, 5, 3149-3171. https://doi.org/10.1039/C3NR33708A

Klejnowski, K., Kozielska, .B., Krasa, A., & Rogula-Kozłowska, W. (2010). Polycyclic aromatic hydrocarbons in PM1, PM2.5, PM10 and tsp in the Upper Silesian agglomeration, Poland. *Archives of Environmnetal Protection*, 36(2), 65–72.

Kroukamp, E. M., Wondimu, T. & Forbes, P. B. C. (2016). Metal and metalloid speciation in plants: Overview, instrumentation, approaches and commonly assessed elements. *TrAC Trends in Analytical Chemistry*, 77, 87-99. https://doi.org/10.1016/j.trac.2015.10.007

Krupadam, R. J. (2012). Nanoporous polymeric material for remediation of PAHs polluted water. *Polycyclic Aromatic Compounds*, 32, 313-333. https://doi.org/10.1080/10406638.2011.633591

Krupadam, R. J., Ahuja, R. & Wate, S. R. (2007). Benzo(a)pyrene imprinted polyacrylate nanosurfaces: Adsorption and binding characteristics. *Sensors and Actuators B: Chemical*, 124, 444-451. https://doi.org/10.1016/j.snb.2007.01.020

Kuppusamy, S., Thavamani, P., Megharaj, M. & Naidu, R. (2015). Bioremediation potential of natural polyphenol rich green wastes: A review of current research and recommendations for future directions. *Environmental Technology & Innovation*, 4, 17-28. https://dx.doi.org/10.1016/j.eti.2015.04.001

Kuppusamy, S., Thavamani, P., Megharaj, M. & Naidu, R. (2016). Biodegradation of polycyclic aromatic hydrocarbons (PAHs) by novel bacterial consortia tolerant to diverse physical settings – Assessments in liquid- and slurry-phase systems. *International Biodeterioration & Biodegradation*, 108, 149-157. https://dx.doi.org/10.1016/j.ibiod.2015.12.013

Kuppusamy, S., Thavamani, P., Venkateswarlu, K., Lee, Y. B., Naidu, R. & Megharaj, M. (2017). Remediation approaches for polycyclic aromatic hydrocarbons (PAHs) contaminated soils: Technological constraints, emerging trends and future directions. *Chemosphere*, 168, 944-968. https://doi.org/10.1016/j.chemosphere.2016.10.115

Lamichhane, S., Bal Krishna, K. C. & Sarukkalige, R. (2016). Polycyclic aromatic hydrocarbons (PAHs) removal by sorption: A review. *Chemosphere*, 148, 336-353. https://doi.org/10.1016/j.chemosphere.2016.01.036

Lao, C., Zeledón, Z., Gamisans, X. & Solé, M. (2005). Sorption of Cd(II) and Pb(II) from aqueous solutions by a low-rank coal (leonardite). *Separation and Purification Technology*, 45, 79-85. https://doi.org/10.1016/j.seppur.2005.02.006

Lawal, A. T. (2017). Polycyclic aromatic hydrocarbons. A review. *Cogent Environmental Science*, 3, 1339841, 1-89. https://doi.org/10.1080/23311843.2017.1339841

Lee, S. M. & Tiwari, D. (2012). Organo and inorgano-organo-modified clays in the remediation of aqueous solutions: An overview. *Applied Clay Science*, 59-60, 84-102. https://doi.org/10.1016/j.clay.2012.02.006

Lee, S. Y., Kim, S. J., Chung, S. Y. & Jeong, C. H. (2004). Sorption of hydrophobic organic compounds onto organoclays. *Chemosphere*, 55, 781-785. https://doi.org/10.1016/j.chemosphere.2003.11.007

Lemić, J., Tomašević-Čanović, M., Adamović, M., Kovačević, D. & Milićević, S. (2007). Competitive adsorption of polycyclic aromatic hydrocarbons on organo-zeolites. *Microporous and Mesoporous Materials*, 105, 317-323. https://doi.org/10.1016/j.micromeso.2007.04.014

Li, J., Zhao, L., Qin, L., Tian, X., Wang, A., Zhou, Y., Meng, L. & Chen, Y. (2016). Removal of refractory organics in nanofiltration concentrates of municipal solid waste leachate treatment plants by combined Fenton oxidative-coagulation with photo – Fenton processes. *Chemosphere*, 146, 442-449. https://doi.org/10.1016/j.chemosphere.2015.12.069

Li, Z. & Bowman, R. S. (2001). Retention of inorganic oxyanions by organo-kaolinite. *Water Research*, 35, 3771-3776. https://doi.org/10.1016/S0043-1354(01)00120-8

Lian, L., Yao, B., Hou, S., Fang, J., Yan, S. & Song, W. (2017). Kinetic study of hydroxyl and sulfate radical-mediated oxidation of pharmaceuticals in wastewater effluents. *Environmental Science & Technology*, 51, 2954-2962. https://doi.org/10.1021/acs.est.6b05536

Liu, L., He, L., Jiang, X., Zhao, W., Xiang, G. & Anderson, J. L. (2014). Macrocyclic polyamine-functionalized silica as a solid-phase extraction material coupled with ionic liquid dispersive liquid–liquid extraction for the enrichment of polycyclic aromatic hydrocarbons. *Journal of Separation Science*, 37, 1004-1011. https://doi.org/10.1002/jssc.201301062

Luo, Z.-h., Wei, C.-l., He, N.-n., Sun, Z.-g., Li, H.-x. & Chen, D. (2015). Correlation between the photocatalytic degradability of PAHs over Pt/$TiO_2$-$SiO_2$ in water and their quantitative molecular structure. *Journal of Nanomaterials*, 284834, 1-11. https://doi.org/10.1155/2015/284834

Luthy, R. G., Aiken, G. R., Brusseau, M. L., Cunningham, S. D., Gschwend, P. M., Pignatello, J. J., Reinhard, M., Traina, S. J., Weber, W. J. & Westall, J. C. (1997). Sequestration of hydrophobic organic contaminants by geosorbents. *Environmental Science & Technology*, 31 (12), 3341-3347. https://doi.org/10.1021/es970512m

Maletic, S. P., Beljin, J. M., Roncevic, S. D., Grgic, M. G. & Dalmacija, B. D. (2019). State of the art and future challenges for polycyclic aromatic hydrocarbons is sediments: sources, fate, bioavailability and remediation techniques. *Journal of Hazardous Material*, 365, 467-482. https://doi.org/10.1016/j.jhazmat.2018.11.020

Martinez, E., Gros, M., Lacorte, S., Barceló, D. (2004). Simplified procedures for the analysis of polycyclic aromatic hydrocarbons in water, sediments and mussels. *Journal of Chromatography A*, 1047, 181-188. https://doi.org/10.1016/j.chroma.2004.07.003

Meng, L., Qiao, M. & Arp, H. P. H. (2011). Phytoremediation efficiency of a PAH-contaminated industrial soil using ryegrass, white clover, and celery as mono- and mixed cultures. *Journal of Soils and Sediments*, 11, 482-490. https://doi.org/10.1007/s11368-010-0319-y

Mohan, S. V., Kisa, T., Ohkuma, T., Kanaly, R. A. & Shimizu, Y. (2006). Bioremediation technologies for treatment of PAH-contaminated soil and strategies to enhance process efficiency. *Reviews in Environmental Science and Bio/Technology*, 5, 347-374. https://doi.org/10.1007/s11157-006-0004-1

Mojiri, A., Zhou, J. L., Ohashi, A., Ozaki, N. & Kindaichi, T. (2019). Comprehensive review of polycyclic aromatic hydrocarbons in water sources, their effects and treatments. *Science of The Total Environment*, 696, 133971, 1-16. https://doi.org/10.1016/j.scitotenv.2019.133971

Montaseri, H. & Forbes, P. B. C. (2018). Molecularly imprinted polymer coated quantum dots for fluorescence sensing of acetaminophen. *Materials Today Communications*, 17, 480-492. https://doi.org/10.1016/j.mtcomm.2018.10.007

Moscoso, F., Ferreira, L., Deive, F. J., Morán, P. & Sanromán, M. A. (2013). Viability of phenanthrene biodegradation by an isolated bacterial consortium: optimization and scale-up. *Bioprocess and Biosystems Engineering*, 36, 133-141. http://dx.doi.org/10.1007/s00449-012-0768-3

Müller, S., Totsche, K. U. & Kögel-Knabner, I. (2007). Sorption of polycyclic aromatic hydrocarbons to mineral surfaces. *European Journal of Soil Science*, 58, 918-931. https://doi.org/10.1111/j.1365-2389.2007.00930.x

Munyeza, C. F., Dikale, O., Rohwer, E. R. & Forbes, P. B. C. (2018). Development and optimization of a plunger assisted solvent extraction method for polycyclic aromatic hydrocarbons sampled onto multi-channel silicone rubber traps. *Journal of Chromatography A,* 1555, 20-29. https://doi.org/10.1016/j.chroma.2018.04.053

Nian, Q., Wang, X., Wang, M., & Zuo, G. (2019). A hybrid material composed of graphitic carbon nitride and magnetite ($Fe_3O_4$) for magnetic solid-phase extraction of trace levels of hydroxylated polycyclic aromatic hydrocarbons. *Microchimica Acta*, 186(8), 497-506. doi:10.1007/s00604-019-3607-2

Novoselov, K. S., Fal′ko, V. I., Colombo, L., Gellert, P. R., Schwab, M. G. & Kim, K. (2012). A roadmap for graphene. *Nature*, 490, 192-200. https://doi.org/10.1038/nature11458

Nsibande, S. A., Montaseri, H. & Forbes, P. B. C. (2019). Advances in the application of nanomaterial-based sensors for detection of polycyclic aromatic hydrocarbons in aquatic systems. *TrAC Trends in Analytical Chemistry,* 115, 52-69. https://doi.org/10.1016/j.trac.2019.03.029

Nsibande, S. A. & Forbes, P. B. C. (2020). Development of a turn-on graphene quantum dot-based fluorescent probe for sensing of pyrene in water. *RSC Advances,* 10, 12119-12128.https://doi.org/10.1039/C9RA10153E

Okere, U. V. (2011), Biodegradation of PAHs in 'pristine' soils from different climatic regions. *Journal of Bioremediation & Biodegradation*, s:1, 1-11. https://doi.org/10.4172/2155-6199.S1-006

Okoli, C. P., Adewuyi, G. O., Zhang, Q., Zhu, G., Wang, C. and Guo, Q. (2015). Aqueous scavenging of polycyclic aromatic hydrocarbons using epichlorohydrin, 1,6-hexamethylene diisocyanate and 4,4-methylene diphenyl diisocyanate modified starch: Pollution remediation approach. *Arabian Journal of Chemistry*. 12(8), 2760-2773. https://doi.org/10.1016/j.arabjc.2015.06.004

Olivella, M. À., Jové, P. & Oliveras, A. (2011). The use of cork waste as a biosorbent for persistent organic pollutants–Study of adsorption/desorption of polycyclic aromatic hydrocarbons. *Journal of Environmental Science and Health, Part A*, 46, 824-832. https://doi.org/10.1080/10934529.2011.579845

Ololade, I. A., Adeola, A. O., Oladoja, N. A., Ololade, O. O., Nwaolisa, S. U., Alabi, A. B. & Ogungbe, I. V. (2018). In-situ modification of soil organic matter towards adsorption and desorption of phenol and its chlorinated derivatives. *Journal of Environmental Chemical Engineering*, 6, 3485-3494. https://doi.org/10.1016/j.jece.2018.05.034

Olsson, A. C., Fevotte, J., Fletcher, T., Cassidy, A., Mannetje, A., Zaridze, D., Szeszenia-Dabrowska, N., Rudnai, P., Lissowska, J., Fabianova, E., Mates, D., Bencko, V., Foretova, L., Janout, V., Brennan, P. & Boffetta, P. (2010). Occupational exposure to polycyclic aromatic hydrocarbons and lung cancer risk: a multicenter study in Europe. *Occupational and Environmental Medicine*, 67(2), 98-103. https://doi.org/10.1136/oem.2009.046680

Oyedotun, K. O., Masikhwa, T. M., Lindberg, S., Matic, A., Johansson, P. & Manyala, N. (2019). Comparison of ionic liquid electrolyte to aqueous electrolytes on carbon nanofibres supercapacitor electrode derived from oxygen-functionalized graphene. *Chemical Engineering Journal*, 375, 121906. https://doi.org/10.1016/j.cej.2019.121906

Pazos, M., Rosales, E., Alcántara, T., Gómez, J. & Sanromán, M. A. (2010). Decontamination of soils containing PAHs by electroremediation: A review. *Journal of Hazardous Materials*, 177, 1-11. https://doi.org/10.1016/j.jhazmat.2009.11.055

Payne, R.B., Ghosh, U., May, H.D., Marshall, C.W. & Sowers, K.R., (2017). Mesocosm studies on the efficacy of bioamended activated carbon for treating PCB-impacted sediment. *Environmental Science & Technology* 51, 10691-10699. https://doi.org/10.1021/acs.est.7b01935

Peng, W., Li, H., Liu, Y. & Song, S. (2017). A review on heavy metal ions adsorption from water by graphene oxide and its composites. *Journal of Molecular Liquids*, 230, 496-504. https://doi.org/10.1016/j.molliq.2017.01.064

Pérez-Gregorio, M. R., García-Falcón, M. S., Martínez-Carballo, E. & Simal-Gándara, J. (2010). Removal of polycyclic aromatic hydrocarbons from organic solvents by ashes wastes. *Journal of Hazardous Materials*, 178, 273-281. https://doi.org/10.1016/j.jhazmat.2010.01.073

Petruzzelli, G., Pedron, F., Rosellini, I., Grifoni, M. & Barbafieri, M. (2016). Polycyclic aromatic hydrocarbons and heavy metal contaminated sites: phytoremediation as a strategy for addressing the complexity of pollution, in: Ansari, A. A.; Gill, S. S.; Gill, R.; Lanza, G. R.; Newman, L. (Eds.), Phytoremediation: Management of Environmental Contaminants, Volume 4. Springer International Publishing, pp. 61-90.

Pourfadakari, S., Ahmadi, M., Jaafarzadeh, N., Takdastan, A., Neisi, A. A.; Ghafari, S.; Jorfi, S. (2019). Remediation of PAHs contaminated soil using a sequence of soil washing with biosurfactant produced by Pseudomonas aeruginosa strain PF2 and electrokinetic oxidation of desorbed solution, effect of electrode modification with $Fe_3O_4$ nanoparticles. *Journal of Hazardous Materials*, 379, 120839, 1-14. https://doi.org/10.1016/j.jhazmat.2019.120839

Quinn, L., Pieters, R., Nieuwoudt, C., Borgen, A. R., Kylin, H. & Bouwman, H. (2009). Distribution profiles of selected organic pollutants in soils and sediments of industrial, residential and agricultural areas of South Africa. *Journal of Environmental Monitoring*, 11, 1647-1657. https://doi.org/10.1039/B905585A

Ran, Y., Huang, W., Rao, P. S. C., Liu, D., Sheng, G. & Fu, J. (2002). The role of condensed organic matter in the nonlinear sorption of hydrophobic organic contaminants by a peat and sediments. *Journal of Environmental Quality*, 31, 1953-1962. https://doi.org/10.2134/jeq2002.1953

Ran, Y., Xiao, B., Huang, W., Peng, P., Liu, D., Fu, J. & Sheng, G. (2003). Kerogen in an aquifer and its strong sorption for hydrophobic organic contaminants. *Journal of Environmental Quality* 32(5), 1701-1709. https://doi.org/10.2134/jeq2003.1701

Reddy, K. R., Ala, P. R., Sharma, S. & Kumar, S. N. (2006). Enhanced electrokinetic remediation of contaminated manufactured gas plant soil. *Engineering Geology*, 85, 132-146. https://doi.org/10.1016/j.enggeo.2005.09.043

Ritchie, H. & Roser, M. (2020). "Clean Water". Published online at OurWorldInData.org. Retrieved from: https://ourworldindata.org/water-access [Online Resource]

Rivas, J., Gimeno, O., de la Calle, R. G. & Beltrán, F. J. (2009). Ozone treatment of PAH contaminated soils: Operating variables effect. *Journal of Hazardous Materials*, 169, 509-515. https://doi.org/10.1016/j.jhazmat.2009.03.136.

Rockne, K.J., Shor, L. M., Young, L.Y., Taghon, G.L. & Kosson, D.S. (2002). Distributed sequestration and release of PAHs in weathered sediment: The role of sediment structure and organic carbon properties. *Environmental Science and Technology*, 36, 2636-2644. https://doi.org/10.1021/es015652h

Roy, S., Labelle, S., Mehta, P., Mihoc, A., Fortin, N., Masson, C., Leblanc, R., Châteauneuf, G., Sura, C., Gallipeau, C., Olsen, C., Delisle, S., Labrecque, M. & Greer, C. W. (2005). Phytoremediation of heavy metal and PAH-contaminated brownfield sites. *Plant and Soil*, 272, 277-290. https://doi.org/10.1007/s11104-004-5295-9

Sabah, E. & Ouki, S. (2017). Adsorption of pyrene from aqueous solutions onto sepiolite. *Clays and Clay Minerals*, 65, 14-26. https://doi.org/10.1346/CCMN.2016.064046

Saichek, R. E. & Reddy, K. R. (2005). Surfactant-enhanced electrokinetic remediation of polycyclic aromatic hydrocarbons in heterogeneous subsurface environments. *Journal of Environmental Engineering and Science*, 4, 327-339. https://doi.org/10.1139/s04-064.

Samanta, S. K., Singh, O. V. & Jain, R. K. (2002). Polycyclic aromatic hydrocarbons: environmental pollution and bioremediation. *Trends in Biotechnology*, 20, 243-248. https://doi.org/10.1016/s0167-7799(02)01943-1.

Schad, H., Haist-Gulde, B., Klein, R., Maier, D., Maier, M. & Schulze, B. (2000). Funnel-and-gate at the former manufactured gas plant site in Karlsruhe: sorption test results, hydraulic and technical design, construction. Proceedings of the seventh international FZK/TNO conference on contaminated soil 18-22 September 2000, Leipzig, Germany, 951-959.

Schoonraad, G.-L., Madito, M. J., Manyala, N. & Forbes, P. (2020). Synthesis and optimisation of a novel graphene wool material by atmospheric pressure chemical vapour deposition. *Journal of Materials Science,* 55, 545-564. https://doi.org/10.1007/s10853-019-03948-0.

Shannon, M. A., Bohn, P. W., Elimelech, M., Georgiadis, J. G., Mariñas, B. J. & Mayes, A. M. (2008). Science and technology for water purification in the coming decades. *Nature*, 452, 301-310. https://doi.org/10.1038/nature06599.

Silva, I. S., Grossman, M. & Durrant, L. R. (2009). Degradation of polycyclic aromatic hydrocarbons (2–7 rings) under microaerobic and very-low-oxygen conditions by soil fungi. *International Biodeterioration & Biodegradation*, 63, 224-229. https://doi.org/10.1016/j.ibiod.2008.09.008

Smol, M. & Włodarczyk-Makuła, M. (2012). Effectiveness in the removal of polycyclic aromatic hydrocarbons from industrial wastewater by ultrafiltration technique.” *Archives of Environmental Protection*, 38(4), 49–58. https://doi.org/10.2478/v10265-012-0040-6

Smol, M., Włodarczyk-Makuła, M., Mielczarek, K. & Bohdziewicz, J. (2014a). Comparison of the retention of selected PAHs from municipal landfill leachate by RO and UF processes. *Desalination and Water Treatment*, 52(19–21), 3889–97. https://doi.org/10.1080/19443994.2014.887451

Smol, M., Włodarczyk-Makuła, M., Bohdziewicz, J., Mielczarek, K. (2014b). The use of integrated membrane systems in the removal of selected pollutants from pre-treated wastewater in coke plant, Monographs of the Environmental Engineering Committee Polish Academy of Sciences, Warsaw-Gliwice, Membranes and Membrane Processes in Environmental Protection. 119, 143–52.

Smol, M., Włodarczyk-Makuła, M., Mielczarek, K., Bohdziewicz, J. & Włóka, D. (2015). The use of reverse osmosis in the removal of PAHs from municipal landfill leachate. *Polycyclic Aromatic Compounds*, 36(1), 20-39. https://doi.org/10.1080/10406638.2014.957403.

Solé, M., Casas, J. M. & Lao, C. (2003). Removal of Zn from Aqueous Solutions by Low-Rank Coal. *Water, Air, and Soil Pollution*, 144, 57-65. https://doi.org/10.1023/A:1022965417124

Soleimani, M. (2012). Bioremediation: An environmental friendly solution for oil contaminated soils. *Journal of Bioremediation and Biodegradation,* 3(4), 1000e109. https://doi.org/10.4172/2155-6199.1000e109

Streat, M. & Sweetland, L. A. (1997). Physical and adsorptive properties of Hypersol-MacronetTM polymers. *Reactive and Functional Polymers,* 35, 99-109. https://doi.org/10.1016/S1381-5148(97)00049-7

Su, Y.-H., Zhu, Y.-G., Sheng, G. & Chiou, C. T. (2006). Linear adsorption of nonionic organic compounds from water onto hydrophilic minerals: silica and alumina. *Environmental Science & Technology,* 40, 6949-6954. https://doi.org/10.1021/es0609809

Sun, J.-H., Wang, G.-L., Chai, Y., Zhang, G., Li, J. & Feng, J. (2009). Distribution of polycyclic aromatic hydrocarbons (PAHs) in Henan Reach of the Yellow River, Middle China. *Ecotoxicology and Environmental Safety*, 72(5), 1614-1624. https://doi.org/10.1016/j.ecoenv.2008.05.010

Sun, K., Liu, J., Gao, Y., Jin, L., Gu, Y. & Wang, W. (2014). Isolation, plant colonization potential and phenanthrene degradation performance of the endophytic bacterium *Pseudomonas sp*. *Scientific Reports*, 4, 5462, 1-9. https://doi.org/10.1038/srep05462

Sun, M., Fu, D., Teng, Y., Shen, Y., Luo, Y., Li, Z. & Christie, P. (2011). In situ phytoremediation of PAH-contaminated soil by intercropping alfalfa (Medicago sativa L.) with tall fescue (Festuca arundinacea Schreb.) and associated soil microbial activity. *Journal of Soils and Sediments*, 11, 980-989. https://doi.org/10.1007/s11368-011-0382-z

Sun, Y., Yang, S., Zhao, G., Wang, Q. & Wang, X. (2013). Adsorption of polycyclic aromatic hydrocarbons on graphene oxides and reduced graphene oxides. *Chemistry – An Asian Journal*, 8, 2755-2761. https://doi.org/10.1002/asia.201300496

Sun, Y. & Zhou, Q. (2016). Uptake and translocation of benzo[a]pyrene (B[a]P) in two ornamental plants and dissipation in soil. *Ecotoxicology and Environmental Safety*, 124, 74-81. https://doi.org/10.1016/j.ecoenv.2015.09.037

Topuz, F. & Uyar, T. (2017). Cyclodextrin-functionalized mesostructured silica nanoparticles for removal of polycyclic aromatic hydrocarbons. *Journal of Colloid and Interface Science*, 497, 233-241. https://doi.org/10.1016/j.jcis.2017.03.015

Torabian, A., Kazemian, H., Seifi, L., Bidhendi, G. N., Azimi, A. A. & Ghadiri, S. K. (2010). Removal of petroleum aromatic hydrocarbons by surfactant-modified natural zeolite: The effect of surfactant. *CLEAN – Soil, Air, Water*, 38, 77-83. https://doi.org/10.1002/clen.200900157

United Nations Information Centre (2017). The sustainable development goals report. https://unstats.un.org/sdgs/files/report/2017/TheSustainableDevelopmentGoalsReport2017.pdf [Online Resource]

USEPA, United State Environmental Protection Agency (2000). Toxic release inventory public data release. Washington, D.C.: Office of Environmental Information, United States Environmental Protection Agency. hppt://www.epa.gov/triinter/tridata/index.htm. [Online Resource]

Valderrama, C., Cortina, J. L., Farran, A., Gamisans, X. & Lao, C. (2007). Kinetics of sorption of polyaromatic hydrocarbons onto granular activated carbon and Macronet hyper-cross-linked polymers (MN200). *Journal of Colloid and Interface Science*, 310, 35-46. https://doi.org/10.1016/j.jcis.2007.01.039

Van der Wat, L. & Forbes, P. B. C. (2019). Comparison of extraction techniques for polycyclic aromatic hydrocarbons from lichen biomonitors. *Environmental Science and Pollution Research*, 26, 11179-11190. https://doi.org/10.1007/s11356-019-04587-3

Vidal, C. B., Barros, A. L., Moura, C. P., de Lima, A. C. A., Dias, F. S., Vasconcellos, L. C. G., Fechine, P. B. A. & Nascimento, R. F. (2011). Adsorption of polycyclic aromatic hydrocarbons from aqueous solutions by modified periodic mesoporous organosilica. *Journal of Colloid and Interface Science*, 357, 466-473. http://doi.org/10.1016/j.jcis.2011.02.013

Viñas, M., Sabaté, J., Espuny, M. J. & Solanas, A. M. (2005). Bacterial community dynamics and polycyclic aromatic hydrocarbon degradation during bioremediation of heavily creosote-contaminated soil. *Applied and Environmental Microbiology*, 71, 7008. https://doi.org/10.1128/AEM.71.11.7008-7018.2005

Wang, J., Chen, Z. & Chen, B. (2014a). Adsorption of polycyclic aromatic hydrocarbons by graphene and graphene oxide nanosheets. *Environmental Science & Technology*, 48, 4817-4825. https://doi.org/10.1021/es405227u

Wang, J., Li, F., Li, X., Wang, X., Li, X., Su, Z., Zhang, H. & Guo, S. (2013). Effects of electrokinetic operation mode on removal of polycyclic aromatic hydrocarbons (PAHs), and the indigenous fungal community in PAH-contaminated soil. *Journal of Environmental Science and Health, Part A*, 48, 1677-1684. https://doi.org/10.1080/10934529.2013.815500

Wang, L., Yang, Z., Niu, J. & Wang, J. (2009). Characterization, ecological risk assessment and source diagnostics of polycyclic aromatic hydrocarbons in water column of the Yellow River Delta, one of the most plenty biodiversity zones in the world. *Journal of Hazardous Materials*, 169, 460-465. https://doi.org/10.1016/j.jhazmat.2009.03.125

Wang, T., Jin, X., Chen, Z., Megharaj, M. & Naidu, R. (2014b). Green synthesis of Fe nanoparticles using eucalyptus leaf extracts for treatment of eutrophic wastewater. *Science of The Total Environment*, 466, 210-213. https://doi.org/10.1016/j.scitotenv.2013.07.022

Wang, W., Wang, Z., Liu, J., Zhang, Z. & Sun, L. (2017). Single-step one-pot synthesis of graphene foam/TiO2 nanosheet hybrids for effective water treatment. *Scientific Reports*, 7, 43755. 1-9. https://doi.org/10.1038/srep43755

WHO/UNICEF, (2012). Global water supply and sanitation assessment report. Geneva: WHO/UNICEF. [Online Resource].

World Health Organization (WHO) (1984), Guidelines for Drinking Water Quality, Geneva.

Wise, D. L. (2000). Remediation engineering of contaminated soils. Series: Environmental Science & Pollution, *Boca Raton: CRC Press*, Taylor and Francis Group, United Kingdom.

Wołowiec, M., Muir, B., Zięba, K., Bajda, T., Kowalik, M. & Franus, W. (2017). Experimental study on the removal of VOCs and PAHs by zeolites and surfactant-modified zeolites. *Energy & Fuels*, 31, 8803-8812. https://doi.org/10.1021/acs.energyfuels.7b01124

Wu, B., Zhang, Y., Zhang, X.-X. & Cheng, S.-P. (2011a). Health risk assessment of polycyclic aromatic hydrocarbons in the source water and drinking water of China: Quantitative analysis based on published monitoring data. *Science of The Total Environment*, 410, 112-118. https://doi.org/10.1016/j.scitotenv.2011.09.046

Wu, C.-H., Chang-Chien, G.-P. & Lee, W.-S. (2004). Photodegradation of polychlorinated dibenzo-p-dioxins: comparison of photocatalysts. *Journal of Hazardous Materials*, 114, 191-197. https://doi.org/10.1016/j.jhazmat.2004.08.008

Wu, M., Chen, L., Tian, Y., Ding, Y. & Dick, W. A. (2013). Degradation of polycyclic aromatic hydrocarbons by microbial consortia enriched from three soils using two different culture media. *Environmental Pollution*, 178, 152-158. https://doi.org/10.1016/j.envpol.2013.03.004

Wu, T., Cai, X., Tan, S., Li, H., Liu, J. & Yang, W. (2011b). Adsorption characteristics of acrylonitrile, p-toluenesulfonic acid, 1-naphthalenesulfonic acid and methyl blue on graphene in aqueous solutions. *Chemical Engineering Journal*, 173, 144-149. https://doi.org/10.1016/j.cej.2011.07.050

Wu, Y., Zhou, S., Ye, X., Chen, D., Zheng, K. & Qin, F. (2011c). Transformation of pollutants in landfill leachate treated by a combined sequence batch reactor, coagulation, Fenton oxidation and biological aerated filter technology. *Process Safety and Environmental Protection*, 89, 112-120. https://doi.org/10.1016/j.psep.2010.10.005

Wu, Z. & Zhu, L. (2012). Removal of polycyclic aromatic hydrocarbons and phenols from coking wastewater by simultaneously synthesized organobentonite in a one-step process. *Journal of Environmental Sciences*, 24, 248-253. https://doi.org/10.1016/s1001-0742(11)60780-8

Xi, Z. & Chen, B. (2014). Removal of polycyclic aromatic hydrocarbons from aqueous solution by raw and modified plant residue materials as biosorbents. *Journal of Environmental Sciences*, 26, 737-748. https://doi.org/10.1016/S1001-0742(13)60501-X

Xu, C., Nasrollahzadeh, M., Selva, M., Issaabadi, Z. & Luque, R. (2019). Waste-to-wealth: biowaste valorization into valuable bio(nano)materials. *Chemical Society Reviews*, 48, 4791-4822. https://doi.org/10.1039/C8CS00543E

Xu, H., Zhan, M.-X., Cai, P.-T., Ji, L.-J., Chen, T. & Li, X.-D. (2019). Adsorption characteristics of polycyclic aromatic hydrocarbons by biomass-activated carbon in flue gas. *Energy & Fuels*, 33, 11477-11485. https://doi.org/10.1021/acs.energyfuels.9b02723

Yakout, S. M. & Daifullah, A. A. M. (2013). Removal of selected polycyclic aromatic hydrocarbons from aqueous solution onto various adsorbent materials. *Desalination and Water Treatment*, 51, 6711-6718. https://doi.org/10.1080/19443994.2013.769916

Yang, K., Chen, B. & Zhu, L. (2015). Graphene-coated materials using silica particles as a framework for highly efficient removal of aromatic pollutants in water. *Scientific Reports*, 5, 11641, 1-13. https://dx.doi.org/10.1038%2Fsrep11641

Yang, X., Li, J., Ren, X., Huang, Y. & Wang, X. (2013). Adsorption of naphthalene and its derivatives on magnetic graphene composites and the mechanism investigation. *Colloid Surface A.*, 422, 118– 125. https://doi.org/10.1016/j.colsurfa.2012.11.063

Yap, C. L., Gan, S. & Ng, H. K. (2012). Ethyl lactate-Fenton treatment of soil highly contaminated with polycyclic aromatic hydrocarbons (PAHs). *Chemical Engineering Journal*, 200-202, 247-256. https://doi.org/10.1016/j.cej.2012.06.036

Ye, S., Yan, M., Tan, X., Liang, J., Zeng, G., Wu, H., Song, B., Zhou, C., Yang, Y., Wang, H. (2019b). Facile assembled biochar-based nanocomposite with improved graphitization for efficient photocatalytic activity driven by visible light. *Applied Catalysis B: Environmental* 250, 78-88. https://doi.org/10.1016/j.apcatb.2019.03.004

Ye, S., Zeng, G., Wu, H., Liang, J., Zhang, C., Dai, J., Xiong, W., Song, B., Wu, S., Yu, J. (2019a). The effects of activated biochar addition on remediation efficiency of co-composting with contaminated wetland soil. Resources, Conservation and Recycling 140, 278-285. https://doi.org/10.1016/j.resconrec.2018.10.004

Yuan, H., Li, T., Ding, X., Zhao, G. & Ye, S. (2014). Distribution, sources and potential toxicological significance of polycyclic aromatic hydrocarbons (PAHs) in surface soils of the

Yellow River Delta, China. *Marine Pollution Bulletin*, 83, 258-264. http://doi.org/10.1016/j.marpolbul.2014.03.043

Zeledón-Toruño, Z. C., Lao-Luque, C., de las Heras, F. X. C. & Sole-Sardans, M. (2007). Removal of PAHs from water using an immature coal (leonardite). *Chemosphere*, 67, 505-512. https://doi.org/10.1016/j.chemosphere.2006.09.047

Zertal, A., Molnár-Gábor, D., Malouki, M. A., Sehili, T. & Boule, P. (2004). Photocatalytic transformation of 4-chloro-2-methylphenoxyacetic acid (MCPA) on several kinds of $TiO_2$. *Applied Catalysis B: Environmental*, 49, 83-89. https://doi.org/10.1016/j.apcatb.2003.11.015

Zhang, C., Wu, L., Cai, D., Zhang, C., Wang, N., Zhang, J. & Wu, Z. (2013). Adsorption of polycyclic aromatic hydrocarbons (Fluoranthene and Anthracenemethanol) by functional graphene oxide and removal by pH and temperature-sensitive Coagulation. *ACS Applied Materials & Interfaces*, 5, 4783-4790. https://doi.org/10.1021/am4002666

Zhang, L., Li, P., Gong, Z. & Li, X. (2008). Photocatalytic degradation of polycyclic aromatic hydrocarbons on soil surfaces using $TiO_2$ under UV light. *Journal of Hazardous Materials*, 158, 478-484. https://doi.org/10.1016/j.jhazmat.2008.01.119

Zhang, L., Luo, L., & Zhang, S. (2011). Adsorption of phenanthrene and 1,3-dinitrobenzene on cation-modified clay minerals. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 377, 278-283. https://doi.org/10.1016/j.colsurfa.2011.01.017

Zhang, M.-h., Dong, H., Zhao, L., Wang, D.-x. & Meng, D. (2019). A review on Fenton process for organic wastewater treatment based on optimization perspective. *Science of The Total Environment*, 670, 110-121. https://doi.org/10.1016/j.scitotenv.2019.03.180

Zhang, S., Niu, H., Cai, Y. & Shi, Y. (2010). Barium alginate caged $Fe_3O_4@C_{18}$ magnetic nanoparticles for the pre-concentration of polycyclic aromatic hydrocarbons and phthalate esters from environmental water samples. *Analytica Chimica Acta*, 665, 167-175. https://doi.org/10.1016/j.aca.2010.03.026

Zhang, S., Yao, H., Lu, Y., Yu, X., Wang, J., Sun, S., Liu, M., Li, D., Li, Y.-F. & Zhang, D. (2017). Uptake and translocation of polycyclic aromatic hydrocarbons (PAHs) and heavy metals by maize from soil irrigated with wastewater. *Scientific Reports*, 7, 12165, 1-11. https://doi.org/10.1038/s41598-017-12437-w

Zhao, G., Jiang, L., He, Y., Li, J., Dong, H., Wang, X. & Hu, W. (2011a). Sulfonated graphene for persistent aromatic pollutant management. *Advanced Materials*, 23, 3959-3963. https://doi.org/10.1002/adma.201101007

Zhao, G. X., Li, J. X. & Wang, X. K. (2011b). Kinetic and thermodynamic study of 1-naphthol adsorption from aqueous solution to sulfonated graphene nanosheets. *Chemical Engineering Journal*, 173, 185–190. https://doi.org/10.1016/j.cej.2011.07.072

Zhao, J., Wang, Z., Zhao, Q. & Xing, B. (2014). Adsorption of phenanthrene on multilayer graphene as affected by surfactant and exfoliation. *Environmental Science & Technology*, 48, 331-339. https://doi.org/10.1021/es403873r

Zhao, W., Yang, L., He, L. & Zhang, S. (2016). Simultaneous enrichment of polycyclic aromatic hydrocarbons and $Cu^{2+}$ in water using tetraazacalix[2]arene[2]triazine as a solid-phase extraction selector. *Journal of Agricultural and Food Chemistry*, 64, 6233-6239. https://doi.org/10.1021/acs.jafc.6b03083

Zimmerman, S. C., Wendland, M. S., Rakow, N. A., Zharov, I. & Suslick, K. S. (2002) Synthetic hosts by monomolecular imprinting inside dendrimers. *Nature*, 418, 399-403. https://doi.org/10.1038/nature00877