

Department of Civil Engineering

**Improve the Efficiency of Constructed Wetlands in Removing Polycyclic
Aromatic Hydrocarbons (PAH) from Stormwater**

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**This thesis is presented for the Degree of
Doctor of Philosophy
of
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DECLARATION

To the best of my knowledge and belief this thesis contains no material previously published by any other person except where due acknowledgement has been made.

This thesis contains no material which has been accepted for the award of any other degree or diploma in any university.

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ABSTRACT

Polycyclic aromatic hydrocarbons (PAHs) are major pollutants in degrading the quality of stormwater due to toxic, mutagenic, carcinogenic and teratogenic nature. PAHs are organic micro pollutants persistent in the environment due to their chemically stable structure and low bioavailable fraction. United States Environmental Protection Agency (USEPA) has categorised 16 PAHs in the priority list due to their adverse impact towards environment and human health. PAHs released from manufacturing industries, vehicular exhaust and other incomplete combustion of organic carbons are discharged into the atmosphere and urban surfaces. PAHs in the air, soil, parking lots, road, highway, and drainage will mix in stormwater with rainfall and snowmelt resulting in poor quality of stormwater.

Among the different types of PAHs removal methods, constructed wetland (CW) system is economic and environmental friendly technique which consists multiple treatment opportunities including filtration, adsorption, phytoremediation and bioremediation. The PAHs removal capacity of different elements of CW is still unsatisfactory. This study focused on improving the performances CWs for PAHs removal by introducing bed materials such as powder activated carbon (PAC), granular activated carbon (GAC), zeolite, bentonite, sand and *Dianella revoluta* plant. Furthermore, the performances of environmental parameters such as dissolved oxygen (DO), pH, oxidation reduction potential (ORP) and temperature of CW have been also examined. In addition to this, the present study has included solubilisation enhancement of PAHs with organic solvents and various types of surfactants which increase the bioavailability of PAHs which is crucial in detoxification of PAHs adsorbed in CW bed media as well as from contaminated soils and sediments. The outcome of this research would add strengths in the sustainable management of urban stormwater.

PAH adsorption order was found as PAC (100%) > GAC (92.79%) > bentonite (80.25%) > zeolite (25.04%) from laboratory experiments. PAC and GAC were further considered for kinetic and isotherm analysis. The PAH adsorption rate was well fitted with second order kinetic model ($R^2 = 1$) for both adsorbents when compared to first-order kinetic ($R^2 = 0.94-0.98$). Furthermore, the adsorption rate was increased with mass of adsorbents. Moreover, adsorption isotherm data were well fitted with Freundlich isotherm models with correlation coefficient of 0.91 and 0.95 for PAC and GAC respectively.

From the analysis of experimental results, organic solvents were found to be effective in phenanthrene solubility. Moreover, there is positive effect of duration of mixing in phenanthrene solubility with result up to 84.16% solubility with methanol at 120 h. The surfactant enhanced remediation (SER) is one of the promising techniques in detoxifying PAHs by enhancing solubility and biodegradability of PAHs. 1:9 anionic-nonionic surfactant system was observed effective in PAH solubilisation when compared to single system and other proportions of mixed systems. Biosurfactants have many potential advantages such as biodegradability, lower toxicity and a wide range of environmental resilience. Moreover, selection of proper type and quantity of synthetic surfactants could also improve PAHs solubilisation and biodegradation without adverse impact to the environment.

From analysis of experimental results, sodium dodecylbenzene sulfonate (SDBS) was found effective in phenanthrene solubilisation when compared to sodium dodecyl sulphate (SDS). Anionic-nonionic mixed surfactants systems are more effective in phenanthrene solubilisation when compared to single surfactant system. The highest phenanthrene solubility was obtained at anionic-nonionic surfactants ratio 1:9 among the various proportions considered in the experiments. Furthermore, phenanthrene solubility increased with increase of surfactant concentration from 1 to 5 mM for all systems. Moreover, polyoxyethylene sorbitan monolaurate (Tween20) was found more effective when compared to polyoxyethylene sorbitan monooleate (Tween80) in phenanthrene solubilisation for all tested proportions of anionic-nonionic systems for all concentrations of surfactants.

Considering suitable plants in CWs to remove PAH, *Dianella revoluta* found to be effective as phenanthrene removal efficiency of CW3 (84.38%) was observed greater than CW2 (78.6%). Positive effect of PAC in CW was found as phenanthrene removal of CW2 (78.6%) was greater than CW1 (53.6%). The adsorption of phenanthrene was increased with increased amount of PAC which could be observed from phenanthrene removal efficiency of CW2 (78.6%) and CW4 (92.2%), however, there might be negative effect of 0.05% PAC on plant health. From analysing the ORP, CWs were under anoxic and anaerobic conditions in most of cases. There was not found any significant trend in pH values for effluent samples of different types of CWs. The temperature of CWs was independent of CW bed media or plant as the temperature measurements were same as that of room temperature.

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LIST OF ABBREVIATIONS

AC	Activated Carbon
CCME	Canadian Council of Ministers of the Environment
CP	Catylpyridinium
CTMAB	Cetyltrimethylammonium Bromide
CW	Constructed Wetland
DPC	Dodecylpyridinumchloride
GAC	Granular Activated Carbon
GO	Graphene Oxide
HA	Humic Acid
IOB	Inorgano-Organo Bentinite
LCEFM	Laccase Carrying Electrospun Fibrous Membrane
LECA	Light Weight Clay Aggregate
LPHM	Low pH Montmorillonite
MPEG	Methoxy Polyethylene Glycol
PLGA	Poly (Lactide-Co- Glycolide)
PAC	Powder Activated Carbon
PAH	Polycyclic Aromatic Hydrocarbon
PDLGA	Poly(D,L-Lactide-Co-Glycolide)
RGO	Reduced Graphene Oxide
RHAC	Rice Husk Activated Carbon
SDBS	Sodium Dodecylbenzene Sulfonate
SDS	Sodium Dodecyl Sulfate
SF	Surface Flow
SSF	Subsurface Flow
USEPA	Unites State Environmental Protection Agency

Chapter 1

Introduction

1.1 Background

Along with the growth of population around the world, the urbanisation rate has been increasing resulting expansion of residential and commercial buildings, roads, parking lots and industrial developments. The natural ground surface, as well as vegetation amount, has been decreasing at an alarming rate due to covering the natural surface with buildings, road, parking lots and other artificial impervious surfaces and structures. This leads to the degradation of the quality of stormwater runoff day by day due to the discharge of residential, commercial and industrial waste to water resources (McIntosh et al. 2013; Liu et al. 2016; Vogel and Moore 2016). Depending on the activities at catchment area, stormwater comprises different types of pollutants such as sediments, nutrients, heavy metals, polycyclic aromatic hydrocarbons (PAHs), pesticides, polychlorinated biphenyls, and biological organisms. Among stormwater pollutants, PAHs are known as one of the major pollutants in degrading the quality of stormwater due to its toxic, mutagenic, carcinogenic and teratogenic properties (USEPA 2008).

PAHs are persistent organic compounds and they are ubiquitous in the environment. Their occurrences in the environment are by natural and anthropogenic means such as pyrolysis of organic matter, chemical industries, use of fossil fuel (Gallego et al. 2008; Manoli and Samara 1999; Ravindra et al. 2008). The major sources of PAHs in stormwater are point sources such as petroleum and carbon black manufacturing industries and nonpoint sources such as wear and leaching of asphalt, tire wear, drips of crankcase oil, and vehicular exhaust (Brown and Peake 2006; Sposito et al. 2009).

PAHs are toxic, mutagenic and carcinogenic organic compounds and the ecological toxicity increased with increasing of molecular weight of PAHs (Liu et al. 2016). Due to the toxic, mutagenic and carcinogenic natures of PAHs, numbers of methods such as physical, chemical, thermal, biological, surfactant enhanced, phytoremediation and combined technology (constructed wetland) have been developed to remove PAHs from contaminated soil, sediment and water (Zhou et al. 2013; Wang, et al. 2014; Li et al. 2015; Sun et al. 2014;

Peng et al. 2014; Li et al. 2014; Hu et al. 2014; Yi et al. 2016; Xu et al. 2016; Al-Sbani et al. 2016).

Sorption method has been extensively used in remediation of PAHs because PAHs have complex chemical structures and having highly sorptive ability into the solid media. Various types of sorption media (activated carbon, biochar, bentonite, zeolite, light weight clay aggregate, etc) have been used in PAHs remediation by sorption method (Amstatter et al. 2012; Li et al. 2014; Kaya et al. 2013; Nkansah et al. 2012; Lemić et al. 2007). Among them activated carbon has been found very effective PAHs sorbent which could remove PAHs up to 100% from aqueous solution (Kong et al. 2011).

PAHs from soil, sediment and water media could also be removed by a chemical method which includes conventional oxidation and advance oxidation process (AOP) (Chen et al. 2015). Conventional oxidation process comprises oxidation by ozone, chlorine, potassium and permanganate whereas AOP involves the combination of different oxidant as O_3 , H_2O_2 ; different source of energy as UV light, electrical energy and different types of catalyst as iron, TiO_2 , ZnO , Pt (Beltrán et al. 1999; Rebola et al. 2008; Miller and Olejnik 2004; Cordeiro and Corio 2009). Another process of PAHs remediation is thermal processes. In-pile thermal desorption, soil venting thermal desorption and rotary kiln incineration are some methods for thermal treatment of PAHs. Thermal process includes vaporization, boiling, oxidation and pyrolysis techniques (Baker et al. 2006, Acharya and Ives 1993, (Harmon et al. 2001).

When compared to chemical and thermal techniques, bioremediation and phytoremediation techniques are environmental friendly and have less operation and maintenance cost to remove PAHs from the environment (Desai et al. 2008; Petruzzelli et al. 2016). In these methods, PAHs are degraded and detoxified with the help of plants and associated microorganisms (USEPA, 2000). Furthermore, a combined technique such as constructed wetland (CW) system is one of the best management techniques to treat urban stormwater and industrial runoff (Kadlec and Wallace 2009). CW treatment system includes multi-treatment opportunities such as adsorption, filtration, sedimentation, phytoremediation and biodegradation without producing by-products to further contaminate the environment (Eifert 2000). CW system thus has been gaining popularity in urban stormwater treatment especially in remediation of toxic, carcinogenic and mutagenic organic micro-pollutant such as PAHs.

1.2 Research significance

The PAHs in urban stormwater is generated from point sources such as residential, commercial and industrial waste disposal and non-point sources such as vehicles and urban surface materials (building roofs, roads, highways, parking lots, streets, driveways and footpaths, tire wear, drips of crankcase oil, and vehicular exhausts). The water from rainfall or snowmelt brings PAHs from air, impervious urban surfaces into rivers, lakes and coastal water bodies. Naturally, the non-point source pollution is difficult to control because water is irregularly discharged (Nakajima et al. 2010). Thus management of non-point source pollution such as PAHs from urban stormwater has become significantly important.

Furthermore, significant interest in developing appropriate PAHs removal processes through understanding remediation mechanisms have been raised (Makkar and Rockne 2003; Chen et al. 2008). A number of methods (physical, chemical, thermal, phytoremediation, bioremediation) have been investigated to treat PAHs from contaminated soil, sediment and water bodies to mitigate the possible risk of ecological toxicity into the environment due to PAHs. The combined technique such as CW system has become popular for urban stormwater treatment (Kadlec et al. 2009) due to its multi-treatment opportunities, environmentally friendly nature and less operational and maintenance cost. There are numbers of studies in aqueous PAHs removal by using CW (Gavin et al. 2006; Terzakis et al. 2008; Wojciechowska 2013; Poerschmann and Schultze-Nobre 2014; Cottin and Merlin 2008; Yi et al. 2016; Tromp et al. 2012), however, past studies have mainly focused on overall removal of PAHs. The PAHs removal in different elements of CW has been scarcely investigated, especially the role of CW bed media and CW vegetation in PAHs removal process.

The significance of this research:

1. Investigated PAHs removal capacity of CW media such as powder activated carbon (PAC), granular activated carbon (GAC), zeolite, bentonite, sand and *Dianella revoluta* plant.
2. Examined the performances of environmental parameters such as dissolved oxygen (DO), pH, oxidation reduction potential (ORP) and temperature of CW system.

3. Evaluated solubilisation enhancement of PAHs with organic solvents and various types of surfactants in single and mixed systems. Moreover, reviewed surfactant enhanced PAHs remediation.
4. Developed efficient and environmental friendly PAHs treatment method which would add strengths in the sustainable management of urban stormwater.

1.3 Objective of study

The main objective of this study is to develop low cost and environmental friendly technique to effectively remove PAHs in urban stormwater.

The specific objectives of the study are:

- To evaluate different types of sorption media and affecting factors in PAHs remediation by using sorption method.
- To investigate the PAHs sorption capacity and PAHs sorption rate of selected adsorbents.
- To investigate performance of selected PAH adsorbents to be used in the constructed wetland.
- To explore solubilisation process of PAHs with different types of organic solvents.
- To evaluate surfactant enhanced solubilisation and remediation of PAHs with various types of surfactants in their single and mixed micelles.
- To investigate the effectiveness of suitable bed materials and plants used for CWs in PAHs removal.
- To assess the integrated impacts of environmental parameters in improving the performance of CWs in PAHs remediation.
- To develop recommendations for CWs to enhance the PAHs removal capacity.

1.4 Organization of thesis

This thesis comprises 7 chapters.

Chapter 1 provides the background and introduction to remove PAHs from stormwater with the significance of this research which leads to develop aims and objectives of the study.

Chapter 2 provides a critical review of past literature related to sources of PAHs, types of PAHs, physical and chemical properties of PAHs, effect of PAHs in the environment and human health and PAHs remediation methods from the environment.

Chapter 3 presents the importance of sorption method in PAHs remediation from soil, sediment and aqueous media along with popular PAHs sorption media, sorption kinetics, sorption isotherm, and affecting factors in PAHs sorption process. The content of this chapter has been already published (published journal paper #1).

Chapter 4 presents the kinetic and isotherm analysis of PAH adsorption with PAC and GAC along with effect of adsorbent mass on PAH adsorption based on laboratory experimental results.

Chapter 5 describes the solubilisation capacity of PAHs with different types of organic solvents such as methanol, hexane, acetone. PAHs solubilisation with organic solvents is important mechanism to decontaminate the PAHs contaminated soil, sediment and CW bed media.

Chapter 6 discusses the types of surfactants, affecting factors in PAHs solubilisation, PAHs biodegradation in the presence of surfactants and mechanisms of surfactants enhanced solubilisation of PAHs with single and mixed micelles. Surfactants enhance the bioavailability of PAHs which is of high importance in detoxification of PAHs adsorbed into CW bed media. This chapter has been also published (published journal paper #2).

Chapter 7 presents the results of the laboratory experiments on solubilisation of PAH with anionic (SDS, SDBS) and nonionic (Tween20 and Tween80) surfactants including effectiveness of different proportion of anionic-nonionic surfactants and effect of surfactants concentration in solubilisation of surfactants.

Chapter 8 presents PAHs treatment by using CW where the significance of CW in stormwater PAHs treatment along with different mechanisms of PAHs treatment involved in CW. Moreover, this chapter analyses laboratory experimental results for PAH removal capacity of different types of the bed media and plant along with the effect of time and spatial variation in PAHs remediation. Furthermore, environmental parameters such as temperature,

pH, dissolved oxygen and oxidation reduction potential for CW have been monitored and presented in this chapter.

Chapter 9 concludes overall research outcome and highlights the specific outcomes of the study performed on improve the efficiency of constructed wetlands in removing polycyclic aromatic hydrocarbons (PAHs) from stormwater. Also this chapter provides the recommendations for application of the outcome of this study and guidelines for further research.

1.5 List of publications

This thesis is based on the following papers, which are referred to in the text by their respective roman numerals.

Paper 1

Shanti Lamichhane, KC Bal Krishna, Ranjan Sarrukkalige, 2016. Polycyclic aromatic hydrocarbons (PAHs) removal by sorption method: A review. *Chemosphere*, 148, 336-353.

Paper 2

Shanti Lamichhane, KC Bal Krishna, Ranjan Sarrukkalige, 2017. Surfactant Enhanced Remediation of Polycyclic Aromatic Hydrocarbons: A review. *Journal of Environmental Management*, 199, 46-61.

Chapter 2

Literature review

2.1 Urbanisation and storm water quality

The urbanisation rate has been increasing along with the growth of population around the world due to continuous changes in aspects of living conditions of society. With the expansion of residential and commercial buildings, industrial infrastructures, highways, roads and parking lots, the natural ground surface as well as the amount of vegetation has been decreasing at an alarming rate. The increase in impervious surface directly impacts on the quality and quantity of stormwater. The natural movement of stormwater has been dramatically changed with rapid urbanisation in Australia resulting in increased urban runoff (National water quality management strategy 2000). The precipitation and snowfall can no longer infiltrate the ground surface resulting significantly larger runoff than that of a rural or natural area and creates a risk of floods. Flood protection, ecological protection, restoration, drainage system, etc. are added to the urban stormwater management system. More importantly, the quality of stormwater runoff is found to be poorer due to pollution by the urban development, causing the concern for the water resources. In addition, urbanisation leads to delegate the stormwater quality from industrial, residential and commercial discharge. Therefore, the urban water has been polluted more and more with time (McIntosh et al. 2013). Depending on the activities at catchment area, stormwater comprises different types of pollutants such as sediments, nutrients, heavy metals, polycyclic aromatic hydrocarbons (PAHs), pesticides, polychlorinated biphenyls, and biological organisms.

2.2 PAHs in stormwater

Among the pollutants in stormwater, PAHs are known as the major pollutants in degrading the quality of water (USEPA 2008) as PAHs are toxic, mutagenic, carcinogenic and teratogenic. PAHs are composed of two or more fused aromatic benzene rings (Chen and Zhu 2011) having lipophilic nature with comparatively high desorption activation energy (Johnsen and Karlson 2005) and exist in different compounds according to the number and position of aromatic rings. PAHs are persistent compounds in the environment due to their chemically stable structure and low bioavailable fraction (Shin et al. 2006) and are identified as one of the

major pollutants in urban stormwater (Sirova 2015; Nakajima et al. 2010). PAHs released from manufacturing industries, vehicular exhaust and other incomplete combustion of organic carbons are discharged into the atmosphere. PAHs in the air, soil, parking lots, road, highway, and drainage will mix in stormwater with rainfall and snowmelt (Prabhukumar 2010; Weerasundara and Vithanage 2016) resulting in poor quality of stormwater.

The major sources of PAH in urban stormwater are anthropogenic activities such as vehicular emissions, leakage from the petroleum industry, manufacturing of carbon black, coal tar pitch and asphalt, heating and power generation, emissions from internal combustion engines, wear and leaching of asphalt and bituminous roads, highways, parking lots, tire wear and drips of crankcase oil (Manoli and Samara 1999; Ravindra et al. 2008; Liu et al. 2016; Brown and Peake 2006). PAHs are ubiquitous in urban runoff (García-Flores 2013; Sirova 2015; Hengren 2010; Hwang and Foster 2006; Hoffman 1984). This could be due to less likely of infiltration to ground water because of the high coverage of buildings, roads, parking lots and other artificial structures. Finally, PAHs are discharged into the nearby waterbodies with rainfall and snowmelt (Weerasundara and Vithanage 2016) which ultimately results in adverse impact in the environment and aquatic life.

2.3 Types of PAHs

PAHs are categorized as low molecular weight PAHs and high molecular weight PAHs based on fused benzene ring numbers in PAHs molecules. Low molecular weight PAHs include two and three ring structures while high molecular weight PAHs comprise four and more ring structures. The aqueous solubility of PAHs decreases almost linearly with increase in molecular mass (Heitkamp and Cerniglia 1989; Balati et al. 2015).

Based on the source of formation, PAHs are categorised as petrogenic PAHs and pyrogenic PAHs. Petrogenic sources include gasoline, diesel fuel, lubricating oil, asphalt, and bitumen while pyrogenic sources include incomplete combustion of coal, petroleum product, wood, garbage incinerators and forest fires.

Furthermore, depending on the ring structures, PAHs are divided into alternant and non-alternant groups. Alternant PAHs are composed of only six-membered benzoid rings while

non-alternant PAHs may contain rings with less than six carbon atoms in addition to six-membered rings. Examples of alternant PAHs are presented in Figure 2.1 and examples of non-alternant PAHs are presented in Figure 2.2.

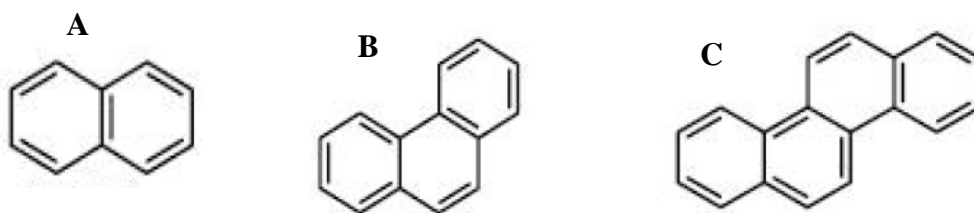


Figure 2.1: Alternant PAH (A: Naphthalene, B: Phenanthrene, C: Chrysene)

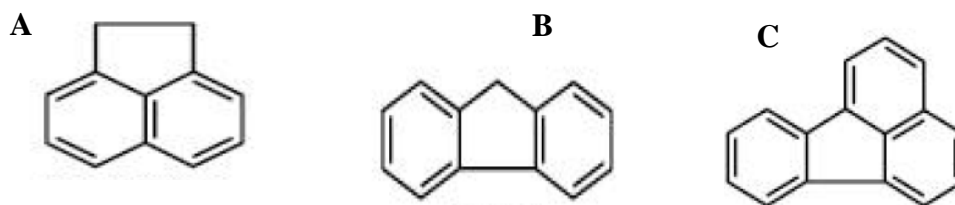


Figure 2.2: Non-alternant PAH (A: Acenaphthene, B: Fluorene, C: Fluoranthene)


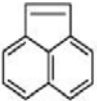
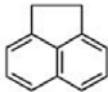
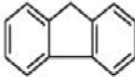
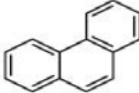
Although there are more than 100 different types of PAHs, United States Environmental Protection Agency (USEPA) has categorised 16 PAHs (Table 2.2) in the priority list due to their adverse impact towards the environment and human health (Zhang et al. 2004).

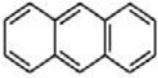
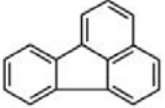
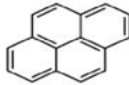
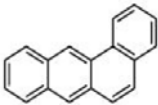
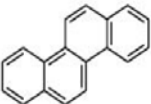
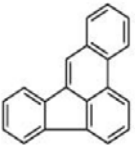
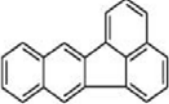
2.4 Physical and chemical properties of PAHs

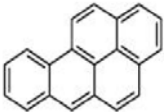
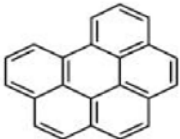
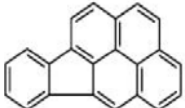
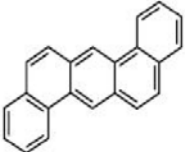
PAHs are less water soluble with lipophilic nature and having comparatively high desorption activation energy (Johnsen and Karlson 2005). PAHs are solid and appear from colorless to white or pale yellow-green in their purest form (Parbhukumar 2010). PAHs are persistence in the environment and less microbial degradable due to their chemically stable structure and low bioavailable fraction (Seo and Bishop 2007; Alcantara et al. 2009; Shin et al. 2006). Transformation, degradation, and sequestration of PAHs depend on molecular weight, water solubility, vapor pressure and ring structures of PAHs. High molecular weight PAHs are relatively less water soluble, less volatile, more lipophilic, high affinity to a solid phase and less biodegradable in comparison to low molecular weight PAHs (Prabhukumar 2010; Balati

et al. 2015; Wammer and Peters 2005). However, PAHs with linear arranged molecules are less soluble than those with angular or peri-fused one. For example, anthracene is less soluble than phenanthrene (Table 2.1). Furthermore, the octanol-water partition coefficient (K_{ow}) and partition coefficients normalized to organic carbon (K_{oc}) are important parameters in controlling PAHs desorption from soil and to predict the environmental contaminants (Hussein and Ismail 2013).

Table 2.1: Physical and chemical properties of USEPA categorised 16 PAHs (Pandey et al. 2016; Kim et al. 2013; Prabhukumar 2010; Lundstedt 2003)

PAHs	Chemical structure	Molecular weight (g/mol)	Vapour pressure (Pa)	Melting point (°C)	Boiling point (°C)	Density (g/cm ³)	Solubility in water at 25 °C (µg/L)	Log K _{ow}	Log K _{oc}
Naphthalene (C ₁₀ H ₈)		128.1705	11.866		218		3.17 x 10 ⁴	3.29	2.97
Acenaphthylene (C ₁₂ H ₈)		152.1919	3.866	92-93	280	0.8987	3.4 x 10 ³	4.07	3.40
Acenaphthene C ₁₂ H ₁₀		154.2078	0.5	95	279	1.222	3.93 x 10 ³	3.98	3.66
Fluorene C ₁₃ H ₁₀		166.2185	0.432	116-117	295	1.202	1.98 x 10 ³	4.18	3.86
Phenanthrene C ₁₄ H ₁₀		178.2292	9.07 x 10 ⁻²	101	339-340	1.18	1.29 x 10 ³	4.45	4.15

Anthracene C ₁₄ H ₁₀		178.2292	3.4 x 10 ⁻³	218	340	1.25	73	4.45	4.15
Fluoranthene C ₁₆ H ₁₀		202.2506	1.08 x 10 ⁻³	110.8	375-393	1.252	260	4.90	4.58
pyrene C ₁₆ H ₁₀		202.2506	5.67 x 10 ⁻⁴	145.148	360-404	1.271	135	4.88	4.58
Benzo(a)anthracene C ₁₈ H ₁₂		228.2879	2.05 x 10 ⁻⁵	158	435	1.19	14	5.61	5.30
Chrysene C ₁₈ H ₁₂		228.2879	1.04 x 10 ⁻⁶	254	441-448	1.274	2.0	5.16	5.30
Benzo(b)fluoranthene C ₂₀ H ₁₂		252.3093	1.07 x 10 ⁻⁵	168	168	1.286	1.2	6.04	5.74
Benzo(k)fluoranthene C ₂₀ H ₁₂		252.3093	1.28 x 10 ⁻⁸	217	217	1.286	0.76	6.06	5.74

Benzo(a)pyrene C ₂₀ H ₁₂		252.3093	6.52 x 10 ⁻⁷	179	493-496	1.24	3.8	6.06	6.74
Benzo(ghi)perylene C ₂₂ H ₁₂		276.3307	1.33 x 10 ⁻⁸	278	525	1.378	0.26	6.50	6.20
Indeno(123cd)pyrene C ₂₂ H ₁₂		276.3307	1.87 x 10 ⁻⁸	163.6	161-163	536	62	6.58	6.20
Dibenz(ah)anthracene C ₂₂ H ₁₄		278.3466	2.80 x 10 ⁻⁹	262	262	1.232	0.5 (27°C)	6.84	6.52

2.5 Sources of PAH

PAHs are released into the environment as a result of natural activities such as terrestrial vegetation synthesis, microbial synthesis, and volcanic activity. However, PAHs released by these processes are minimal when compared to PAHs produced from forest fires, grassland fires and anthropogenic sources (Sims and Overcash 1983). Anthropogenic activities (such as military operations, vehicular emissions, agricultural production, residential waste burning, combustion of fossil fuels, leakage from the petroleum industry, manufacturing of carbon black, coal tar pitch and asphalt, heating and power generation, and emissions from internal combustion engines) release a significant amount of PAHs in to the environment (Manoli and Samara 1999; Ravindra et al. 2008; Liu et al. 2016). High molecular weight PAHs are produced by the light-duty vehicles which use gasoline and low molecular weight PAHs are produced by heavy-duty vehicles which use diesel (Aryal et al. 2010). According to William et al. (1999), gasoline, coal, leaching of creosoted wood products, fossil fuel burning, tanker spills, oil seeps, and petroleum-related industries induce 2.4×10^{-4} to 0.56 mg/L PAHs .

PAHs are detected in different media such as in air (Liu et al. 2015; Manoli et al. 2016), in soil, sediments and street dust (Vane et al. 2014; Wang et al. 2015; Sun et al. 2016; Sarria-Villa et al. 2016; LiDong et al. 2016; Bandowe and Nkansah 2016), in water bodies (Chang et al. 2004; Balati et al. 2015; Sun et al. 2016; Sarria-Villa et al. 2016) and in the tissues of animal and plants (USEPA 2008; Li, Dong et al. 2016; Barhoumi et al. 2016; Chen et al. 2015; Waręzak et al. 2015) signifying their wider presence in the environment. According to (Witter and Nguyen 2016), PAHs level are found 2.4 times more in an urban watershed in comparison to a rural area. PAHs infiltration into the urban ground is less likely than country region due to the high cover of buildings, roads, highway, parking lots and other artificial structures. The accumulated PAHs on those impervious surfaces are discharged into the nearby water body with rainfall and snowmelt runoff (Weerasundara and Vithanage 2016).

2.6 Standard limit of PAHs

There have been efforts at international level and national level to regulate the amount of PAHs in water, in order to protect both human and animal lives. The standard limit for the total PAHs concentration permitted in drinking water is 0.2 µg/L (WHO, 2003), while Environmental Protection Agency (EPA) set as 0.1 µg/L for benzo(a)anthracene, 0.2 µg/L for Benzo(b)fluoranthene, benzo(k)]fluoranthene, benzo(a)pyrene and chrysene, 0.3 µg/L for

dibenz(a,h)anthracene and 0.4 µg/L for indeno(1,2,3-cd)pyrene (Giridhar Prabhukumar 2010). Moreover, Chinese Standards for Drinking Water Quality (GB5749-2006) reports the concentration limit value of benzo(a)pyrene as 0.01µg/L and total concentration limit value for 6 PAHs (fluoranthene, Benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(g, h, i)perylene and indeno(1,2,3-cd)pyrene) is 0.2 µg/L (Chen and Zhu 2011).

Regarding the limit of PAHs for safe aquatic life, Canadian Council of Ministers of the Environment ((CCME) 1999) sets the concentration of PAHs as 1.1 µg/L for naphthalene, 5.8 µg/L for acenaphthene, 3.0 µg/L for fluorene, 0.4 µg/L for phenanthrene, 0.0012 µg/L for anthracene, 0.025 µg/L for pyrene, and 0.0015 µg/L for benzo(a)pyrene.

2.7 Environmental and health impact of PAHs

PAHs released from both natural and anthropogenic sources are directly or indirectly deposited in sediment, water, plants, soils, aquatic organisms and human bodies. Since they are present throughout the environment, it is not unusual for human and animals to be exposed through inhalation, skin contact and consumption of contaminated water, grains, vegetables and seafoods (Nielsen et al. 1996; Barhoumi et al. 2016).

PAHs are very crucial pollutants due to their carcinogenic, mutagenic and toxic properties and their persistent nature (Manoli and Samara 1999). The carcinogenicity of PAHs increased with increasing molecular weight (Eisler 1987). There is a risk of developing cancer in human organs (such as lung, bladder, stomach, skin, larynx, scrotum, breast, oesophageal, prostate, kidney and pancreas) due to exposure to PAHs. Furthermore, they are known to suppress the immune system and are suspected of being endocrine disrupters (Siddens et al. 2012; Xu et al. 2013; USEPA 2008). Furthermore, studies on the tumorigenicity of individual PAH metabolites in animals concluded that vicinal or bay-region diol epoxides are the ultimate mutagenic and carcinogenic species of alternant PAHs (Graslund 1989). The various studies have presented the adverse biological and biochemical effects of PAHs to aquatic organisms (Schiedek 2006; Fragoso 2006; Barhoumi et al. 2016). Many other studies (Grova and 2009; Hakura et al. 1998; Eisler 1987; Labib et al. 2013; Sposito et al. 2009; Sean 2013; Zhang, Shen et al. 2016; Xu, Ho, et al. 2016; Wang, Kobayashi, et al. 2016; Wang, Zhang, et al. 2016; Sun et al. 2016; Sarria-Villa et al. 2016; Pruneda-Alvarez et al. 2016; Mohammed et al. 2016; Manoli et al. 2016; Li, Dong, et al. 2016; Kamal et al. 2016; Godschalk 2003; Bandowe

and Nkansah 2016; Chen et al. 2015) have also demonstrated the ecological and toxicological aspects of PAHs in human health and environment.

The USEPA has classified seven PAHs (benz(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, chrysene, dibenz(a,h)anthracene, and indeno(1,2,3cd)pyrene) as possible human carcinogens (Kumar 2011). Additionally, other PAH-compounds such as benzo(j)fluoranthene, benzo(g,h,i) perylene, coronene, and ovalene are known as carcinogenic, mutagenic and teratogenic (Luch 2005). Relative cancer potency of some high molecular weight PAHs are shown in Table 2.2.

Table 2.2: Relative cancer potency of six PAHs from EPA (Patra 2003)

PAH	Relative cancer potency
Benzo(a)pyrene	1.0000
Benzo(a)anthracene	0.1450
Benzo(a)fluoranthene	0.1670
Benzo(k)fluoranthene	0.0200
Chrysene	0.0044
Dibenzo(a,h)anthracene	1.1100

2.8 PAHs treatment methods

Due to the toxic, mutagenic and carcinogenic natures of PAHs, significant interests in developing appropriate removal processes through understanding remediation mechanisms have been raised (Makkar and Rockne 2003; Chen et al. 2008). A number of methods have been investigated to treat PAHs from contaminated soils and waters to mitigate the possible risk of PAHs on the environment and human health. Physical, chemical, thermal, biological and phytoremediation processes (which comprise sorption, incineration, thermal desorption, radio frequency heating, oxidation, ion exchange, photolysis, adsorption, electrolysis, chemical precipitation, natural attenuation, biostimulation, bioaugmentation, surfactant enhanced, rhizofiltration, phytoextraction, phytostabilisation and phytodegradation techniques) are the major treatment methods of PAHs contaminated soil, sediment and water (Zhou et al. 2013; Wang et al. 2014; Li et al. 2015; Sun et al. 2014; Peng et al. 2014; Li et al. 2014; Hu et al. 2014; Tian et al. 2017; Hernandez-Vega et al. 2017; Guo et al. 2017; Weerasundara and Vithanage 2016).

2.8.1 Chemical method

Chemical method is one of the conventional methods which have been practiced to remove PAHs from contaminated media. In this process, oxidants such as ozone, chlorine, and potassium permanganate are employed to break down the PAHs (Beltrán et al. 1999; Brown et al. 2003; Miller and Olejnik 2004; Rebola et al. 2008). Chlorine, however, reacts with natural organic matter containing in water resulting in the formation of carcinogenic and mutagenic halogenated hydrocarbons like trihalomethanes and halo acetic acids (Shih and Lederberg 1976).

Oxidation of PAHs by ozone includes two pH-dependent mechanisms; direct oxidation of PAHs by ozone (at low pH) and indirect oxidation by $^{\circ}\text{OH}$ from ozone transformation (at high pH) (Miller and Olejnik 2004). Ozonolysis of benzo(a)pyrene, chrysene, and fluorene in synthetic water demonstrated that direct ozonolysis was the main degradation reaction pathway at low pH and participation of $^{\circ}\text{OH}$ in PAHs degradation become significant at elevated pH (Miller and Olejnik 2004). Intermediate products (such as ring-opened aldehydes, phthalic, aliphatic derivatives) of benzo(a)pyrene after the ozonolysis were found to be more biodegradable (Zeng et al. 2000).

Advance oxidation process (AOP) has been also employed to treat PAHs. AOP involves the combination of different oxidants (such as O_3 , H_2O_2), an energy sources (UV light, electrical energy) and catalysts (iron, TiO_2 , ZnO , Pt) (Cordeiro and Corio 2009; Psillakis et al. 2004; Wen et al. 2003; Ning 2015; Li et al. 2016). In AOP, several chemical oxidation methods are involved with an aim of producing $^{\circ}\text{OH}$ which attacks and destroys the most persistent and toxic organic molecules (Glaze et al. 1987; Andreozzi et al. 1999). The efficiency of AOP depends on various parameters such as oxidant concentrations, UV intensity, reaction time, pH, free radical generation rate and initial concentration of PAHs (Crittenden et al. 1999; Lair et al. 2008; Manariotis et al. 2011). AOP is effective in removing PAHs, however, this process generates toxic intermediate products (Woo et al. 2009). Moreover, AOP uses relatively high operational costs and the increased energy consumption that makes the treatment process cost ineffective (Comninellis et al. 2008; Oller et al. 2011).

2.8.2 Thermal method

In thermal treatment process, heat is applied to volatilise the PAHs from different media. One of the thermal treatment methods is in-pile thermal desorption which includes vaporization, boiling, oxidation and pyrolysis processes. This method is found to be highly effective (99.8% efficiency) in removing benzo(a)pyrene (Baker et al., 2006). A similar high removal efficiency (> 99%) of PAHs was achieved from lampblack (a product of incomplete combustion of a carbonaceous material containing PAHs) contaminated soil using soil venting thermal desorption process (Harmon et al. 2001). Acharya and Ives (1993) treated creosote-contaminated soil which comprises 15 different PAHs with concentrations of > 1000 mg/kg using rotary kiln incinerator (temperature 870-1200 °C) and removal efficiency achieved was > 90%. A very high removal efficiency (99.9%) of 16 USEPA categorised PAHs was reported by (Renoldi et al. 2003) using thermal desorption process (temperature > 450 °C). Despite achieving higher removal efficiency using the thermal process, energy demand is significantly high to maintain the required temperature.

The addition of chemicals could significantly reduce the temperature required in the thermal treatment process. For example, the addition of persulfate in the thermal activation method could achieve a very high removal efficiency (> 99.0%) of PAHs at temperature 60 °C with persulfate consumption of 0.45 to 1.38 g/kg soil (Zhao et al. 2013). According to Ali and Aydin (2001), PAHs from soil could be removed up to 99% using hot water extraction technique although 28 to 100% of extracted PAHs were measured in the water phase demonstrating thermal process alone could not completely eliminate PAHs from the environment.

The moisture content of the contaminated soil and production of HCl, SO_x, NO_x, dioxins, furans and metals emission would be a problem associated with the thermal treatment process (Acharya and Ives 1993). Furthermore, management of high temperature in a real setting would create a major challenge. It is well known that preferential convection as a result of soil heterogeneity can result in significant heat transfer resistance in the field, thereby detracting from the efficiency of the thermal PAHs treatment process. Thermal process is an expensive process compare to other treatment processes such as adsorption, bioremediation, and phytoremediation because of high cost of initial thermal instrumental set up.

2.8.3 Sorption method

Sorption includes absorption, adsorption, and ion exchange process among which adsorption is one of the main processes to remove PAHs. In adsorption, mass transfer process involves the accumulation of substances at the interface of two phases (such as liquid-liquid, gas-liquid, gas-solid, and liquid-solid). The constituents of adsorbents are mainly responsible for the removal of any particular pollutants from water (Khattari and Singh 2009). If the interaction between the solid surface and the adsorbed molecules has a physical nature, the process is called physisorption where the interactions are by van der Waals forces and the process results are reversible. On the other hand, if the attraction forces between adsorbed molecules and the solid surface are due to chemical bonding, the adsorption process is called chemisorption. Chemisorption occurs only as a monolayer. Under favorable conditions, both processes can occur simultaneously or alternatively. Physical adsorption is accompanied by a decrease in free energy and entropy of the adsorption system (Grassi et al. 2012). According to International Union of Pure and Applied Chemistry recognized definition, “chemisorption is adsorption in which the forces involved are valence forces of the same kind as those operating in the formation of chemical compounds while physisorption is adsorption in which the forces involved are intermolecular (van der Waals) forces of the same kind as those responsible for the imperfection of real gases and the condensation of vapours, and which do not involve a significant change in the electronic orbital patterns of the species involved” (Everett 1971). The sorption process is generally studied by plotting the equilibrium concentration of a compound in the sorbent as a function of its equilibrium concentration in solution or solid at a given temperature.

PAHs sorption by carbonaceous material onto soil and sediment involves dual sorption mechanism where absorption process occurs with organic carbon and adsorption process occurs with black carbon (Liu et al. 2015; Sangiorgi et al. 2014). Thus, adsorption is the main process in removal of PAHs from aqueous and solid media by using black carbon based sorbents such as activated carbon and biochar (Xu and Sparks 2013; Wang et al. 2015; Gupta 2015).

Many studies (Reddy et al. 2014; Tang et al. 2016; Rasheed et al. 2015; Kaya et al. 2013; Zhang 2016; Cobas et al. 2014) demonstrated that activated carbon, biochar, bentonite, zeolite, sediment, calcite, sepiolite and iron are popular PAHs sorption media. The details of

PAHs removal capacity with different media along with factors affecting in PAHs sorption and PAHs adsorption kinetic and isotherm analysis are presented in chapter 3 and chapter 4.

2.8.4 PAHs treatment by using organic solvents

PAHs remediation technique with organic solvents is popular from contaminated soil and sediment (Gan et al. et al. 2009). Lau et al. (2014) reported that result from previous study with three-stage cross current solvent was able to remove more than 95% of extractable PAHs. Similarly, according to Oluseyi (2011), PAHs recovery from contaminated soil was observed from 63.6 to over 100 % with organic solvents (acetone, cyclohexane, 2- propanol, methanol, acetonitrile and dichloromethane). Haleyur et al. (2016) studied the extraction of USEPA 16 PAHs from aged contaminated soil with five organic solvents systems as dichloromethane:acetone, chloroform:methanol, dichloromethane, acetone:hexane and hexane. In their study, acetone:hexane, dichloromethane and chloroform:methanol were found effective in PAHs extraction, however, acetone:hexane was healthiest system based on solvent toxicity.

Furthermore, Chen et al. (2015) studied the extraction of 16 PAHs from dissolved phase, from suspended partical and from sediment where organic solvents such as dichloromethane, hexane and methanol were used by using different techniques. For instance, solid phase extraction was used for dissolved PAHs, gravimetry method was used for PAHs from suspended particles and ultrasonic method was used for PAHs from sediment. The concentration of \sum PAHs observed was 351 to 4427 ng/L with a mean value of 835.4 ng/L in dissolved water phase; 3557 to 147,907 ng/L with a mean value of 20,780 ng /L in suspended particulate matter and 362 to 15,667 ng/g with a mean value of 2000 ng/g in sediment. Moreover, Sanchez-Trujillo et al. (2013) also reported the extraction of 16 PAHs by using sonication technique where dichloromethane and hexane were used as extracing solvent in 1:1 ratio. The concentration of individual PAH was found from 0.77 to 270 mg/kg. Other several organic solvents for instance esters, ketones, alkyl amines and aromatics in conjunction with water are used in remediation of PAHs from the soil and sediment (Gan et al. 2009). In PAHs remediation by using organic solvents from contaminated soils and sediments, solubility of PAHs in organic solvents plays an important role (Lau et al. 2014). Therefore, further study has been carried out on solubility of PAH with different types of solvents and presented in chapter 5.

2.8.5 Bioremediation

Bioremediation is an economic and environmentally friendly technique for PAHs remediation which involves the use of naturally occurring bacteria, fungi and algae to degrade organic contaminants by their metabolic processes (Cerniglia and Crow 1981; Zeyuallah et al. 2009; Mesbaiah et al. 2014; (Chen et al. 2008; Desai et al. 2008). Because of the multiple benefits of the biological process over other methods, in the recent past, a number of studies (Li et al. 2015; Sun, Ye et al. 2014; Jiao et al. 2014; Tejeda-Agredano et al. 2013; Abd-Elsalam et al. 2009; Zhao et al. 2009) have been extensively carried out by employing various microbial species which utilize PAHs as an energy source. However, the bioavailability of PAHs is often limited by their low solubility and strong sorption to soil due to its complex chemical structure (Seo and Bishop 2007; Alcantara et al. 2009). The solubility of PAHs decreases linearly with the increase of molecular mass (Heitkamp and Cerniglia 1989). Accordingly, the biodegradability of PAHs decrease with the increase molecular mass of PAHs demonstrating the molecular weight of PAHs influences their biological treatability (Wammer and Peters 2005). Since numbers of microorganisms are sensitive to toxic pollutants, biological processes alone might not be effective in degrading PAHs (Gogate and Pandit 2004; Oller et al. 2011). Use of the indigenous microorganisms in the contaminated site could achieve an efficient removal of PAHs in the biodegradation process (Das and Chandran, 2011).

Furthermore, the bioavailable fraction of PAHs could be enhanced by using surfactants (Bezza and Chirwa 2017) by increasing the solubility of PAHs (Tiwari et al. 2016). Recent studies (Bezza and Chirwa 2016; Zhang, Yang, et al. 2016; Wei et al. 2016; Wang, Li, et al. 2016; Singleton et al. 2016; Sales and Fernandez 2016) reported the surfactants enhanced dissolution and biodegradation of PAHs from contaminated soil and aqueous media indicating the proper combination of surfactants and microorganisms for selected PAHs could degrade up to > 99.99% PAHs (Pan et al. 2016). The detail study of surfactant enhanced remediation (SER) of PAHs including mechanisms of PAHs solubilisation and affecting factors in SER has been presented in chapter 6 and PAHs solubilisation with different types of surfactants in their single and mixed micellar form, effective proportion of anionic and nonionic surfactants for mixed micelles (based on laboratory experimental results) have been presented in chapter 7.

2.8.6 Phytoremediation

In this method, plants associated microorganisms and agronomic techniques are used to degrade and detoxify PAHs. The main mechanisms are phytovolatilisation, phytodegradation, phytoextraction, rhizodegradation and stabilization (USEPA, 2000). The different processes involved in phytoremediation method are presented in Figure 2.3.

Study of endogenous genetic, biochemical and physiological capabilities of the plants demonstrated that the phytoremediation can detoxify the PAHs (Gan et al. 2009). Similarly, Petruzzelli et al. (2016) demonstrated that phytoremediation is a very effective process in remediation of toxic pollutants including PAHs with further speed-up the natural attenuation process efficiently by improving the physical and biological properties of soils.

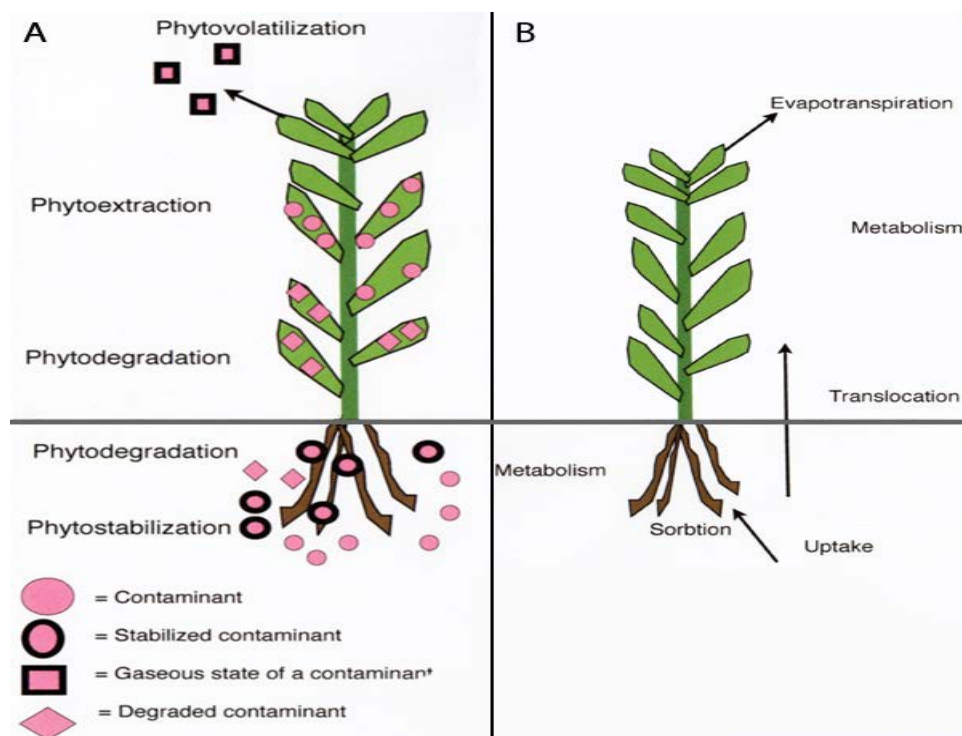


Figure 2.3: A: Schematic model for different mechanisms involved in removal and containment of contaminant in phytoremediation process, B: Physiological processes happen in phytoremediation process (Greipsson 2011)

The process of phytostabilization immobilises the contaminants in soil. In phytodegradation process, the contaminants are uptaken or mobilised by root, stem or leaves. Phytoextraction is the process of accumulation and uptake of contaminants to be removed. The contaminants are uptaken and volatised in phytovolatisation process. Furthermore, the contaminants can be removed by evapotranspiration process through plant leaves as presented in Figure 2.3B.

Phytoremediation technique is efficient and environmentally friendly technique for PAHs remediation from soil, sediment, and water. (Tian et al. 2017; Hernandez-Vega et al. 2017; Guo et al. 2017; Weerasundara and Vithanage 2016; Li, Liu, Zhu, et al. 2016; Ingrid et al. 2016; Su et al. 2015; Liu et al. 2015; Kawasaki et al. 2015 2015; He and Chi 2015).

The plants which have been widely used in phytoremediation of PAHs are ryegrass (Sun et al. 2014; Khan et al. 2014; Yu et al. 2011; Gao et al. 2006), tall fescue (Huang et al. 2004), coneflower (Liu et al. 2014), sunflower (Tejeda-Agredano et al. 2013), *Juncus subsecundus* (Zhang et al. 2012), alfalfa (Gao et al. 2011), *Baumea juncea* (Zhang et al. 2010), arabidopsis and rice (Peng et al. 2014). Moreover, *Brassica juncea*, *Pteris vittata*, *Zea mays*, *Medicago sativa*, *Panicum virgatum*, *Sorghastrum nutans*, *Festuca rubra*, *Festuca arundinacea*, *Echinacea purpurea*, *Fire Phoenix*, *Trifolium pretense*, *Glycine max* have also been used in PAHs remediation (Petruzzelli et al. 2016). *Festuca arundinacea* and *Panicum virgatum* degraded about 38% of pyrene within 190 days (Chen et al. 2003) and *Eichhornia crassipes* removed 45% of naphthalene within 7 days (Nesterenko-Malkovskaya et al. 2012). Phenanthrene (initial concentration 50 mg/L) removal by using endophytic bacterium *Pseudomonas* species in ryegrass was observed as 81.1% within 15 days (Sun, Liu et al. 2014).

2.8.7 Combined method by using constructed wetland

Constructed wetlands (CWs) are engineered structures (Puigagut et al. 2008) which have been gaining popularity in flood control, flow attenuation, runoff pollutants treatment because of its several advantages. CWs consist low construction and operational cost, provide additional wildlife habitat, environmental friendly, aesthetic and generally well received by the public (Eifert 2000; Fournel et al. 2013). CWs are widely accepted over past two decades as innovative urban stormwater treatment system and are increasingly being integrated into water sensitive urban design as best management practice (Kadlec and Wallace 2009; Crowe 2007; Headley and Tanner 2012).

Constructed wetlands have been used for more than fifty years and traditionally CWs have been used to treat domestic and municipal wastewater but for the last two decades, the application of CWs has expanded in treatment of industrial (petrochemical, abattoir, meat

processing, dairy, olive mills, pulp, paper, textile and wine industries) wastewater and stormwater runoff (Vymazal 2014; Vymazal and Kröpfelová 2011). Furthermore, CWs have been used in removing industrial runoff and urban stormwater contaminants including organic substance, heavy metal, suspended and colloidal materials, nutrients and pathogens (Eifert 2000; Yi et al. 2016; Xu, Liu, et al. 2016; Al-Sbani et al. 2016; Herrera-Cardenas et al. 2016; Vymazal 2014; Vymazal and Kröpfelová 2011). PAH is one of the major runoff pollutants having high affinity to be adsorbed into the CW bed media (Wojciechowska 2013; Fountoulakis et al. 2009).

Thus use of CWs is considered to be as most effective management practice in removing storm runoff pollutants including PAHs (EPA 2014; Wojciechowska 2013; Kadlec 2008; Tromp et al. 2012; Fountoulakis et al. 2009; Kadlec and Wallace 2009) with no dead-end products to further contaminate the environment. Moreover, other studies (Yi et al. 2016; Al-Sbani et al. 2016; Warężak et al. 2015) have also presented the effective PAHs removal capacity of CWs.

The basic PAHs removal mechanisms in a constructed wetland are, adsorption, plant uptake, rhizodegradation, biodegradation and volatilization (Fountoulakis et al. 2009; Wojciechowska 2013; Yi et al. 2016; Herrera-Cardenas et al. 2016; Al-Sbani et al. 2016). Among different mechanisms, adsorption is the main mechanisms to remove aqueous PAHs in CW (Wojciechowska 2013). Thus detail study on PAH adsorption including various adsorbing media, affection factors in PAHs adsorption, adsorption kinetic and adsorption isotherm has been carried out based on literatures and presented in chapter 3.

2.8.7.1 Types of constructed wetland

Based on direction of flow, CWs are categorised as horizontal flow CW (Figure 2.4), vertical flow CW (Figure 2.5), and combined horizontal and vertical flow CW. All of these types of CWs have been used in PAHs treatment purpose. For example, The phenanthrene removal efficiency in pilot scale horizontal flow CW has been found 92.47% in front quarter upper layer (Yi et al. 2016) and PAHs removal efficiency in vertical flow CW in combination with detention basin has been found up to 95% in presence of reed bed (Tromp et al. 2012). Furthermore, combined horizontal and vertical flow structure has also been in practice with various combinations of flow types and vegetation types to achieve better PAHs removal efficiency in CW (Vymazal 2014; Wojciechowska 2013; Machate et al. 1997; Vymazal

2008). A very high removal efficiency of phenanthrene (about 99.9%) has been found in combined horizontal and vertical flow constructed wetland planted with *Typha* species and *Scirpus lacustris*. (Machate et al. 1997).

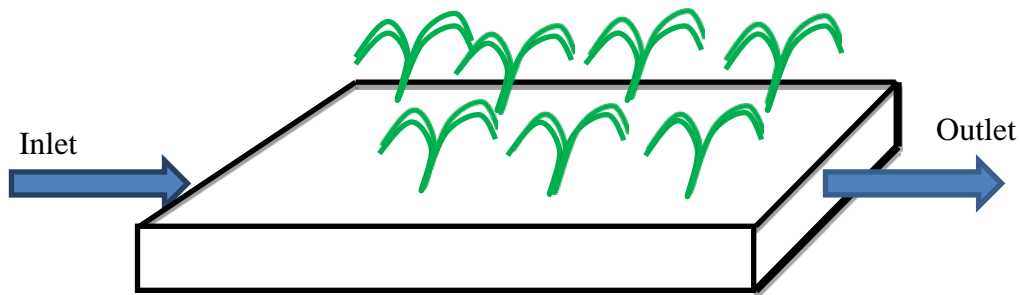


Figure 2.4: Schematic diagram of horizontal flow CW

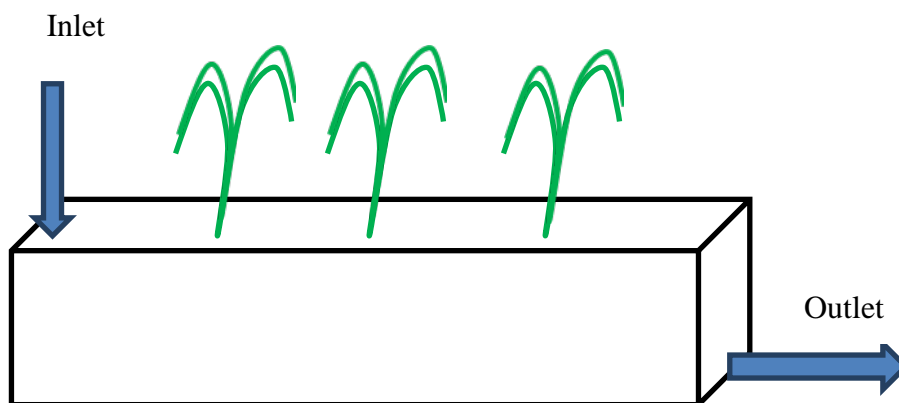


Figure 2.5: Schematic diagram of vertical flow CW

Generally, based on the water flow pattern there are two types of CWs; surface flow (SF) type (Figure 2.6) and subsurface flow (SSF) type (Figure 2.7). The bed media of SSF wetlands provide support to emergent vegetation and greater surface area for physical and microbiological treatment process than the SF constructed wetland (US EPA, 1993).

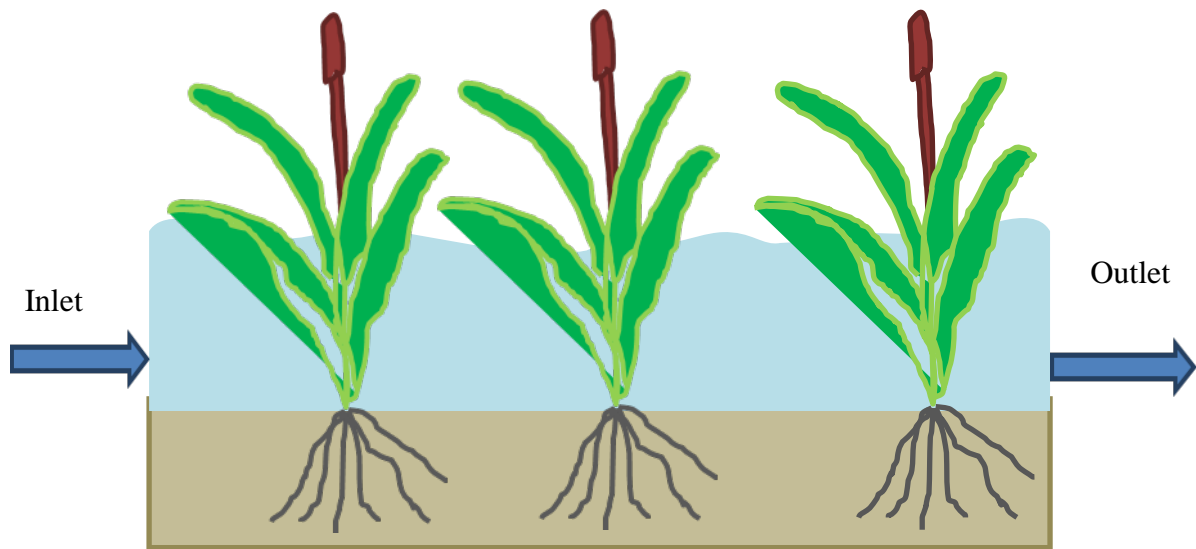


Figure 2.6: Subsurface flow CW

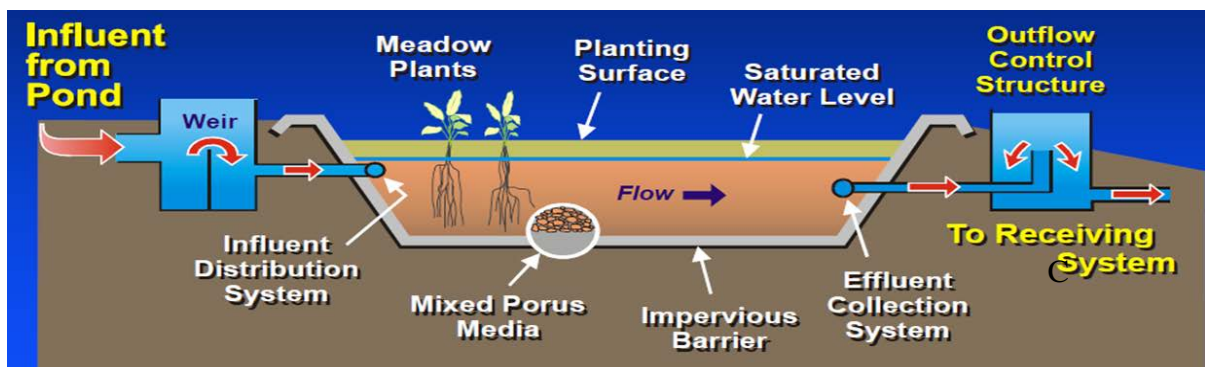


Figure 2.7: Subsurface flow constructed wetland (Walter 2000)

The SSF CW system shows better performance on PAHs removal when compared to SF CW. For example, the average removal of PAHs was found as 79.2% for the SSF CW while 68.2% for the SF case (Fountoulakis et al. 2009). Furthermore, the recent studies by (Yi et al. 2016) and (Al-Sbani et al. 2016) have presented effective PAHs removal efficiency in SSF CW as 92.47 and 96% respectively.

As CWs comprise multiple treatment techniques such as adsorption, phytoremediation and biodegradation, the environmental parameters which affect the individual process play the important role in PAHs remediation in CWs. Among the environmental parameters, dissolved oxygen (DO), oxidation, reduction potential (ORP), temperature and pH have been commonly studied (Al-Sabani et al. 2016, Meng et al. 2014). The DO and ORP are the measures to

identify the aerobic and anaerobic condition of aquatic environment in CW system (Ong et al., 2009) where ORP > 100mV represents an aerobic environment and < 100mV represents an anaerobic environment (Suthersan, 2002). The ORP condition in CWs affects in mineralization of organic matter (Paredes et al. 2007). Temperature and pH are also important parameters which are related to each other and have significant role in contaminant treatment in CW systems. For example, pH was found greater in summer when compared to winter (Yin et al. 2016). Furthermore, pH > 8.5 affects adversely into the components of CWs such as decay of plant assimilation and inhibition of microbiological activities in summer season due to elevated pH (Yin et al. 2016). Similarly, Other studies also presented that more alkaline condition could affect in DO reduction, intracellular metabolic activities of plant, cell growth, and biomass (Buchanan et al. 2000; Cosgrove 2000; Ranieri et al. 2013 Rorslett et al. 1986). The denitrification and nitrification processes were found hampered at pH > 8 in previous study by Vymazal (2007).

Chapter 3

PAHs removal by sorption method (A review)

Note: The contents of this chapter has been published as journal paper.

Shanti Lamichhane, KC Bal Krishna, Ranjan Sarrukkalige, 2016. Polycyclic aromatic hydrocarbons (PAHs) removal by sorption method: A review. *Chemosphere*, 148, 336-353

3.1 Introduction

Sorption method has been found to be superior techniques for PAHs removal because of its multiple benefits such as simplicity in design and operation, low investment and maintenance cost and no undesirable by-products formation. ADDIN EN.CITE (Due to the nature (low aqueous solubility and strong sorption affinity to the solid media) of PAHs, sorption method has become a promising technique (Wang et al. 2014; Liu et al. 2014; Wang et al. 2015; Hu et al. 2014; Alcantara et al. 2009). The selection of proper sorbent and optimizing the influencing environmental factors would be important in removing PAHs from various sources such as water, contaminated soil and sludge (Wang et al. 2015; Hale et al. 2012; Oleszczuk et al. 2012).

Several studies have been carried out to find the effective and economic sorption media and environmental factors affecting the PAHs removal processes (Wang et al. 2015; Liu et al. 2015; Wang et al. 2014; Liu et al. 2014; Li et al. 2014; Hu et al. 2014; Staniska et al. 2015; Kobayashi and Sumida 2015). However, there has been scarcely investigated detailed information about sorption media used to remove PAHs from aqueous solution and factors influencing their effectiveness. The main aim of this chapter therefore, is to summarize the past literatures on PAHs removal by sorption process which detailed sorption media including operating parameters that affect sorption process and sorption mechanisms. Furthermore, this chapter comprises kinetic and isotherm analysis of powder activated carbon and granular activated carbon based on laboratory experiments.

3.2 Sorption media used to remove PAHs

3.2.1 Activated carbon

Activated carbon is being a very popular in PAHs sorption due to their high specific surface area (ranging from 300 m²/g to 3000 m²/g) (Awoyemi 2011). Activated carbon is produced from various materials (bituminous coal, petroleum coke, shells, sewage sludge and plant derived material) (Awoyemi 2011; Kong et al. 2011; Gupta 2015) through carbonization followed by activation processes. Activated carbon is prepared in the form of powder, granules or briquette depending on its specific application. However, granular activated carbon (GAC) and powder activated carbon (PAC) are common in practice for PAHs sorption. GAC is one of the most commonly used porous media for organic contaminants removal by sorption process (Ania et al. 2007; Paune et al. 1998; Valderrama et al. 2008).

(Amstaetter et al. 2012) carried out adsorption test of phenanthrene, anthracene, fluorene, pyrene, benzo(a)pyrene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)anthracene, indeno(1,2,3cd)pyrene, benz (g,h,i) perylene in aqueous solution using activated carbon and achieved a very high adsorption capacity (Table 3.1). Furthermore, better removal efficiency of PAHs (phenanthrene, anthracene, fluorene, pyrene, benzo(a)pyrene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)anthracene, indeno(1,2,3-cd)pyrene, benzo(g,h,i)perylene) could be achieved from the pore water of contaminated soil using PAC than using GAC (Table 3.1) (Hale et al. 2012). Similarly, (Oleszczuk et al. 2012) reported the removal efficiency of freely dissolved PAHs (phenanthrene, fluoranthene, pyrene, benzo(a)pyrene, benzo(g,h,i)perylene) from sewage sludge was 95% with the use of activated carbon (Table 3.1). A very high removal efficiency (99%) of PAHs (USEPA PAHs except naphthalene) in drainage water of moderately contaminated soil was observed when investigation was carried out by adding 2% PAC (Brandli et al. 2008). PAHs (naphthalene, phenanthrene, pyrene) removal efficiency of rice husk (agricultural residue) based activated carbon observed to have higher adsorption capacity than other agricultural and industrial adsorbents (such as chitosan, chitin, sugar bagasse, coconut shells, leonardite and mesoporous organo silica) (Yakout, Daifullah, and El-Reefy 2013). Similarly, as detailed in Table 3.1, soybean stalk (agricultural based) activated carbon was able to achieve significantly high PAHs removal efficiency (95.6 to 100%) from aqueous solution (Kong et al. 2011).

Table 3.1: Details of adsorption media, experiment type, removal efficiency and sorption isotherm

Materials	Study type	Types of PAHs	Description of the study	PAHs removal efficiency	Sorption isotherm model	Isotherm coefficients for best model	Reference
Powder activated carbon (PAC) anthracite based and coconut shells based	Batch	phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3cd)pyrene, benzo(g,h,i)perylene	5 g sediment with total PAHs concentration 30±6 mg/kg (pyrene 3.8 mg/kg) mixing with 50 mg activated carbon (AC) in 40 ml solution and shaken for 30 d.	phenanthrene 95%, anthracene 97.5%, fluoranthene 96.5%, pyrene 98%, benzo(a)pyrene 88%, chrysene 94.5%, benzo(b)fluoranthene 86%, benzo(k)fluoranthene 88%, benzo(a)anthracene 94.5%, indeno(1,2,3-cd)pyrene 73%,	Freundlich, Polanyi-Dubinin-Manes	Log(K_f) for pyrene sorption is 7.2 for anthracite based AC and 8.15 for coconut shells based AC and their respective n values are 0.952 and 1.111 in the absence of sediment. In presence of sediment pyrene sorption reduced by factor 5 in coconut shells based carbon than anthracite based AC.	Amstaetter et al. (2012)

				B(g,h,i)perylene 69%. 8.17			
Activated carbon (AC)	Batch	napthalene, fluorene	12 mg/L napthalene and 1 mg/L fluorene mixed with 50 mg CO ₂ -activated petroleum cokes at 25°C for 15 min.	> 97% napthalene and > 98% fluorene at 75 rpm	Langmuir, Freundlich, linearized Dubinin-Radushkevich	Maximum adsorption of napthalene and fluorene are 13.57 and 12.95 mg/g respectively.	Awoyemi et al. (2011)
Granular activated carbon (GAC)	Batch	napthalene, acenaphthene, fluorene, anthracene, pyrene, fluoranthene	200 ml of 0.2-10 mg/L PAH at 21±1°C mixed with 0.3 g GAC with size 3-6 mm, specific surface area 1000 m ² /g and specific volume 1.5 cm ³ /g for 400 min.		Langmuir, Freundlich, Redlich–Peterson	Maximum sorption of napthalene, acenaphthene, fluorene, anthracene, pyrene and fluoranthene are 140, 111, 145, 232, 109 and 93 g/kg respectively.	Valderrama et al. (2008)
PAC/GAC	Batch	15 USEPA PAHs (excluding napthalene among 16 USEPA PAHs)	Addition of 2% AC to urban soil with freely dissolved Σ15 PAH 38 mg/kg.	Aqueous PAH removal by PAC was 99% and by GAC was 64%			Brändli et al. (2008)

PAC/ GAC	polyoxymethylene passive samples	phenanthrene, anthracene, fluorene, pyrene, benzo(a)pyrene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)A, indeno(1,2,3cd)pyrene, benzo(g,h,i)perylene	2 % by weight AC was added to the soil where pore water PAHs concentration was 31 ng/L	93% and 84% by PAC and GAC respectively after 17 months and 76% and 69% by PAC and GAC respectively after 28 months.			Hale et al. (2012)
Biochar	Batch	phenanthrene, fluoranthene, pyrene	Phenanthrene 9.07 mg/L, fluorene 10.05 mg/L, pyrene 10.57 mg/L, Triton X-100 4.55g/L mixed with 1 to 8 g/L biochar formed at 400, 600 and 800 °C having surface area 427, 537 and 652 m ² /g	95.8- 98.6% by biochar 800 °C, 71.8-88.1% for biochar 400 °C and 82.4-93.4% for biochar 600 °C and Triton X-100 recovery > 87%			Li et al. (2014)

			respectively.				
Biochar	Batch	2-5 ring PAHs	5 g of contaminated soil mixed with 10 mL 1:1 acetone and hexane. Solution shaken at 200 rpm for 2 h for extraction.	> 50 of HMW PAHs and > 40% of the LMW PAHs reduction after 60 d			Beesley et al. (2010).
Pine needle biochar	Batch	napthalene	15, 9, 7.5, 7.5, 2.5, 3, 4 and 4 mg of boichar from at 100, 200, 250, 300, 400, 500, 600 and 700 °C respectively having (surface area of 0.65 to 490.8 m ² /g mixed with napthalene	Maximum adsorption is 136.8 mg/g	Freundlich, Linear	Log (K _f) is 5.085 L/kg and n is 8.0645, distribution coefficient K _d is 1086 mL/g.	Chen et al. (2008)

			initial-concentrations of 0.03- 0.94 and agitated at 20 rpm for 3 d. Maximum adsorption occurs on BC formed at 700°C.				
AC/Biochar	Batch	napthalene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno (1,2,3cd)pyrene, B(g,h,i)perylene	0.5-10% AC and biochar mixed with sewage sludge containing 13.2 ng/L dissolved PAHs.	56- 95% removed by AC and 0-57% by biochar	Freundlich	Average log (K_f) values for different activated carbon dose are 6.4-9.3 L/ng and for different dose of biochar are 6-8.9 L/ng.	Oleszczuk et al. (2012)

AC/Biochar	Batch	d ₁₀ PYR	AC and biochar with surface area 859-792 and 167-190 m ² /g respectively. 200 mg soil containing 5% biochar, 10 mg AC or biochar and 3g soil only mixed with d ₁₀ PYR 1-100 mg/L.		Freundlich	Log(K _f) values for AC are 7.80 - 8.21 L/ng and for biochar are 5.22 - 6.21 L/ng.	Hale et al., (2011)
Coke-derived porous carbon	Batch	naphthalene, fluorene, phenanthrene, pyrene, fluoranthene	0.1 g of the porous carbon with specific area 562- 1904 m ² /g added with 100 mL of 3.250–6.250 µg/mL PAHs and mixed for 18 h at 25 °C.	> 99% for all PAHs at 7 h	Freundlich	For naphthalene K _f values are 146-457.5 mg/kg and n values are 0.53-0.71, for fluorene K _f values are 35.7-45.6 mg/kg and n values are 0.49-0.52, for phenanthrene K _f values are 11.7-46.3 mg/kg and n values are 0.5-0.54 for pyrene K _f values are 6.2-12.3 mg/kg and n values are 0.55-0.59.	Yuan et al. (2010)

Wood ashes	Batch	fluorene, pyrene, chrysene, benzo(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenz(a,h)anthracene, indeno(1,2,3-cd)pyrene, benzo(g,h,i)perylene	10 mg/mL wood ashes mixed with 3 mg/L fluorene and 5mg/L benzo(b)fluoranthene and benzo(g,h,i)perylene and stirred at 25°C for 24 h.	100% for ashes obtain at 800 °C and > 99 for ashes obtained at 500 °C	Freundlich	K _f values for wood ashes (formed at 800) °C are 9.4-32.8 with acetonitrile and n values are 1.698-2.564.	Pérez-Gregorio et al. (2010)
Aspen wood fibre	Batch / Column	pyrene, anthracene, fluorene	For isotherm study 2-50 µg/L each PAH mixed with 2 g saturated aspen wood and shaken at 24 °C for 7- 12.5 d. For column experiment 2.25-3.43 g wood fibre having porosity 68- 75% pumped of	Removal of pyrene, anthracene, fluorene are 74, 67 and 25.5 µg/g respectively over 300 pore volume.	Linear	Average n value for Freundlich isotherm model is 0.93 which is close to 1 concluding best fit is linear.	Boving and Zhang (2004)

			50 µg/L each PAH with flow rates of 0.5 mL/min for 3 months.				
Wood char	batch	pyrene, phenanthrene, benzo(a)anthracene	5 mg original or 1mg treated char mixed with pyrene 2.8 to 112 µg/L and shaken at 25 °C at 150 rpm for 9 d. Solid to solution ratio maintained was 30-80% to determine the PAH adsorption by wood char. pyrene 22.4 µg/L as main sorbate with other co-solute	≥ 60%	Freundlich	Log(K _f) for pyrene, phenanthrene, benzo(a)anthracene are 4.924-5.667, 4.832-5.130, 5.283-5.882 L/µg respectively and their respective n values are 1.25- 1.55, 1.043-1.229, 1.04-1.129.	Wang et al. (2006)

			(phenanthrene, benzo(a)anthracene).				
Soybean stalk based carbon	Batch	napthalene, phenanthrene, acenaphthene	Carbon formed at 700 °C with specific surface area 287.63 m ² /g. 0.04 g of carbon mixed with 32 mL of PAH (phenanthrene 1 mg/L, napthalene 10 mg/L and acenaphthene 3 mg/L) at 25±1 °C for 24 h.	NAP 100%, PHE 99.89%, ACENAP 95.64%	linear	K _d values for napthalene, phenanthrene and acenaphthene are 52.23, 3198.22 and 36.55 L/g respectively at activated concentration 0.01mg/32mL.	Kong et al. (2011)

Quercus cerris cork	Batch	phenanthrene, fluorene, anthracene, acenaphthene	0.3 g of cork mixed with 100 mL PAHs 1-50 µg/L oscillating 700/min for 3 h.	phenanthrene 95%, fluorene 90%, anthracene 96%, acenaphthene 80%	Freundlich	K _f values for phenanthrene, fluorene, anthracene, acenaphthene are 6.647, 3.163, 8.433, 1.386 L/g respectively and their respective n values are 0.98, 1.01, 1.02, 1.03.	Olivella et al. (2011)
Rice husk activated carbon (RHAC)	Batch	napthalene, phenanthrene, pyrene	For kinetic test 5 ml of 8 mg/L of each PAH mixed with 2 mg of activated RHAC and shaken at 200 rpm for 1-7 d. For isotherm study RHAC 0.1-7 mg mixed with 5 mL of 8 mg/L each PAH and shaken at 25±1 °C until equilibrium.	maximum pyrene adsorption is 104.5 mg/g	Freundlich for napthalene, Redlich Peterson for phenanthrene and Langmuir for pyrene	K _f for napthalene is 15.7 L/mg and n is 1.408. For phenanthrene Redlich isotherm constant b _r is 0.54 and β is 1.4.	Yakout et al. (2013)

Organogeolite	Batch Column	fluorene, fluoranthene, pyrene, phenanthrene, benzo(a)anthracene	For batch experiment, 5 g of organozeolite 0-0.4, 0.4-0.8 and 0.8-3 mm size in presence of 31.81 mg/mL stearyldimethylbenzylammoniumchloride surfactant mixed with 500 mL 50 µg/L mixed PAHs. For column test, 2 g organozeolite mixed with 50 µg/L PAHs and flow rate maintained was 6 mL/min.	98% for all PAHs for adsorbent particle size (0-0.4) mm. Upto 83% for other size range.			Lemic' et al. (2007)
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Cetyltrimethyl ammonium bromide (CTMAB)-bentonite	Batch	phenanthrene, pyrene, fluorene, acenaphthene	For kinetic study, 20 mg/L PAHs mixed with 1g/L CTMAB-bentonite for 12 h at 20 ± 1 °C. For isotherm study, sorbent 1-4 g/L mixed and shaken for 6 h.	acenaphthene 49.6%, fluorene 54.5%, phenanthrene 63.3%, pyrene 69.4%.	Linear isotherm for phenanthrene on organo-bentonite	K_d values for phenanthrene are 50.727, 7.687, 2.242 L/g for CTMAB-bentonite concentration 1, 2, 4 g/L respectively.	Zhou et al. (2013)
Natural bentonite (NB) and Hexadecyltrimethyl ammonium (HDTMA) modified bentonite (HB)	Batch	naphthalene	For kinetic study, 0.05 g of NB and HB mixed with 50 mL of naphthalene with concentration 10 mg/L at 20 °C stirred for 60 min. For isotherm study, the PAHs concentration used are 7.5-20 mg/L for same amount of bentonite at 10, 15	Adsorption of naphthalene by HB is 22.45 mg/g	Freundlich, Langmuir	K_f values for NB and HB are 0.397-0.706 L/g and 1.581-3.657 L/g respectively and their respective n values are 0.725-0.846 and 0.488-0.599.	Kaya et al. (2013)

			and 20°C.				
Quartz, goethite-coated quartz, quartz-montmorillonite mixture	Batch	phenanthrene, pyrene, benzo(a)pyrene	For kinetic study, PAHs about 10 % of aqueous solubility with sorbate to solution ratio 1:5 at different time intervals 4-120 h. For isotherm study, 5 different concentrations 1-50 % aqueous solubility at 20 ±1 °C and shaken 15 min for each hour.		Freundlich for phenanthrene and pyrene for two mineral combinations. Linear for phenanthrene, quartz and benzo(a)pyrene	K _f values for phenanthrene and pyrene are 0.21–2.46 L/kg and 0.36–3.43 L/kg respectively. k _d values for benzo(a)pyrene are 48–154 L/kg. For phenanthrene to quartz, K _d is 0.2 L/kg.	Muller et al. (2007)

Cation-modified clay minerals (smectite, kaolinite, vermiculite)	Batch	phenanthrene	0.025-1 mg/L phenanthrene mixed with 0.6 g each mineral sorbent modified by Na, K and Ca cations and shaken at 105 rpm at 25±1 °C for 48 h.		Freundlich	K _f values for Ca, K and Na modified smectite are 20.72, 14.65, 13.72 L/kg respectively and respective n values are 1.124, 1.266, 1.316, for kaolinite K _f values of respective cations are 7.39, 6.83, 6.61, and n values are 1.136, 1.22, 1.235 and for vermiculite K _f values of respective cations are 7.22, 7.8 9,6.94, and n values are 1.266, 1.25, 1.205.	Zhang et al. (2011)
In organo-bentonite (IOB)	Batch	phenanthrene	For isotherm study, 20 mg of IOB mixed with 20 mL of 0-350 mg/L PHE solution and shaken at 180 rpm at 25±1°C for 4 h. For kinetic study, 20 mg IOB and 30 mg/L phenanthrene was used.	Removal efficiency was 99% in 30 min. Maximum removal efficiency is 99.63%.	Langmuir, Linear	K _d values are 84.5- 355.3 L/g, the maximum adsorption capacity 9.82- 13.32 mg/g and b ranges 0.144-0.188 for CTMAB modification 728.9 - 3644.5 mg/L.	Ma and Zhu (2006)

Sepiolite	Batch	phenanthrene, pyrene	Sepiolite 100-200 μm to PAHs (phenanthrene 17.823 mg/L and pyrene 20.225 mg/L) ratio 1:50 g/mL and shaken at 150 rpm at 24.85 °C for 32 h.		Freundlich, Langmuir, Dubinin–Radushkevich isotherm, Temkin	K_f is 0.027 and n is 0.891 for phenanthrene and K_f is 0.043 and n is 0.977 for pyrene. For mixed PAHs, K_f is 0.037 and n is 0.96.	Cobas et al. (2014)
Dodecylpyridinium-chloride (DPC) modified bentonite (organoclays)		naphthalene, phenanthrene	50 mg of bentonite with 25 mL of 1.5-7.5 mg/L naphthalene and 25 mg bentonite with 25 mL of 50-250 $\mu\text{g/L}$ phenanthrene were mixed and shaken at 150 rpm for 18 h at room temperature.		Linear	K_d for naphthalene is 0.151- 1.675 L/g with DPC maintaining cation exchange capacity twice of bentonite. K_d for phenanthrene is 0.426-36.184 L/g with DPC maintaining cation exchange capacity 1.25 times of bentonite.	Changchaivong and Khaodhiam (2009)
Catylpyradinium exchanged	Column	benzo(a)pyrene, benzo(b)fluoranthene, chrysene,	100 g (particle size 125-300 μm) of mixture of 40 mL of	> 99%			Ake et al. (2003)

low-pH montmorillonite CP/LPHM - sand		benzo(k)fluoranthene, dibenz(a,h)anthracene, benzo(a)anthracene	dilute mucilage, 200 g of washed sand and 200 g of CP/LPHM used for column test. Total PAH concentration of field sample was 206.044 µg/L. Flowrate < 25 mL/min for 78h.				
(CP/LPHM):GAC (3:2)	Column	naphthalene, fluorene, phenanthrene, pyrene, total PAHs	4 g of (CP-LPHM/GAC) used in column test. Field sample with total PAH concentration 3.202 µg/L and flow rate of 25 mL/min for 48h.	naphthalene: 61%, fluorene: 99%, phenanthrene: 99% pyrene: 97%, total PAHs: 94%			Wiles et al. (2005)
(CP/LPHM):sand (3:8)	Column	naphthalene, fluorene, phenanthrene, pyrene, total PAHs	13 g of (CP-LPHM/sand) used in column test. Field sample with total	naphthalene: 70% fluorene: 94% phenanthrene: 95%, pyrene:			Wiles et al. (2005)

			PAH concentration 3.202 µg/L was used and flow maintained was about 25mL/min for 48h.	93%, total PAHs: 86%			
Humic acid (HA) and fulvic acid (FA)	Batch	phenanthrene	1 mg/L PHE mixed with HA and FA 0-10 g/kg soil for pH range 3-6 temperature 25 °C and shaken at 180 rpm for 24 h. Temperature effect is examined at pH 3 and temperature 15 and 25 °C.	Highest adsorption was at pH 3 for HA 10 g/kg and FA 205 g/kg. Adsorption was higher at 15 °C than at 25 °C.	Freundlich	At pH 3 and 15 °C, K_f and n values for HA are 220.59 L/kg and 0.815, respectively and for FA 175.55 L/kg and 0.708 respectively.	Ping et al. (2006)

Graphene oxide(GO)/reduced graphene oxide (rGO)	Batch	napthalene, anthracene, pyrene	napthalene, anthracene, pyrene 25.63-30760.8, 1.7823-44.5575, 2.0225-129.44 $\mu\text{g/L}$ respectively mixed with rGOs and GOs concentration 0.2-0.4 g/L and shaken at room temperature for 7 d.	Maximum adsorption of napthalene, anthracene and pyrene with rGOs are 5.912 g/g, 0.183 g/g and 0.979 g/g respectively and maximum adsorption of PYR with GOs is 0.223 g/g.	Langmuir, Freundlich, Polanyi-Dubinin-Ashtakhov (PDA)	Energy values are 94.14, 90.56, 9.75 J/g for pyrene, anthracene, napthalene respectively with rGO and 77.75 J/g pyrene for GO.	Sun et al. (2013)
Hydrophobic molecular sieve (MCM-41)	Batch	phenanthrene	PHE 600 $\mu\text{g/L}$ mixed with 0.2 g/L MCM-41 with specific area 37.2 m^2/g and specific volume 0.14 cm^3/g . The mixture was shaken at 170 rpm at room	Maximum adsorption capacity 2712 $\mu\text{g/g}$	Linear, Langmuir, Freundlich	K_d at 25 °C is 983.9 L/g.	Hu et al. (2014)

			temperature for 24 h.				
Grafted cellulose	Column	16 PAHs	500 ng/L of 16 PAHs mixed with 4g cellulose/L. Cellulose C2 with hydroxide group and cellulose C4 with amine group. Experiment duration 400 min.	C2 94%, C4 98%			Euvrard et al. (2014)

Electrospun nano fibrous membranes (poly(ϵ -caprolactone), poly(d,l-lactide), poly(lactide-co-caprolactone), poly(d,l-lactide-co-glycolide) and methoxy polyethylene glycol-poly(lactide-co-glycolide))	Batch	anthracene, benzo(a)anthracene, benzo(a)pyrene	50-55 mg of Electrospun nano fibrous membrane was mixed with 100 mL of 10-100 μ g/L PAH at room temperature.		Partition, Freundlich, Polanyi Dubinin-Ashtakhov	Sorption of anthracene on poly(ϵ -caprolactone) > 4112.3 μ g/g, benzo(a)anthracene and benzo(a)pyrene on poly(lactide-co-caprolactone) > 1338.8 and 712.1 μ g/g, respectively. Sorption rate of poly(ϵ -capro- lactone) for anthracene, benzo(a)anthracene and benzo(a)pyrene are 75.6, 78.3 and 73.5 μ g/g respectively.	Dia et al. (2011)
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<p>Laccase carrying electrospun fibrous membranes as poly(D,L-lactide) (PDLGA), poly(lactide-co-caprolactone) (P(LA/CL)), poly(D,L-lactide-co-glycolide) (PDLGA) and methoxy polyethylene glycol–poly(lactide-co-</p>	<p>Batch</p>	<p>naphthalene, phenanthrene, benzo(a)anthracene, benzo(a)pyrene</p>	<p>60-70 mg ECEFM mixed with 100 mL of 1-500 µg/L PAHs shaken at 100 rpm at 25±1°C, pH 6.5 for 3h. For sorption kinetic study 50 mL of 50 µg/L PAHs</p>	<p>Highest sorption rate is around 100 % at 1 h for naphthalene, phenanthrene and benzo(a)anthracene by P(LA/CL).</p>		<p>Sorption of phenanthrene, benzo(a)anthracene and benzo(a)pyrene by P(LA/CL) are 2238.8 , 1339.1 and 872.5 µg/g respectively.</p>	<p>Dia et al. (2013)</p>
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glycolide) (MPEG- PLGA)							
Laccase loading spider type reactor (LSTR) with Poly (d,l-lactide-co-glycolide) (PDLGA) surfactant	Batch	napthalene, phenanthrene, anthracene, benzo(a)anthracene, chrysene, benzo(a)fluoranthene, benzo(a)pyrene	6 mg of laccase 150-160 mg LSTR added with 50 mL of mixed 10 µg/L PAHs and shaken at 150 rpm for 24 h.	95.3 - 97.6 %			Niu et al. (2013)
Leonardite (immature coal)	Batch	fluorene, pyrene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(g,h,i)perylene	For kinetic study 0.5 g Leonardite with surface area 19.1 m ² /g mixed with 500 mL PAHs having concentration 100	Pyrene: 95%, fluorene: 78%, benzo(k)fluoranthene: 82%, benzo(g,h,i)perylene: 91%,	Freundlich	K _f values for fluorene, pyrene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(g,h,i)perylene are 8530, 13110, 10990, 12650, 15240 L/kg, respectively and their respective n values are 1.57, 1.62, 1.88, 1.96, 1.78.	Zeledo'n-Torun˜o et al. (2007)

			<p>µg/L and shaken at 25 °C for 24 h. For isotherm study PAHs concentration 5-100 µg/L mixing with 1 g/L leonardite for 2 h.</p>	<p>benzo(a)pyrene: 88%</p>			
<p>Light weight clay aggregate (LECA)</p>	<p>Batch</p>	<p>phenanthrene, pyrene, fluoranthene</p>	<p>For kinetic study, 100 ml of 0.02 mg/L each PAHs added with 0.2 g LECA and shaken for 1-21 h at 300 rpm. To find sorbent concentration effect, 0.2 and 4 g LECA compared for 21 h. For Isotherm study: 0.0005-0.02 mg/L each PAH mixed with 0.2 g LECA for 6 h.</p>	<p>Phenanthrene: 92.61%, fluoranthene: 93.91%, pyrene: 94.15 %</p>	<p>Freundlich, Langmuir</p>	<p>K_f and n values for phenanthrene 0.22 mg/g and 1.48, for fluoranthene 2.02 mg/g and 0.95 and for pyrene 1.7 mg/g and 0.95 respectively.</p>	<p>Nkansah et al. (2012)</p>

River sediment	Batch	phenanthrene, pyrene, fluoranthene	Each PAH 10-100 $\mu\text{g/L}$ mixed with 4g sediments at $25\pm 1^\circ\text{C}$ at 160 rpm for 8h. Best result was for sediment size size < 38 μm .		Freundlich	K_f and n values for phenanthrene 88.54 L/g and 1.053, for fluorene 188.71 L/g and 1.37 and for pyrene 91.46 L/g and 1.266 respectively.	Wang et al. (2015)
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Note: The coefficients of isotherm models are given for the best fitted model only.

Table 3.2: PAHs adsorption capacity of activated carbon produced at different temperature

Feed stocks	Activating agent	Temperature (°C)	BET surface area (m ² /g)	PAHs	Adsorption capacity	Reference
Soybean stalk	H ₃ PO ₄	300	143.17	naphthalene, acenaphthene, phenanthrene	K _d for naphthalene, acenaphthene and phenanthrene are 19.90, 9.91 and 80.05 L/g respectively.	Kong et al. (2011)
		400	148.38		K _d for naphthalene, acenaphthene and phenanthrene are 19.77, 13.41 and 106.61 L/g respectively.	
		500	197.49		K _d for naphthalene, acenaphthene and phenanthrene are 18.53, 12.49, 104.08 L/g respectively.	
		600	231.01		K _d for naphthalene, acenaphthene and phenanthrene are 27.47, 18.36, 520.84 L/g respectively.	
		700	287.63		K _d for naphthalene, acenaphthene and phenanthrene are 52.23, 36.55, 3198.22 L/g respectively.	
Petroleum coke	KOH	600	925.0 for KOH to Coke ratio 2	pyrene, fluoranthene, naphthalene,	Adsorption capacity for pyrene, fluoranthene, naphthalene and phenanthrene are 6.5, 37.0, 175.3 and 11.9 µg/g	Yuan et al. (2010)

				phenanthrene, fluoranthene	respectively.	
		700	562.0 for KOH to Coke ratio 1 and 1904.0 for KOH to Coke ratio 3		Adsorption capacity for pyrene, fluoranthene, naphthalene and phenanthrene are 6.2, 35.7, 146.1 and 11.7 μ g/g, respectively for KOH to Coke ratio 1 and 12.3, 45.6, and 457.7 and 46.3 μ g/g, respectively for KOH to Coke ratio 3.	
		800	1573.0 for KOH to Coke mass ratio 2		Adsorption capacity for pyrene, fluoranthene, naphthalene and phenanthrene are 10.1, 41.7, 427.6, 14.6 μ g/g respectively	

Moreover, making a change in activation process parameters such as temperature, activating agent and oxidant flow rate, activated carbon with different adsorptive properties could be produced from the same material (Bansal 1988). For example, as detailed in Table 3.2, increasing the temperature during the activation process of soybean stalk based activated carbon specific surface area could be increased which resulted increase in the adsorption capacity (Kong et al. 2011). Similar observation for adsorption of aqueous PAHs (Table 3.2) was noted when activating agent (KOH) to carbon ratio was changed during the oil sands petroleum coke based activated carbon production process (Yuan et al. 2010).

High usable surface area and a porous structure of activated carbon facilitate to enhance the sorption capacity (Burchell 1999). Depending on types of activated carbon, the normalised specific surface area capacity could be varied. For example, CO₂-activated petroleum coke has a higher normalised specific surface area of 0.27 mg/m² with maximum naphthalene adsorption capacity of 112.6 mg/g whereas coal-derived commercial activated carbon has specific surface area capacity of 0.19 mg/m² with the maximum naphthalene adsorption capacity of 196.4 mg/g (Awoyemi 2011).

3.2.2 Biochar

High surface area, porous structure available to adsorb organic contaminants, make biochar a favourable adsorbent (Yargicoglu et al. 2015) in the removal of PAHs from aqueous solution and in remediation of PAHs contaminated soil. Similar to activated carbon, biochar is produced by pyrolysis of agricultural, industrial and forest residues (such as wheat residue, corn stover, rice husks, pine needle, peanut hulls, pecan shells, apricot stones, coniferous sawmill residue) in the absence or near-absence of oxygen at temperatures from 300 to 700 °C (Chun et al. 2004; Anderson 2013; Xu and Sparks 2013; Laird 2008).

Biochar has been widely used as soil amendment as it alters soil properties, assist in retain nutrients and organic compounds and encourages microbial activities (Ogbonnaya and Semple, 2013). Use of biochar has been extended towards removing PAHs from aqueous solutions as it has high adsorptive capacity. (Oleszczuk et al. 2012) reported that biochar could reduce about 57% of dissolved PAHs in sewage sludge (Table 3.1). Similarly, use of biochar in PAHs contaminated soil removed > 50 and > 40% of the HMW and LMW PAHs, respectively reducing the toxicity effect to microorganisms and plants due to immobilization

of soil PAHs (Beesley, Moreno-Jimenez, and Gomez-Eyles 2010). Furthermore, Wang et al. 2006) demonstrated that using wood based biochar PAHs(pyrene, phenanthrene and benzo(a)anthracene) removal efficiency of $\geq 60\%$ from aqueous solution could be achieved.

It has been demonstrated that particle size of biochar has little or no effect on sorption of PAHs (Hale et al. 2011). However, the smaller the particle size, the shorter the time for sorption equilibrium to be achieved (Zheng 2010). Sorption of organic contaminants by biochar is governed by types of feed stocks, production processes, sorbate concentration and the age Wang et al. 2006).

A recent study (Li et al. 2014) revealed that wheat straw based biochar produced at 400, 600 and 800 °C achieved PAH removal efficiency of 71.8 to 98.6% from soil washing effluent (Table 3.3). Their adsorption capacity found to be increased with increasing the biochar production temperature. Similar relationship, as detailed in Table 3.3, maximum amount of naphthalene adsorption (136.8 mg/g) by pine needle biochar produced at 700 °C was observed (Chen et al. 2008). They have further demonstrated a non-linear relationship between production temperature and adsorption capacities of biochar which could be a result of destruction of aliphatic alkyl and ester groups at the time of biochar production. Additionally, the increased heat enhances the carbonisation that leads to form high microporous in biochar surface (Bornemann et al. 2007; Chen and Yuan 2011). However, further investigations should be carried out considering the production processes of biochar in removing PAHs.

Table 3.3: PAHs adsorption capacity of biochar produced at different temperatures

Feed stocks	Temperature (°C)	BET surface area (m ² /g)	Pore volume (cm ³ /g)	PAHs	PAHs removal efficiency/ adoption capacity	Reference
Wheat straw	400	427	0.526	phenanthrene, fluoranthene, pyrene	71-88%	Li et al. (2014)
	600	537	0.574		82.4-93.4%	
	800	652	0.634		95.8-98.6%	
Pine needle	250	9.52	-	naphthalene	1.724 mg/g	Chen et al. (2008)
	400	112.4	0.0442		25.69 mg/g	
	500	236.4	0.0952		27.40 mg/g	
	600	206.7	0.0764		15.14 mg/g	
	700	490.8	0.186		136.8 mg/g	

Biochar contains both glassy and rubbery fractions where the glassy fraction is categorised as non-linear competitive adsorption of organic contaminants and the rubbery fraction is associated with linear non-competitive partitioning of organic contaminants (Chen and Yuan 2011). The adsorption of PAHs to wood chars is rapid and is assisted by π - π electron interactions and pore-filling mechanisms (Chen and Chen 2009). Multilayer adsorption, surface coverage, condensation in capillary pores, and adsorption into the polymeric matrix are some of the other processes involved during the adsorption process using biochar (Werner and Karapanagioti 2005).

3.2.3 Modified clay mineral

As demonstrated in Table 3.1, clay minerals such as bentonite, sepiolite, montmorillonite, zeolite, and their modified forms have been widely used to remove phenanthrene, pyrene and benzo(a)pyrene through the adsorption process (Zhang, Luo, and Zhang 2011; Muller, Totsche, and Kogel-Knabner 2007; Ma and Zhu 2006; Cobas et al. 2014; Changchaivong and Khaodhiar 2009; Staniska et al. 2015). Employing organo-zeolite could remove 98% of fluorene, fluoranthene, pyrene, phenanthrene, benzo(a)anthracene (Table 3.1) (Lemić et al.,

2007). Particles size of zeolite is about a millimetre or greater and they are free of shrink-swell behaviour. Thus, zeolite exhibit superior hydraulic characteristics and are suitable for use in filtration systems (Tarasevich et al. 1995).

During the modification of clay minerals, the exchangeable inorganic cations are replaced by organic cations including quaternary ammonium compounds which have cationic head groups with long chain hydrocarbon molecule forming the surfactant tail (Park et al.2008). The obtained organo clay can be effectively used to remove PAHs from aqueous solutions. Cetylpyridinium (CP) exchanged low-pH montmorillonite clay (LPHM) is an effective sorbent for variety of PAHs measured in water (Ake et al. 2003). It has been suggested that GAC mixed with organoclay may be more effective than GAC or CP/LPHM alone. Further study carried out by Wiles et al. (2005) using a combination of different media revealed that PAHs could be removed $\geq 99\%$ by employing CP-LPHM/GAC and 90% with combined CP-LPHM/sand. In addition to this, soil containing smectite minerals is able to retain large amount of phenanthrene (Hundal et al. 2001). The sorption capacity of modified quartz sand with montmorillonite maintaining 5% clay fraction found to be significantly increased the phenanthrene removal efficiency $> 99\%$ (Justyna et al. 2015) demonstrating a positive impact of clay mineral on sorption media.

3.2.4 Other media

In addition to common media, studies have been further extended towards investigating other media for efficient removal of PAHs from aqueous solution and some of them are detailed in Table 3.1. (Sun et al. 2013) employed graphene oxide (GO) and reduced graphene oxide (rGO) to adsorb naphthalene and removal efficiencies of GO and rGO were reported to be 60 and 95%, respectively. Similarly, a media called electrospun nanofibrous membranes have been reported to have a very high sorption capacity from aqueous solution (Table 3.1) (Dai et al. 2011). (Dai et al. 2013) performed adsorption test using four types of laccase-carrying electrospun fibrous membranes (LCEFMs) poly(D,L-lactide) (PDLA), poly(lactide-co-caprolactone) (P(LA/CL)), poly(D,L-lactide-co-glycolide) (PDLGA) and methoxy polyethylene glycol-poly (lactide-co-glycolide) (MPEG-PLGA) to remove benzo(a)pyrene, benzo(a)anthracene, phenanthrene and naphthalene from aqueous solutions. Among those sorbents deactivated P(LA/CL) was found to be a good sorbent for phenanthrene, benz(a)anthracene and benzo(a)pyrene removal (Table 3.1). On the other hand, MPEG-PLGA

appeared to be better for naphthalene removal which could be as a result of their hydrophilic nature. The result observed from these studies further concludes the sorption capacity of media is influenced by the specific surface area and the hydrophilic-hydrophobic property.

Furthermore, (Niu et al. 2013) reported efficient adsorption of seven PAHs named naphthalene, phenanthrene, anthracene, chrysene, benzo(b)fluoranthene, benzo(a)pyrene in aqueous solution at different pH (1.0 to 9.0), temperature (5.0 to 45.0 °C) and dissolved organic matter concentration (0.0 to 36.7 mg/L) using laccase loading spider type reactor. The removal efficiency of these seven PAHs was found to be in the range of 95.3 to 97.6%. Mesoporous molecular sieve MCM-41-dry (surface area 37.2 m²/g), adsorption media was used to remove phenanthrene and the removal efficiency of 97.5% was achieved (Table 3.1) (Hu et al. 2014). This media has great values in using PAHs adsorption media due to its miscible nature to aqueous solution, high adsorption capacity, good settle ability and re-usability. Using two types of grafted cellulose with hydroxide and amine group in a closed-loop column reactor 94 to 98% of 16 PAHs (categorised by USEPA) removal efficiencies were noted (Euvrard 2014)).

As detailed in Table 3.1, adsorption of 5 PAHs on leonardite and adsorption of 3 PAHs on light weight clay aggregate were tested by (Zeledon-Toruno et al. 2007; Nkansah et al. 2012). From their experimental observation, the sorption capacity of the sorbents found to be very high (95%) showing leonardite and light weight clay aggregate are good alternative for sorption of PAHs from water. Recently, the adsorption of three PAHs using river sediment with different particle size (< 38µm, 38-74µm, 74-200µm) demonstrated that the sediments having particle size of < 38µm were found to be most efficient adsorbent (Table 3.1) (Wang et al. 2015) for aqueous PAHs. (Perez-Gregorio et al. 2010) reported 99 to 100% removal efficiency of wood ashes (produced at temperatures of 500 to 800 °C) to remove fluorene, pyrene, chrysene, benzo(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenz(a,h)anthracene, indeno(1,2,3-cd)pyrene, benzo(g,h,i)perylene from aqueous solutions (Table 3.1).

3.3 Factors Affecting Adsorption Process

3.3.1 Particle size and surface area

PAHs adsorption capacity of adsorbent or media is inversely proportional to the particle size of the media (Wang et al. 2015). For example, the adsorption of benzene, naphthalene, and anthracene found to be higher in estuarine colloids than in the soil and sediment (Wijayarathne and Means 1984; Hundal et al. 2001). This is due to adsorption is a surface phenomenon and the extent of adsorption is proportional to the specific surface area which is the portion of the total surface area that is available for adsorption (El-Sheikh et al. 2004; Naeem et al. 2007). In agreement with this theory, investigations carried out using various particles sizes of adsorption media demonstrates the smaller size particles possess the largest surface area for mass transfer resulting the highest adsorption capacity (Lemić et al. 2007; Wang et al. 2015). Similarly, accumulation of hydrophobic organic pollutants such as phenanthrene found to be increased with the decrease of particle size of sediments as a result of increased surface area (Cornelissen and Gustafsson 2004).

3.3.2 Solubility

The solubility of the adsorbate greatly influences the adsorption capacity of adsorbents. In general, an inverse relationship was observed between the extent of adsorption of a solute and its solubility in the solvent where the adsorption takes place (Chiou et al. 1998). For example, the adsorption capacity of sediment found to be increased with decrease in solubility of PAH in aqueous solution (Hu et al. 2008).

Furthermore, there is an inverse relationship between the solubility and molecular weight of PAHs. For example, the solubility found to be in decreasing order with increasing molecular weight for the tested three PAHs as naphthalene, acenaphthylene and phenanthrene (Balati et al. 2015). The relationship between aqueous solubility and octanol-water partition coefficients for the partitioning of PAH between water and organic matter in soils could be explained by Eq. 3.1.

$$K_{ow} = \frac{\text{amount of organic chemical in octanol (mg/L)}}{\text{amount of organic chemical in water (mg/L)}} \quad \text{Eq 3.1}$$

The octanol-water coefficient is expressed as $\log K_{ow}$ whose value increases with increase in molecular weight of PAHs. For example, $\log K_{ow}$ of naphthalene is 3.37 and indeno(1,2,3-cd)pyrene is 6.50 which means naphthalene is more soluble than indeno(1,2,3-cd)pyrene. This observation further clarified that the influence of chemical structure on their solubility.

3.3.3 Salinity

PAHs adsorption capacity found to be increased with increasing the salinity. Inorganic ions (such as Na^+ , K^+ , Cl^- and SO_4^{2-}) bind water molecules tightly into hydration shells (Weston et al. 2010) reducing the water solubility of PAHs and the cavity volume to accommodate organic solute which force more PAHs molecules onto the adsorbent surface. In corroboration with the theory, adsorption coefficient of phenanthrene increased by 15% when it was transferred from pure water to 0.34M KCl solution (Karickhoff et al. 1979). Similar observation was reported by (El-Nahhal and Safi 2004) demonstrating the adsorption of phenanthrene on clay surface dramatically increased with increasing NaCl concentration (up to 150 g/L) in the aqueous solution. It was also observed that the adsorption of phenanthrene increased in saline water due to decrease of solubility to 0.97 from 1.12 mg/L in fresh water (Sun et al. 2009). Furthermore, PAHs adsorption capacity on the sediments found to be increased with increasing salinity and changing the physico-chemical properties of the sediments (Hu et al. 2008; Wang et al. 2015).

3.3.4 Temperature

The effect of temperature on PAHs sorption could be described by Van't Hoff equation (2) which was derived using the concept of Gibbs free energy.

$$\ln K_{eq} = -\frac{\Delta H}{R} * \frac{1}{T} + \frac{\Delta S}{TR} \quad \text{Eq. 3.2}$$

where, ΔH is change in enthalpy KJ/mol, T is absolute temperature (K), ΔS is change in entropy KJ/mol/K, R is gas constant (8.314×10^{-3} kJ/K/mol) and K_{ep} is equilibrium partition coefficient at a given temperature cm^3/g . According to Eq. 3.2 if the slope ($\Delta H/R$) is negative sorption process is endothermic and if slope is positive process is exothermic.

The sorption of PAH decreased by average values of 27.3, 17.0, and 27.4% for naphthalene, phenanthrene, and pyrene, respectively with increasing temperature from 4 to 27 °C (Edgar Hiller 2008) where enthalpies of sorption (ΔH_s) calculated using Eq. 3.2 were negative indicating the process was exothermic. Similarly, sorption coefficients of fluoranthene on soil and lava observed to be decreased by 1.6 times when temperature was raised from 5 to 25 °C (He et al. 1995). Furthermore, adsorption of naphthalene on soil containing 1.6% of organic carbon decreased when temperature was increased from 15 to 35 °C (Podoll et al. 1989). Similar decreased trend of adsorption of naphthalene on other media was observed at temperature range of 22 to 90 °C (Sleep and McClure 2001). In brief, the adsorption reactions are normally exothermic thus the extent of adsorption generally increases with decreases of temperature (Bekci 2006).

In contrast to the previous results, the adsorption of benzene, toluene, ethylbenzene to the soil comprising 0.16% of organic carbon, increased with increasing temperature from 5 to 45 °C (Steinberg 1992). Similarly, adsorption of naphthalene, acenaphthylene and phenanthrene from wastewater onto NH₂-SBA-15 found to be high at the higher temperature (Balati et al. 2015) and the endothermic nature of the adsorption process was also conformed from positive values of enthalpy (using Eq. 3.2). Lower adsorption capacities are normally expected at higher temperature for the compounds whose solubility increase with temperature, whereas higher adsorption capacity could be expected for the compounds whose solubility decreases with temperature (Kipling 1965) which explain the effect of temperature on sorption capacity is the result of combined contribution of sorption and solubility.

3.3.5 pH

pH of the solution affects the extent of adsorption capacity due to distribution of surface charge of the adsorbent varying the extent of adsorption according to the adsorbate functional groups (Gao and Pedersen 2005; Putra et al. 2009). For example, phenanthrene adsorption on activated carbon was maximum (> 90%) at pH 2 and minimum (< 40%) at pH 12.0 which is due to increase of positive charge on the adsorbent surface at low pH resulted to higher interaction between the adsorbent surface and PAH molecule. However, at higher pH, the positive charge on the adsorbent surface is decreased and OH⁻ ions interact with the PAH molecules for the adsorption on the active sites, reducing the adsorption efficiency of the adsorbent (Gupta, 2015). In agreement to this, the removal of naphthalene increased with the

reduced pH from 8.0 to 2.0 and maximum removal (79.3%) occurred at pH 2.0 onto silica-based organic-inorganic nan-hybrid material (NH₂-SBA-15). Such a higher removal at low pH is due to formation of NH₃⁺ on NH₂-SBA-15 surface, thus, increase of electrostatic interaction between surface charges of adsorbent and PAHs (Balati et al. 2015). Sorption of anthracene on estuarine colloids had significantly decreased at elevated pH from 8.0 to 9.0 or decreased pH from 8.0 to 5.0 (Wijayarathne and Means 1984). When experiment was carried out at various pH (3.0 to 6.0) to remove phenanthrene using soil comprising humic and fulvic acid, an improved removal efficiency was noted at pH 3.0 (Ping et al. 2006).

However, it has been also reported that pH is not a significant influencing factor for adsorption of PAHs (naphthalene, phenanthrene, anthracene, fluoranthene and pyrene) into the different media (Mader 1997). Raber (1998) demonstrated that pyrene and benzo(k)fluoranthene have no effect on the binding capacity in pH range of 3.5 to 6.0. Similarly, pH in the range of 2.0 to 6.0 of the solutions did not significantly affect the adsorption process of pyrene, benzo(k)fluoranthene, benzo(a)pyrene and benzo(g,h,i)perylene on leonardite (Zeledon-Toruno et al. 2007). Not a significant influence of pH (3.0 to 11.0) on adsorption of phenanthrene onto hydrophobic molecular sieve MCM-41 was observed (Hu et al. 2014). (DePaolis and Kukkonen 1997) also reported that pH did not greatly affect the binding capacity of humic substances for benzo(a)pyrene and pyrene. Similarly, pH values ranging from 1.0 to 9.0, the maximum difference in efficiency of each PAH removal by free laccase was 16.4 to 28.1%, while the maximum difference for poly (d,l-lactide-co-glycolide) laccase-loading spider-type reactor was between 9.3 and 16.3% (Niu et al. 2013) which further confirm no significant impact of pH on PAHs adsorption process. Further investigation is required to clarify the role of pH in sorption of PAHs

3.3.6 Initial PAH concentrations

Adsorption of phenanthrene found to be increased with increasing the initial PAHs concentration (Ping et al. 2006). Awoyemi (2011) performed experiment using naphthalene with various initial concentrations (1.6, 4.2 and 8.2 mg/L) and demonstrated the adsorption rate is proportional to the initial concentration. Similarly, adsorption capacity of acenaphthene onto the silica gel increases from 0.178 to 1.296 mg/g for an increase of initial concentration from 0.376 to 1.795 mg/L (Hall et al. 2009). Furthermore, Gupta (2015) studied adsorption of phenanthrene on activated carbon for phenanthrene concentrations range of 10 to 50 mg/L and

reported that adsorption capacity of adsorbent increased with PAH concentrations. Similar result was also reported by Gong et al. (2007) when test was carried out using three different oil solutions having different PAHs concentrations. The positive influence of high initial PAHs concentrations could be due to availability of larger number of PAHs to interact with active sites of the activated carbon.

3.3.7 Contact time

When hydrophobic organic compound comes into contact with soil, a portion is rapidly adsorbed to soil components (such as organic matter, clay minerals) through a physisorption, whilst remaining fractions take longer time to reach sorption equilibrium (Semple 2007). In order to prove such hypothesis, Zeledon-Toruno et al. (2007) carried out experiment using pyrene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(g,h,i)perylene and fluorene with initial PAHs concentration of 100 µg/L. The experimental result showed 70% of PAHs removal was achieved within 2 h of contact time and then gradually reached to the equilibrium within 24 h with maximum removal efficiency of > 82% for pyrene, benzo(k)fluoranthene, benzo(a)pyrene and benzo(g,h,i)perylene and 78.4% for fluorene. The sorption of anthracene, benzo(a)anthracene and benzo(a)pyrene into electrospun nanofibrous membranes (Table 3.1) mostly achieved within 30 min and equilibrium reached within 3 h (Dai et al. 2011). Similarly, phenanthrene adsorption rate on mesoporous molecular sieve MC-41 was rapid for the first 20 min, and then slowly reached to the equilibrium within 60 min and no further significant change in adsorption has been observed until 2 h (Hu et al. 2014). Phenanthrene adsorption rate on activated carbon increases rapidly at the first 75 min contact time then reached to the equilibrium state at 150 min (Gupta 2015). Amount of PAH adsorbed onto the activated carbon increased with contact time (Awoyemi 2011) which could be due to the greater importance of migration effect for longer time on adsorption of PAHs.

3.3.7.1 Adsorption kinetics

Kinetic study is performed to ascertain the minimum time required to achieve equilibrium condition during the adsorption process. The adsorption rate of persistent organic compound such as PAHs on adsorbents is important parameter in designing effective sorption system. Many attempts have been made for describing the expression of adsorption kinetics of PAHs on different types of adsorbents and most common types of adsorption kinetic models found

in the literatures are pseudo-first-order kinetics, pseudo-second-order kinetics and Elovitch equation which are detailed in Table 3.4.

Table 3.4: Summary of adsorption kinetics

Kinetic Types	Equations	PAHs	Adsorbents	R ²	References
pseudo-first-order	$\text{Log}(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad \text{Eq.3.3}$ <p>where, q_e: sorption capacity at equilibrium (mg/g), q_t : sorption capacity at time t (mg/g), k_1: rate constant of pseudo-first-order sorption per minute.</p>	naphthalene, acenaphthylene, phenanthrene	Silica-based organic-inorganic nanohybrid material (NH ₂ -SBA-15)	0.837 to 0.975	Balati et al. (2015)
		phenanthrene, naphthalene, acenaphthene, pyrene	Plant residue based sorbent	0.855 to 0.993	Xi and Chen (2014)
		naphthalene	Clay sediment	0.82	Owabor et al. (2013)
		naphthalene, acenaphthene, fluorene, fluoranthene, pyrene	Mesoporous organosilica	0.921 to 0.989	Vidal et al. (2011)
		fluorene	Activated carbon	0.974	Awoyemi (2011)
		naphthalene	Organo-sepiolite	0.922	Gök et al. (2008)
		naphthalene	Zeolite	0.946	Chang et al. (2004)
Pseudo-second-order	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad \text{Eq.3.4}$	naphthalene, acenaphthylene,	Silica-based organic-inorganic	0.914 to 0.988	Balati et al. (2015)

	Where, k_2 : pseudo-second-order rate constant (g/mg/min).	phenanthrene	nanohybrid material (NH2-SBA-15)		
		phenanthrene, naphthalene, acenaphthene, pyrene	Plant residue based sorbent	0.941 to 0.994	Xi and Chen (2014)
		naphthalene	Clay sediment	0.035	Owabor et al. (2013)
		naphthalene, acenaphthene, fluorene, fluoranthene, pyrene	Mesoporous organosilica	0.930 to 0.997	Vidal et al. (2011)
		fluorene	Activated carbon	0.996	Awoyemi (2011)
		naphthalene	Activated carbon	N/A	Cabal et al. (2009)
		naphthalene	Organo-sepiolite	0.999	Gök et al. (2008)
		naphthalene	Zeolite	0.996	Chang et al. (2004)
		Elovitch	$q_t = \frac{1}{b} \ln(ab) + \frac{1}{b} \ln(t) \quad \text{Eq.3.5}$ Where, q_t : sorption capacity at time t (mg/g), a : Elovich parameter referring	naphthalene	Clay sediment
		fluorene	Activated carbon	0.852	Awoyemi (2011)
		naphthalene	Organo-sepiolite	0.941	Gök et al. (2008)

	to the initial sorption rate (mg/g/min), b: the desorption constant (g/mg).	acenaphthene, phenanthrene, anthracene, fluoranthene	Soil	N/A	Javier et al. (2008)
		naphthalene	Zeolite	0.990	Chang et al. (2004)

It has been reported that in most of the cases pseudo-first-order equation does not fit well for the whole range of contact time, and is generally applicable over the initial 20 to 30 min of the sorption process (Ho and McKay 1998). The review of sorption kinetics concluded the pseudo-second-order equation might be applied for chemisorption processes with a high degree of correlation (HO 1998). For example, experimental data fitted very well with the pseudo-second-order kinetic model for PAH adsorption using a variety of adsorbents (Table 3.4), such as zeolite (Chang et al. 2004), activated carbon (Cabal et al. 2009; Awoyemi 2011), organo-sepiolite (Gök et al. 2008), NH₂-SBA-15 (Balati et al. 2015) and plant residue based sorbent (Xi and Chen 2014). Similar to the second order, many PAHs adsorption in to the media found to be followed Elovitch kinetic as detailed in Table 3.4. PAHs (acenaphthene, phenanthrene, anthracene, fluoranthene) sorption onto the soil fitted well in Elovitch equation (Javier 2008) which also revealed that the fast sorption occurred in the beginning following the slower rate at last.

3.3.8 Soil organic matter

It is well documented that organic matter of soil and sediments play a significant role to govern the sorption of PAHs. The sorption capacity and affinity of organic matter greatly rely on their compositions (Ahangar 2010). Many studies (Gregory, Shea, and Guthrie-Nichols 2005; Cao et al. 2008) reported that PAHs sorption is proportional to the organic matter content in soil water system. It has been further demonstrated that sorption of hydrophobic organic compound by soil organic matter is controlled by the polarity of soil organic matter and aromatic carbon (Abelmann et al. 2005; Kang and Xing 2005). Studies have shown that the aliphatic groups of organic matter are responsible for the sorption properties of non-ionic organic pollutants such as PAHs. On the other hand, several studies have suggested that the key role in the sorption of PAHs played by aromatic domains of organic matter in soil and sediments (Ahangar 2010).

Phenanthrene adsorption found to be enhanced at pH 6 with increasing exogenous humic and fulvic acid (Ping et al. 2006). Conte et al. (2001) carried out adsorption test of fluorene, phenanthrene, fluoranthene, pyrene, anthracene, benzo(a)anthracene, benzo(a)pyrene, chrysene and benzo(k)fluoranthene using soil with humic acid. Adsorption capacity of soil found to be increased by adding humic acid concluding exogenous humic acid along with natural soil organic carbon could enhance the PAHs adsorption capacity. Since the interactions

between PAHs and soil matrices are hydrophobic, the clay humic complexes in soil matrices are essential in stabilizing these interactions (Piccolo 1994). The increase of the hydrogen and metals ion concentration change the structure of the humic polymer resulting less hydrophilic due to neutralization of charge which would bind hydrophobic compounds more effectively (Carter and Suffet 1982). Testing of 14 different types of soil and sediment, demonstrated a strong correlation between PAHs sorption capacity and the organic carbon present in clay and soil (Kile et al. 1999). Staniska et al. (2015) further demonstrated the strong relationship with humic acids and phenanthrene sorption.

Understanding of stability of PAH on soil media is very important to know the effect of organic matter on PAH sorption on soil. Soils contain a wide range of physically and chemically different forms of organic matter such as different humic substances, black carbon and kerogen. They are categorised as rubbery and glassy domain (Huang et al. 2003; Xiao et al. 2004). Both domains consist holes which interact with organic pollutants Semple et al. 2003) during sorption. The soft domains of soil organic matter may consist of fulvic and humic acids in their rubbery states which are characterized by linear sorption isotherms having relatively rapid sorption rate. The hard domains of soil organic matter may include kerogen, black carbon and humic acids in their glassy states and are possibly responsible for nonlinear sorption isotherms with slow sorption rate (Huang and Weber 1997). PAHs with a HMW undergo sorption by the fraction of humins to a greater degree, while LMW PAHs are bonded more strongly by humic and fulvic acids (Meyer 2011).

Sorption of PAHs on soil and natural sediments from air could be explained using dual sorption model. Absorption into biogenic organic carbon (OC) fraction and adsorption into combustion-derived, black carbon (BC) fraction (Lammel 2004; Liu et al. 2015) for gas-particle partitioning coefficient, K_P ($m^3/\mu g$) is,

$$K_P = 10^{-12} \left(f_{OM} \frac{MW_{Oct} \gamma_{Oct}}{MW_{OM} \rho_{OM}} K_{Oa} + f_{BC} \frac{a_{atm-BC}}{a_{soot} \rho_{BC}} K_{soot-air} \right) \quad \text{Eq. 3.6}$$

Where, f_{OM} and ρ_{OM} are the fraction and density of organic matter, f_{BC} and ρ_{BC} are the fraction and density of black carbon, K_{Oa} is octanol air partitioning coefficient, MW and γ are molecular weight of organic matter and octanol, $K_{(soot-air)}$ is the partitioning coefficient between soot and air and $a_{(atm-BC)}$ is surface area of atmospheric black carbon.

(Liu et al. 2015) demonstrated the prediction of gas-particle partitioning of 16 PAHs found to be better attribution with dual sorption model as a result of absorption into organic carbon and adsorption onto the black carbon. Similarly, Lohmann (2005) reported that the overall partitioning of PAHs attributed to dual sorption model with good agreement between predicted and observed values of partitioning coefficient for phenanthrene and pyrene. The partitioning of 13 types of PAHs found to be well fitted with dual sorption model (Sangiorgi et al. 2014), however, this model always underestimates the particle sorption for PAHs.

3.4 Adsorption Isotherms

Capacities of adsorbents, adsorbents' surface properties, adsorption mechanisms pathways which are essential parameters to design an effective adsorption system, could be determined with the help of adsorption isotherm. Adsorption isotherm describes how the contaminants such as PAHs interact with the adsorbent materials. In general, an adsorption isotherm is a curve which describes the phenomenon leading the mobility of a substance from the aqueous or aquatic environments to a solid-phase at a constant temperature and pH. In order to determine the maximum adsorption capacity of adsorbents and to understand the adsorption mechanisms, many studies have been employed Langmuir, Freundlich and Linear isotherm models as detailed in Table 3.5.

Table 3.5: Summary of adsorption isotherms

Isotherm	Equation	Significance
Langmuir	$q_e = \frac{K_L q_m C_e}{(1 + K_L C_e)} \quad \text{Eq. 3.7}$ <p>Where, q_e: amount of adsorbate per mass unit of adsorbent at equilibrium (mg/g), C_e: adsorbate concentration at equilibrium (mg/L), q_m: maximum adsorption capacity (mg/g) and K_L: Langmuir constant related to the energy of adsorption (L/mg).</p>	<p>Assumes that all the adsorption sites have equal solute affinity and adsorption at one site does not affect the adsorption at an adjacent site.</p> <p>Follows homogeneous adsorption, which each molecule possess constant enthalpies and sorption activation energy (Kundu and Gupta 2006), with no transmigration of the adsorbate (Perez-Marin et al. 2007).</p>

Freundlich	$q_e = K_f C_e^{1/n} \quad \text{Eq. 3.8}$ <p>Where, q_e: amount of adsorbate adsorbed per unit mass of adsorbent (mg/g), C_e: concentration of adsorbate in equilibrium solution (mg/L), K_f: Freundlich adsorption coefficient and $1/n$: measure of intensity of adsorption.</p>	<p>Describe the surface heterogeneity with non-uniform distribution of adsorption heat and affinities over the sorbent surface Hameed et al. 2007(Hameed et al. 2007).</p> <p>Amount adsorbed is the summation of adsorption on all sites, with the stronger binding sites are occupied first, until adsorption energy are exponentially decreased upon the completion of adsorption process (Zeldowitsch 1934).</p>
Linear	$q_e = K_d C_e \quad \text{Eq. 3.9}$ <p>Where, q_e: amount of adsorbate adsorbed per unit mass of adsorbent (mg/g), C_e: concentration of adsorbate in equilibrium solution (mg/L), K_d: the equilibrium distribution coefficient (L/g).</p>	<p>Special condition of Freundlich isotherm equation. When the exponent of Freundlich isotherm is 1, the Freundlich isotherm becomes Linear isotherm.</p>

Langmuir, Freundlich and Linear isotherm models have been employed to determine the PAHs adsorption capacity of the adsorbents and to understand the adsorption mechanisms. Table 3.1 detailed different types of isotherm tested with various adsorbent media. Freundlich isotherm model has been described as the most common in sorption of hydrophobic organic carbon (Huang et al. 2003). Moreover, from the studies carried out with varieties of media as detailed in Table 3.1, majority of PAHs adsorption data appeared to be well fitted with Freundlich isotherm. However, the nature of adsorption isotherm depends on source, formation process and properties of adsorbent, PAHs combination and concentration, contact time etc.

3.5 Conclusion

PAHs could be removed from aqueous media and immobilized in the contaminated soil using various types of adsorbents such as activated carbon, biochar, organic mineral, amended clay, sand, sediments, cellulose, and membranes. The effectiveness of sorption process depends not only on the properties of the adsorbent and adsorbate but also on operating variables such as pH, ionic strength, temperature, existence of competing organic or inorganic compounds and contact time including the adsorbent production processes. Moreover, studies demonstrated that selecting a right adsorbent media and operating parameters, removal efficiency could be achieved up to 100%. Findings of this review study would definitely be helpful for researchers in exploring and identifying the sorption media and factor affecting them to remove PAHs from aqueous solution and PAHs immobilised in contaminated soil environment. Based on this review, activated carbons are considered for further study because of effective PAHs adsorption capacity. Detail study on PAHs adsorption with activated carbons (adsorption kinetic, adsorption isotherm, effect of adsorbent mass) has been presented in chapter 4 based on laboratory experimental results.

Chapter 4

PAHs adsorption by powder activated carbon and granular activated carbon

4.1 Introduction

PAHs remediation from stormwater has become of particular concern due to carcinogenic, mutagenic, teratogenic property of PAHs to human and aquatic lives (Barhoumi et al. 2016; Siddens et al. 2012). Due to high sorption affinity to solid and less water solubility of PAHs, sorption method is an effective method in remediation of PAHs (Alcantara et al. 2009; Liu et al. 2014). Activated carbon (AC) has high adsorption capacity due to well-developed porous structures and large surface area (Ge et al. 2016) and has increasing demand in remediation of wastewater contaminated due to varying anthropogenic activities (Ge et al. 2015). AC has excellence performance in removal of organic pollutants from aqueous media (Shaarani and Hameed 2011). For instance, > 99% PAHs were removed by using AC from aqueous media (Rasheed et al. 2015).

There are many studies available in PAHs adsorption by AC (Rasheed et al. 2015; Awoyemi 2011; Brandli et al. 2008; Hale et al. 2012; Xiao et al. 2014; Kalmykova et al. 2014; Saad et al. 2014). However, most of them are for PAHs adsorption from contaminated soil and pore-water of contaminated soil. Comparative study of PAC and GAC for stormwater PAHs adsorption has been scarcely investigated. Therefore, the objective of this study was to perform comparative study of PAC and GAC for PAH adsorption capacity, PAH adsorption rate and effect of adsorbents mass in PAH adsorption from stormwater.

Phenanthrene is one of the most common PAHs found in the environment. Phenanthrene is an alternant PAH with 3 fused benzene rings with colourless to white crystallized solid normally having faint odour. According to the study by Zgheib et al. (2012), out of USEPA 16 PAHs, phenanthrene, fluoranthene, pyrene and chrysene are commonly found in urban stormwater. In agreement with this, other studies (Walker et al. 1999; Terzakis et al. 2008; Department of Water 2009) also have reported that phenanthrene is one of the four commonly available

PAHs in stormwater. Therefore, phenanthrene has been considered as a model PAH throughout laboratory experiments in present study.

The concentration of phenanthrene in stormwater used in this study is 40 µg/L and laboratory experiments were performed at temperature (20±1°C). The stormwater characteristic of this study is different from past literatures. The concentration of mix PAHs (naphthalene, acenaphthylene, acenaphthene, phenanthrene, fluorene, Anthracene) used in the study by Smol et al. (2014) was 1µg/L and experimental temperature was 20 °C. The phenanthrene concentration used in the study by Rad et al. (2014) was 5 to 40 mg/L and experimental temperature was 24±2°C. The concentration of mixtures of PAHs in petrochemical wastewater was 5 to 15 mg/L at temperature 28±2°C (Crisafulli et al. 2008).

4.2 Materials and Methods

GAC with size 3-4 mm was purchased from Rowe Scientific, PAC (density 0.25-0.6 g/cm³) purchased from Sigma Aldrich, phenanthrene (99% pure) obtained from Supelco and 100% pure ethanol was purchased from Westlab.

4.2.1 Adsorption kinetic study

The phenanthrene adsorption kinetic study was carried out using PAC and GAC. During batch kinetic test, 2 mg PAC and 10 mg GAC were mixed in 100 ml aqueous solution in 250 ml conical flasks separately. The solution was prepared by using Milli-Q water. The concentration of phenanthrene in solution was 40 µg/L. The concentration of ethanol in all solution was not exceeded 1%. The duplicate samples were prepared for all samples. The flasks were sealed with parafilm and then aluminum foil to prevent evaporation of organic solvent and placed on platform shaker (Innova 2100, Brunswick Scientific) at 100 rpm. The kinetic batch test was carried out at room temperature (20±1°C).

Table 4.1: summary of experimental condition

Test	Volume of solution (ml)	PAC (mg)	GAC (mg)	Phenanthrene concentration ($\mu\text{g/L}$)	Shaker rotating speed (rpm)	Water used
Adsorption batch test	100	2	10	40	100 rpm	Milli-Q water

The experimental set up for adsorption test is shown in Figure 4.1.



Figure 4.1: Batch test for adsorption of PAH with PAC and GAC

The phenanthrene concentration of supernatant was measured periodically until it reaches equilibrium.

The data obtained for rate of PAH adsorption with ACs were fitted in pseudo-first-order and second-order kinetic models for further analysis.

The linearized form of pseudo-first-order model is

$$\text{Log } (q_e - q_t) = \log q_e - \frac{K_1 t}{2.303} \quad \text{Eq.4.1}$$

Where, q_e is sorption capacity at equilibrium ($\mu\text{g}/\text{mg}$), q_t is sorption capacity at time t ($\mu\text{g}/\text{mg}$), k_1 is rate constant of pseudo-first-order sorption per hour. K_1 and q_e were calculated from slope and intersection of linear plot of $\text{Log } (q_e - q_t)$ versus t and q_t was calculated by using following equation

$$q_t = \frac{(C_o - C_t)V}{m} \quad \text{Eq.4.2}$$

Where, C_o is the initial phenanthrene concentration ($\mu\text{g}/\text{L}$), C_t is concentration ($\mu\text{g}/\text{L}$) at time t , V is volume (L) of solution and m is mass of adsorbents (mg).

The linearized form of pseudo-second-order model is

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad \text{Eq.4.3}$$

Where, k_2 is pseudo-second-order rate constant ($\mu\text{g}/\text{mg}/\text{h}$). K_2 and q_e were determined from the slop and intercept of plot of t/q_t versus t .

4.2.2 Effect of mass of adsorbents on adsorption kinetics

To evaluate effect of mass of adsorbents on phenanthrene adsorption, amount of PAC considered was 20 and 200 mg whereas amounts of GAC considered was 20, 100 and 200 mg. The adsorbents were placed separately in 250 ml conical flasks and mixed with 150 ml solution containing 40 $\mu\text{g}/\text{L}$ phenanthrene at room temperature ($20 \pm 1^\circ\text{C}$). The duplicate samples were prepared for all samples. The flasks were sealed with parafilm and aluminum foil and then placed on platform shaker at 175 rpm. The phenanthrene concentration of supernatant measured at different interval of time untill equilibrium.

4.2.3 Adsorption isotherm study

Adsorption isotherm study was carried out for 2 mg PAC and 10 mg GAC in 100 ml solution for five different concentrations (5, 10, 20, 30, 40 µg/L) of phenanthrene. The speed of shaker was maintained as 100 rpm. The isotherm batch experiment was run 24h for PAC dosed samples and 48h for GAC dosed samples at room temperature (20±1°C). The equilibrium times were obtained from kinetic experiments for both types of adsorbents. The isotherm data were fitted in Lagmuir and Freundlich models. The linearized equation for Lagmuir model is

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_1 q_m} \quad \text{Eq.4.4}$$

Where, q_m (µg/mg) is the maximum capacity of phenanthrene adsorbed, K_1 (L/µg) is Langmuir constant and C_e is phenanthrene concentration at equilibrium (µg/L). The maximum adsorption capacity and the Lagmuir constant were determined from slop and interception of the plot of C_e/q_e versus C_e . In addition to this, Langmuir adsorption isotherm can be expressed by separation factor R_L as presented in equation 4.5.

$$R_L = \frac{1}{(1 + q_m * K_1)} \quad \text{Eq.4.5}$$

The R_L value indicates the nature and the feasibility of adsorption process. The process is irreversible if $R_L = 0$, the process is favourable if $0 < R_L < 1$, the process is linear if $R_L = 1$ and process is unfavourable if $R_L > 1$.

The linear equation for Freundlich model is

$$\text{Log}q_e = \text{Log}K_f + 1/n\text{Log}C_e \quad \text{Eq.4.6}$$

Where, q_e is phenanthrene adsorbed per unit mass of activated carbon (µg/mg), K_f is Freundlich adsorption coefficient and $1/n$ is measure of intensity of adsorption. K_f and n values were calculated from slop and interception of plot of $\text{Log}q_e$ versus C_e .

4.2.4 Method development for PAH analysis

Spectrofluorophotometer RF- 5301PC from Shimadzu was used to analyse PAH. The excitation and emission band width set as 5 nm with high sensitivity. The excitation wavelength was 250 nm and emission wavelength set in the range of 290 to 475 nm based on spectrum peaks from number of trials. For standard calibration curve, phenanthrene samples were prepared with concentration range from 0.006 to 100 $\mu\text{g/L}$. The sample prepared was diluted serially by half from 100 $\mu\text{g/L}$ to 0.006 $\mu\text{g/L}$. Phenanthrene solution was prepared in 1% ethanol in all cases.

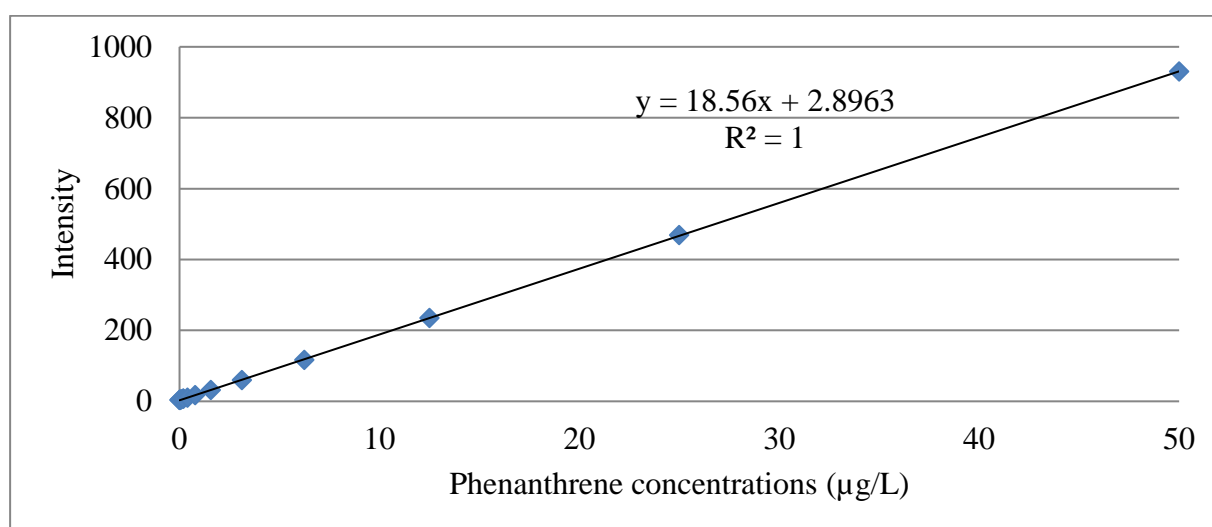


Figure 4.2: Calibration curve developed for standard phenanthrene analysis with spectrofluorophotometer

Linear calibration graph was obtained with correlation coefficient of 1 (Figure 4.2) with considering phenanthrene concentration from 0.006 to 50 $\mu\text{g/L}$. This curve was used to determine phenanthrene concentration of all samples.

Data for 100 $\mu\text{g/L}$ was not fitted in linear plot of calibration curve. Therefore, data for 100 $\mu\text{g/L}$ was excluded during plotting calibration curve. Spectrum analysis was performed to see the nature of peak for 100 $\mu\text{g/L}$ and also to compare with peaks developed with lower concentrations. For the spectrum analysis phenanthrene concentration were tested in the range from 1.563 to 100 $\mu\text{g/L}$. The concentration of phenanthrene was diluted by half from 100 $\mu\text{g/L}$ to 1.563 $\mu\text{g/L}$. The spectrum analysis is presented in Figure 4.3.

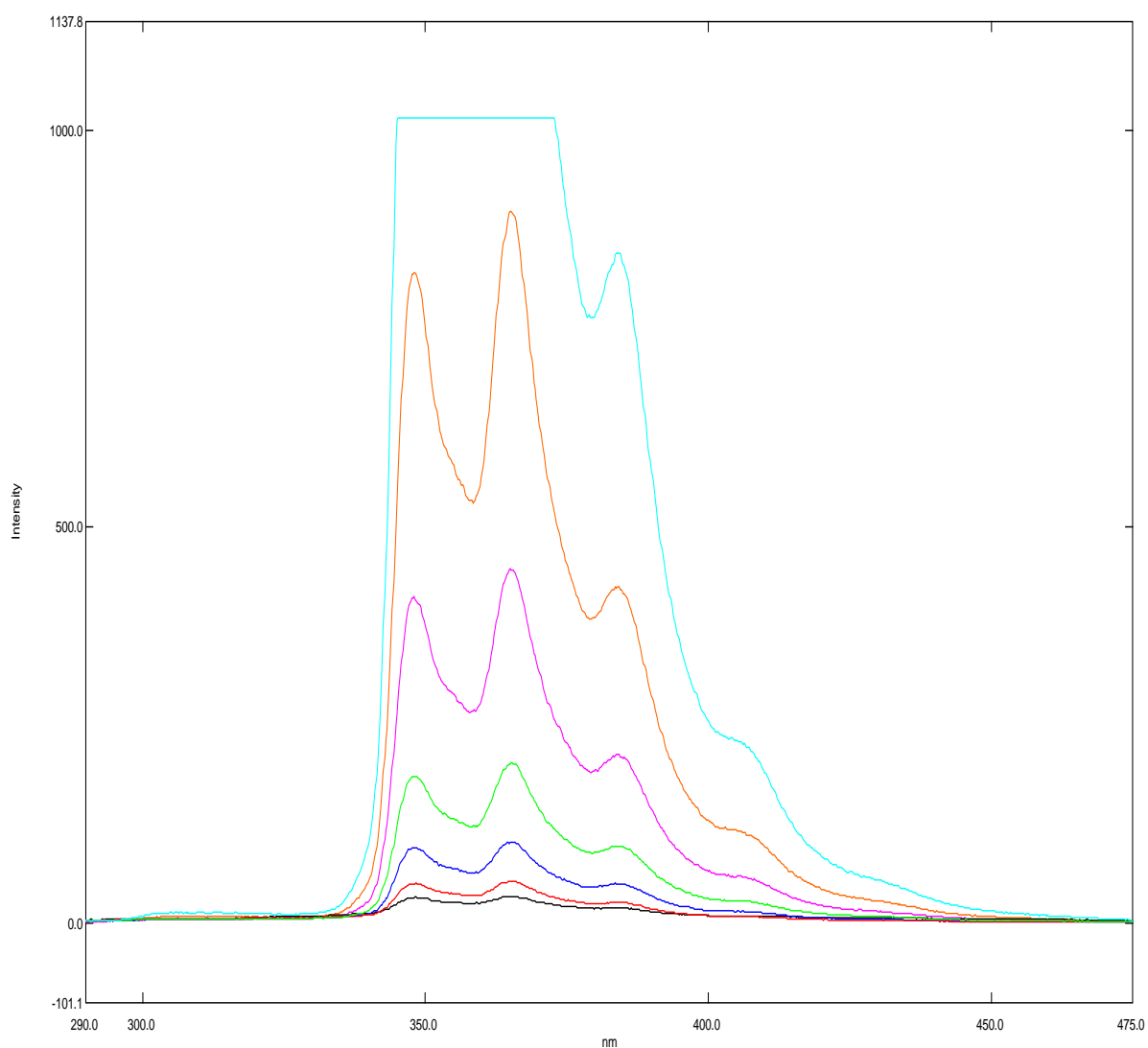


Figure 4.3: Spectrum for 1.563 to 100 µg/L phenanthrene

The spectrum of 100 µg/L showed different nature than peak of other concentrations as the top of spectrum is flat for 100 µg/L phenanthrene. However, proper peaks were developed for other concentrations. To further varify the higher detection limit of the machine for particular excitation-emission range, 54 µg/L phenanthrene was also tested to evaluate the nature of spectrum. The spectrum for 54 µg/L was found similar to the nature of that 100 µg/L (Figure A1 in Appendix). Therefore, in all laboratory tests phenanthrene concentration was maintained less than 50 µg/L to avoid possible error due to ditECTION limit of Spectrofluorophotometer. Moreover, standards were measured regularly to make sure the reliability of method used.

4.3 Results and Discussion

4.3.1 Performance of GAC and PAC

Adsorption kinetic study predicts the rate of removal of pollutant from aqueous media and provides the information related to sorption reactions mechanisms. Therefore, adsorption kinetic study is important in pollutants removal by adsorption method.

The phenanthrene removal efficiency was 98.75% within 0.25 h and this result increased up to 99.43% within 5 h. Beyond this point, phenanthrene removal efficiency was not increased when the test was carried out until 24 h (Figure 4.4) indicating the equilibrium condition was reached at 5 h. The maximum removal efficiency of phenanthrene by PAC from synthetic stormwater was observed as 99.43% with residual phenanthrene concentration in the supernatant was 0.227 μ g/L (Table A2 in Appendix).

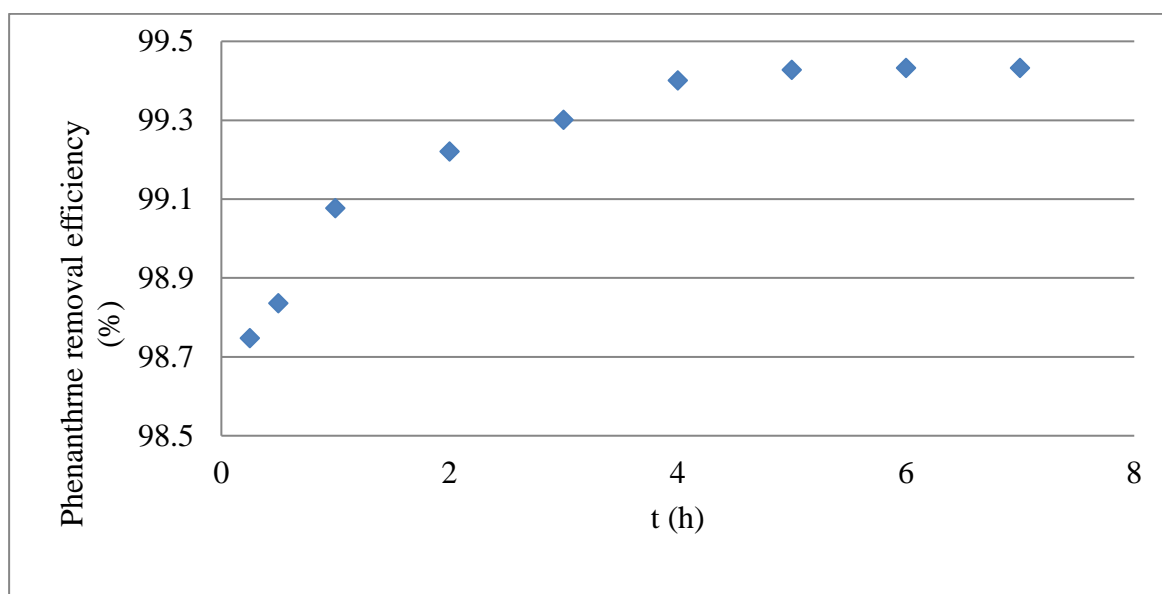


Figure 4.4: Phenanthrene adsorption by PAC during batch kinetic experiment

Phenanthrene removal efficiency was observed 11.62% at 0.25 h and 75.15% at 7 h with GAC. The removal efficiency was further increased up to 97.51% at 48 h which was remaining constant with further increasing of test time as the removal efficiency of 72 h was also 97.51% indication equilibrium stage reached at 48 h (Figure 4.5).

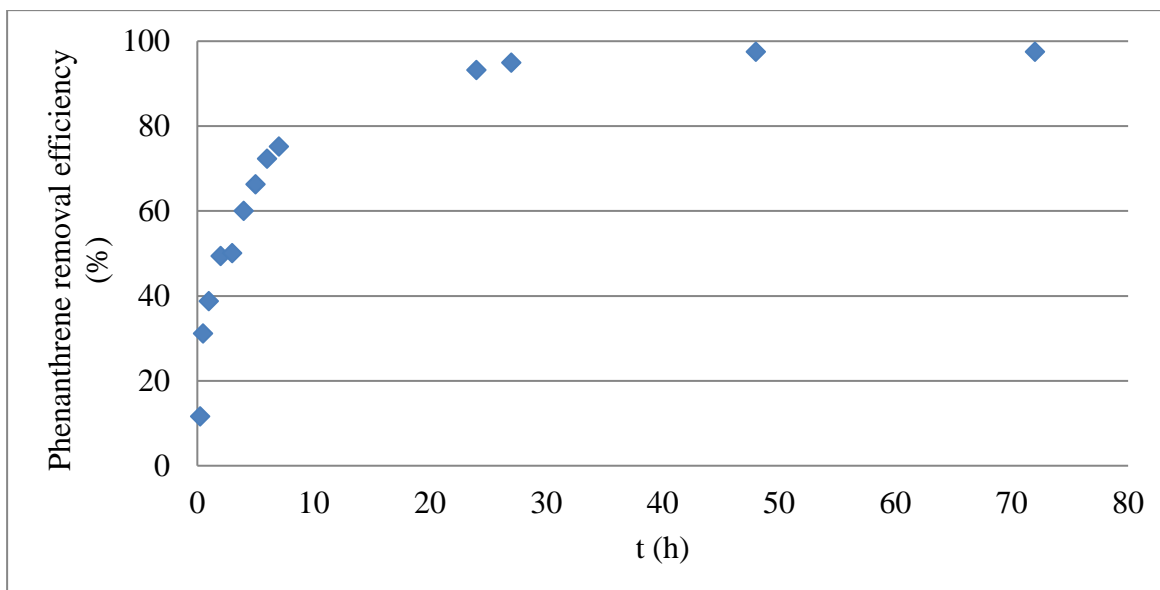


Figure 4.5: Phenanthrene adsorption by GAC from aqueous solution

From the analysis of experimental results, both ACs are found effective in PAHs remediation. The removal efficiency of Σ 6 PAHs from synthetic wastewater was obtained as 98.1% and removal efficiency of phenanthrene was obtained as 100% by using AC (Smol et al. 2014). The reason for higher percentage of phenanthrene removal in Smol et al. (2014) is due to use of greater amount of AC (50 g) when compared to amount of AC used in present study (2 to 10 mg). Thus the result of present study has been found effective in aqueous PAHs remediation.

The comparative results for phenanthrene adsorption by PAC and GAC from aqueous solution, is presented with column diagram (Figure 4.6) where equilibrium time for PAC is less than equilibrium time of GAC. The fast rate of phenanthrene removal with PAC than GAC is due to greater specific surface area of PAC due to small particle size when compared to GAC.

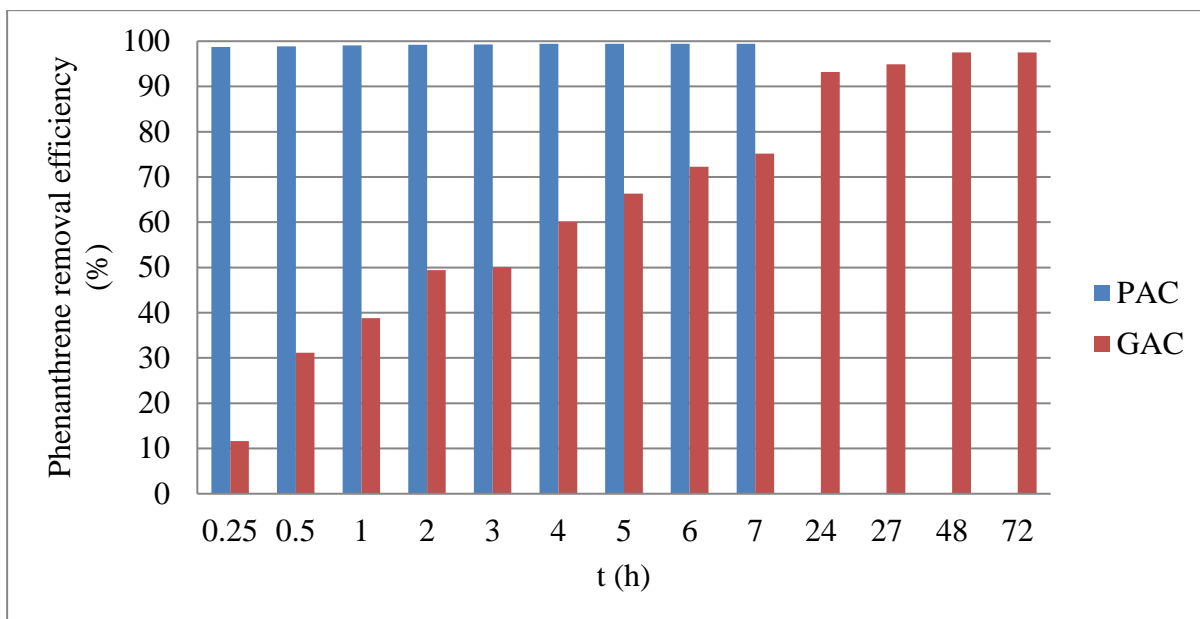


Figure 4.6: Phenanthrene adsorption by PAC and GAC at different interval of time

4.3.2 Adsorption kinetic model

To better elucidate the mechanism of rate-controlling steps in the sorption process of PAC and GAC, pseudo-first-order and pseudo-second-order kinetic models were used to fit the experimental data. The parameters of kinetic models for phenanthrene adsorption with PAC and GAC are tabulated in Table A4 and Table A5 respectively in Appendix section.

The graphs were developed for $\text{Log}(q_e - q_t)$ versus t to analyse data with pseudo-first-order model where coefficient of correlation for phenanthrene adsorption with PAC was found as 0.94 and with GAC was found as 0.98 (Figure 4.7), revealing adsorption data with GAC fitted better than adsorption data with PAC.

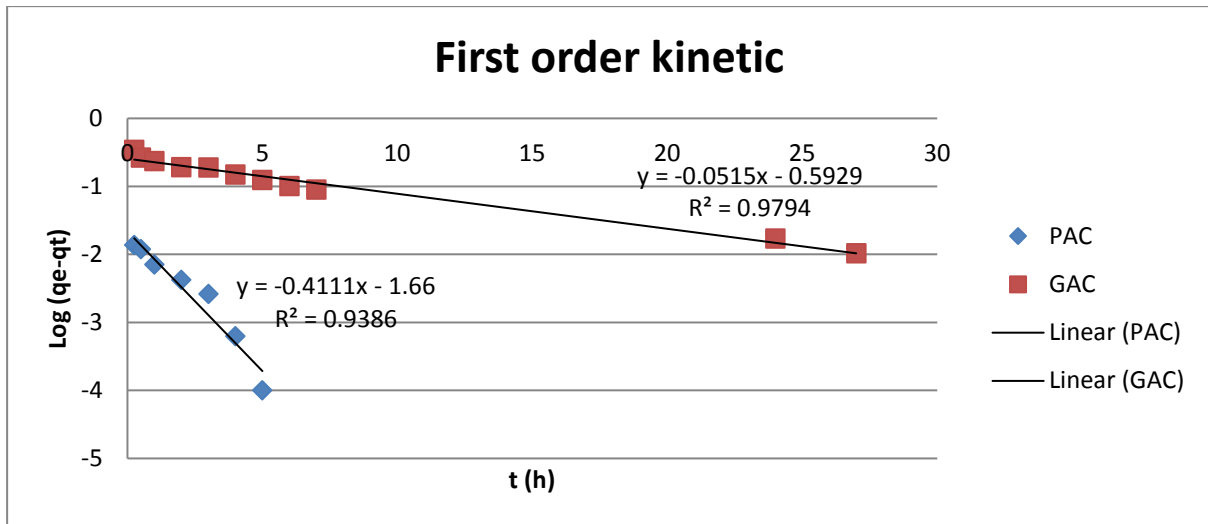


Figure 4.7: First order kinetic model for phenanthrene adsorption by PAC and GAC

Further, parameters of pseudo-second-order kinetic models were also plotted in graphs where coefficients of correlation found higher than that of first-order. In this case coefficients of correlation value for PAC was 1 and for GAC was also very close to 1 (Figure 4.8).

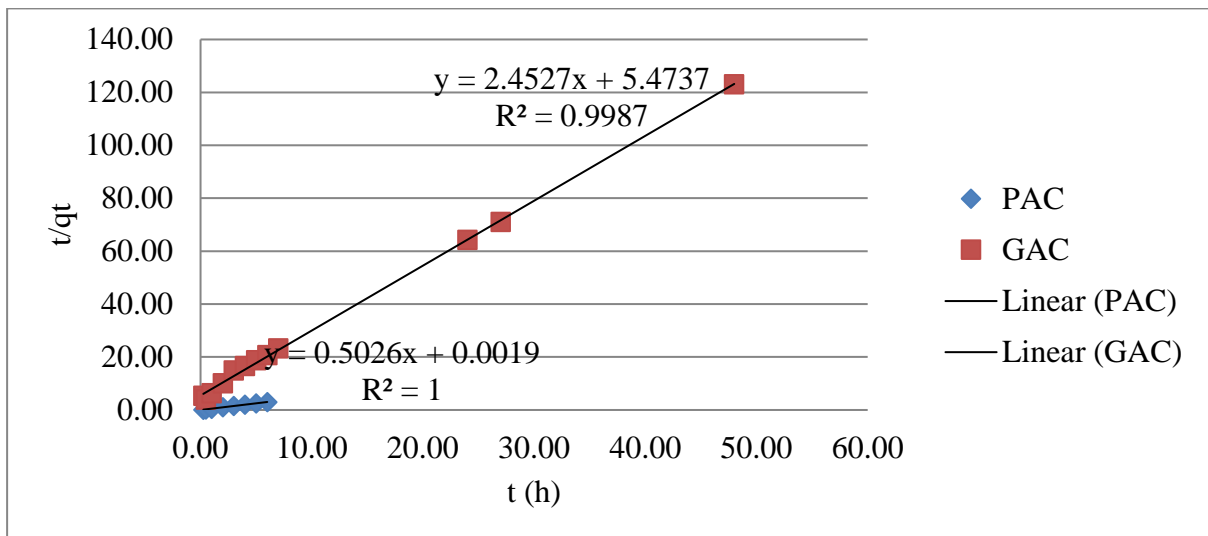


Figure 4.8: Second order kinetic model for phenanthrene adsorption by PAC and GAC

Thus the experimental data fitted with both first and second-order kinetic models, however, high correlation coefficients were obtained in second-order kinetic model when compared to first-order for both adsorbents (PAC and GAC).

Table 4.2: Pseudo-second-order and pseudo-second-order kinetic parameters for phenanthrene adsorption by PAC and GAC

PAH adsorbents	q_{exp}	Pseudo first -order model		Pseudo second- order model	
		q_e ($\mu\text{g}/\text{mg}$)	K_1 (h^{-1})	$q_e(\mu\text{g}/\text{mg})$	K_2 ($\mu\text{g}/\text{mg}/\text{h}$)
PAC	1.99	0.022	0.95	1.99	132.95
GAC	0.39	0.255	0.12	0.41	1.1

The q_e values obtained from Pseudo second-order kinetic model is more closed to q_{exp} when compare to q_e obtained from Pseudo first-order model (Table 4.2) indicating Pseudo second-order model better fits than first order model in PAH adsorption with activated carbon. According to Rad et al. (2014), the adsorption processes and equilibrium data for phenanthrene adsorption with AC was well fitted by pseudo-second-order kinetic model. Similar results for PAHs adsorption kinetic study have been also reported in other studies (Cabal et al. 2009; Awoyemi, 2011), indicating the adsorption process was driven by chemisorption process (Ho and McKay, 1998). Phenanthrene adsorption data onto NH₂-SBA-15 from wastewater was also well fitted in Pseudo second- order model (Balati et al. (2015). In agreement with the trend of adsorption capacity, phenanthrene removal rates (K_1 and K_2) of PAC found to be greater than the removal rates (K_1 and K_2) of GAC (Table 4.2).

4.3.3 Effect of mass of adsorbents on adsorption of phenanthrene

Phenanthrene removal efficiency increased with increasing mass of adsorbents. The adsorption equilibrium for PAC was obtained within 24 h and in case of GAC, adsorption equilibrium was observed within 24 h for 20 and 100 mg, however, 120 h for 200 mg. For PAC, the effect of mass could be seen only for data obtained at 2 h as other results obtained were similar (Figure 4.9). Phenanthrene removal efficiency was > 99.8% at four hours for both cases of PAC amounts and complete removal occurred within 24 h. However, the effect of

mass of GAC in phenanthrene adsorption was observed for longer period as 24 h (Figure 4.10).

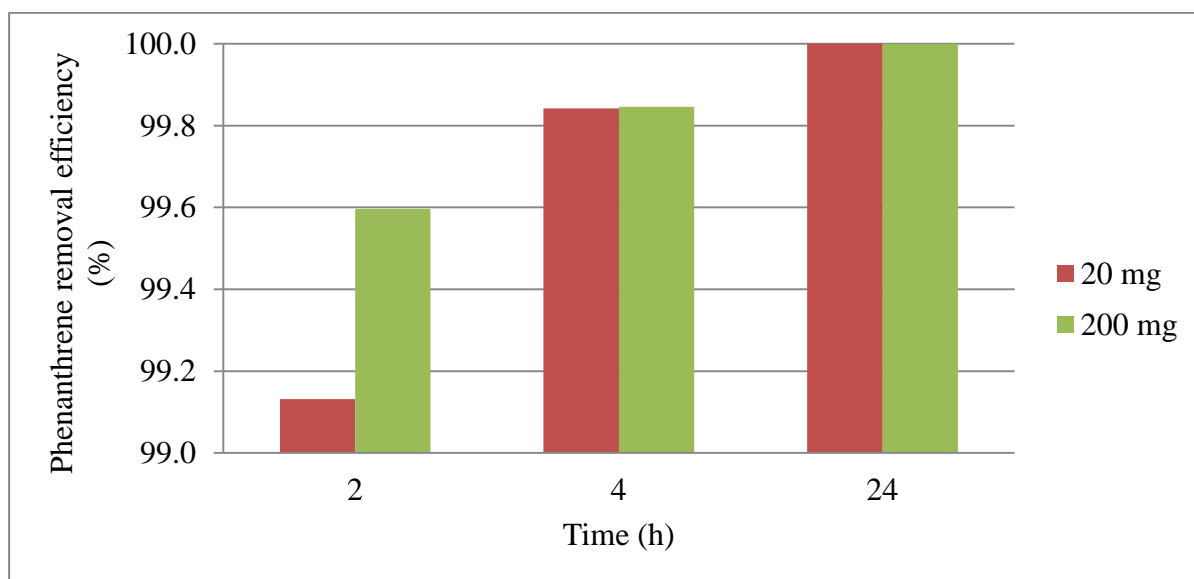


Figure 4.9: Phenanthrene removal efficiency with time for varying amount of PAC

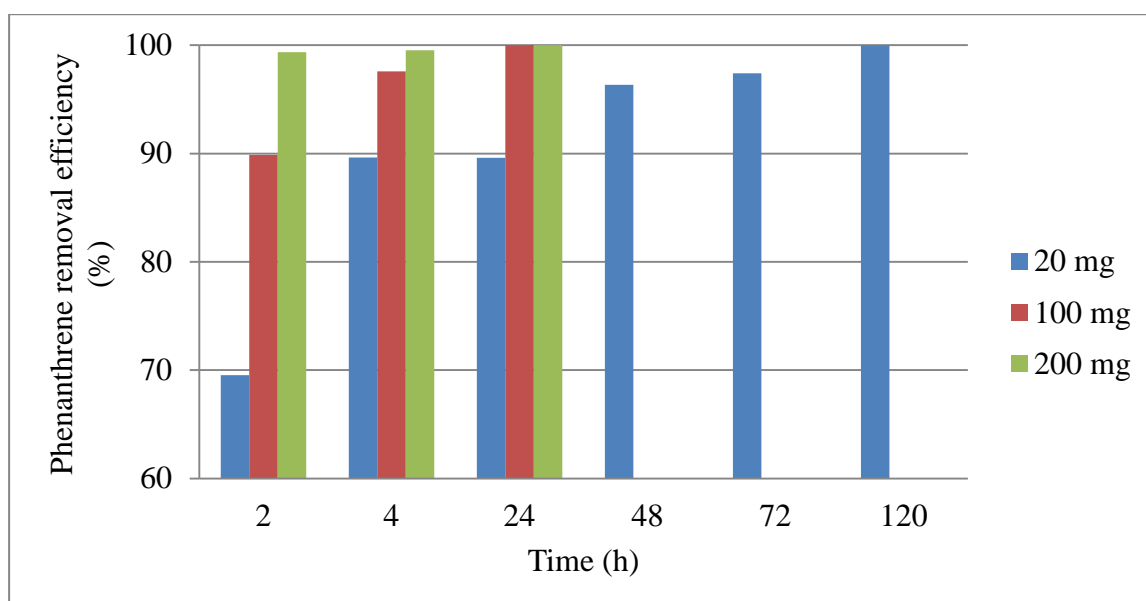


Figure 4.10: Phenanthrene removal efficiency with time with varying amount of GAC

Phenanthrene removal efficiency with GAC also enhanced with increase of mass of adsorbent similar to the case of PAC. With 20 mg GAC the all phenanthrene (initial concentration of 40 $\mu\text{g/L}$) was removed within 120 h where as complete removal of phenanthrene for same initial

concentration was observed within 24 h with 100 and 200 mg GAC. The similar results of enhancement of PAHs removal efficiency with increasing of AC concentration have been reported in other studies (Kong et al. 2011; Garg et al., 2003, Rad et al. 2014) which is due to increase in available sorption sites. Moreover, the adsorption enhancement of phenanthrene with increasing amount of AC was presented by Gupta (2015).

4.3.4 Adsorption isotherm analysis

The equilibrium of adsorption is important aspects for the evaluation of the adsorption process as a unit operation. Batch isotherm study was carried out for different concentrations (5-40 $\mu\text{g/L}$) of phenanthrene (Table A8 and Table A9 in Appendix) for constant mass of adsorbents.

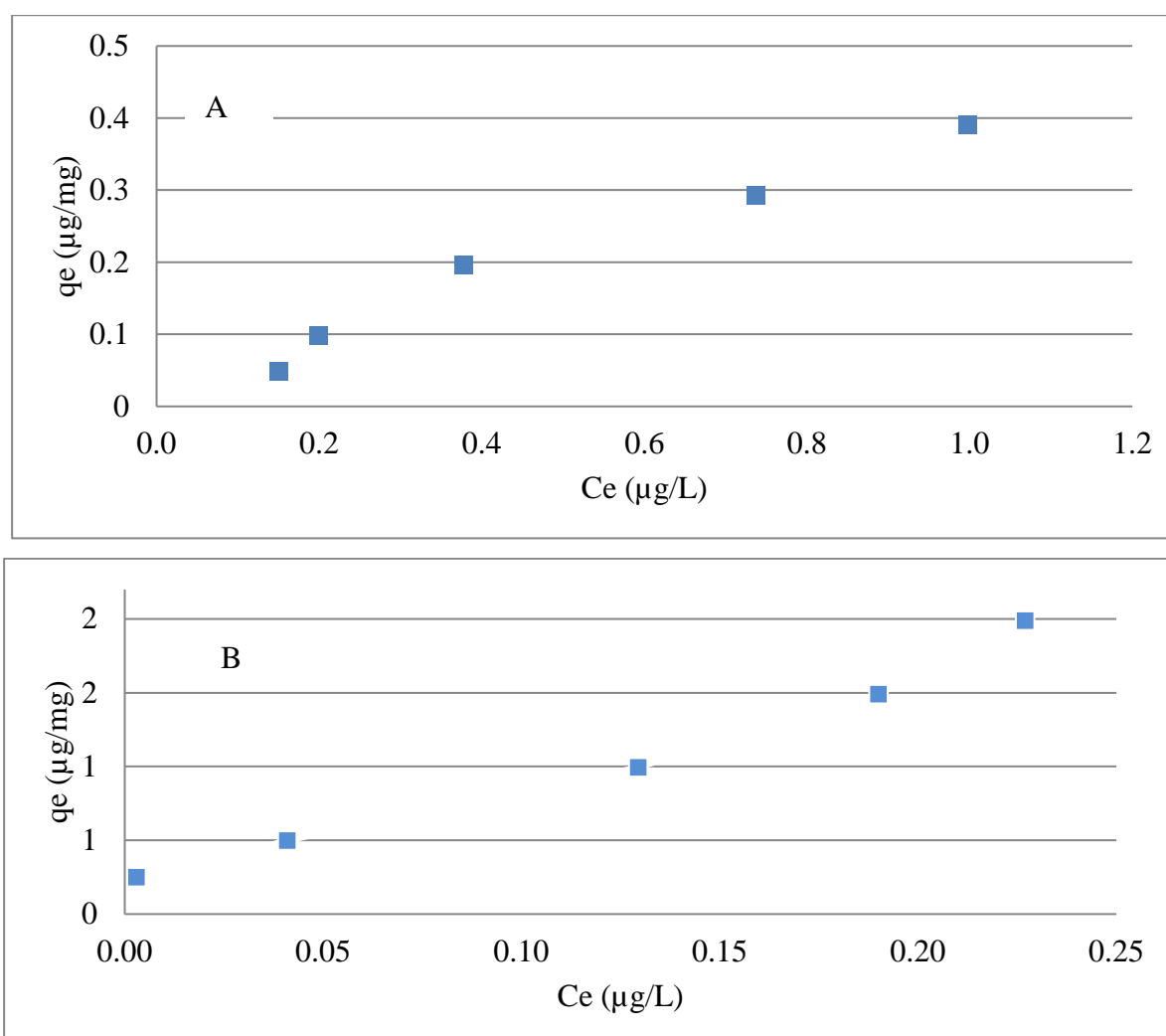


Figure 4.11: Adsorption isotherm for phenanthrene adsorption: with PAC (A), with GAC (B)

Figure 4.11(A) and Figure 4.11(B) depict the adsorption isotherm (q_e versus C_e) where adsorption capacity increased with increasing equilibrium of phenanthrene concentrations. This is in agreement with the adsorption of phenanthrene with AC (Rad et al. 2014) and anthracene (three ring structure PAH) with activated carbon (Saad et al., 2014). Generally isotherm study is analysed by fitting the adsorption data in different types of isotherm models. Common models for PAHs adsorption with activated carbon (Langmuir and Freundlich) have been considered in present study.

4.3.5 Adsorption isotherm modelling

In order to obtain the information about mechanism of the adsorption process, the experimental data of phenanthrene adsorption on PAC and GAC were fitted in Langmuir and Freundlich isotherm models. The graphs developed for Langmuir and Freundlich model are presented in Figure 4.12 and Figure 4.13 respectively.

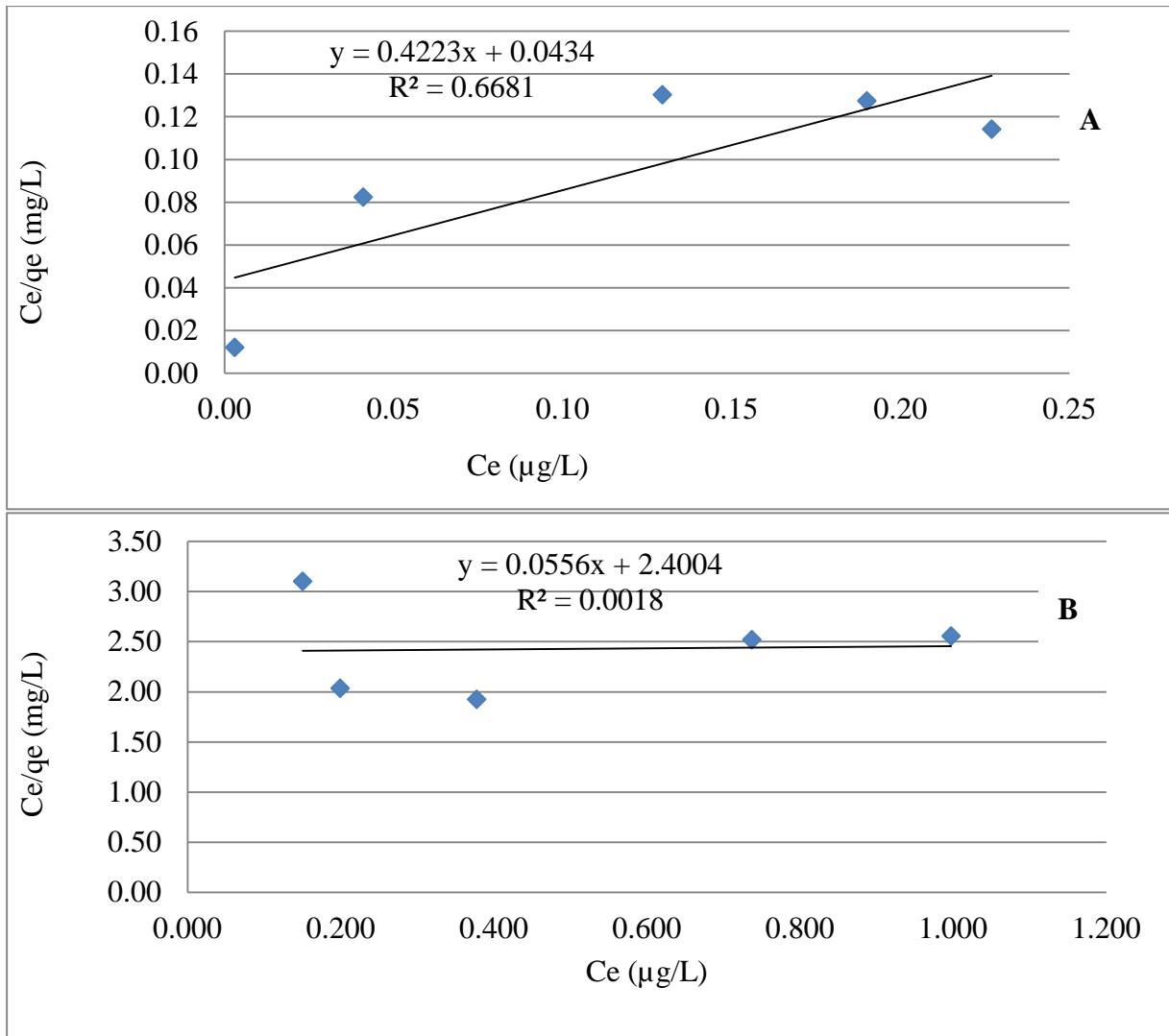


Figure 4.12: Langmuir isotherm analysis for phenanthrene adsorption with PAC (A) and with GAC (B)

The adsorption data were not fitted in Langmuir isotherm model for both PAC and GAC (Figure 4.12) where as Freundlich model exhibited a better fit with higher correlation coefficient values (Figure 4.13) describing the surface heterogeneity with non-uniform distribution of adsorption and affinities over the sorbent surface (Hameed et al. 2007).

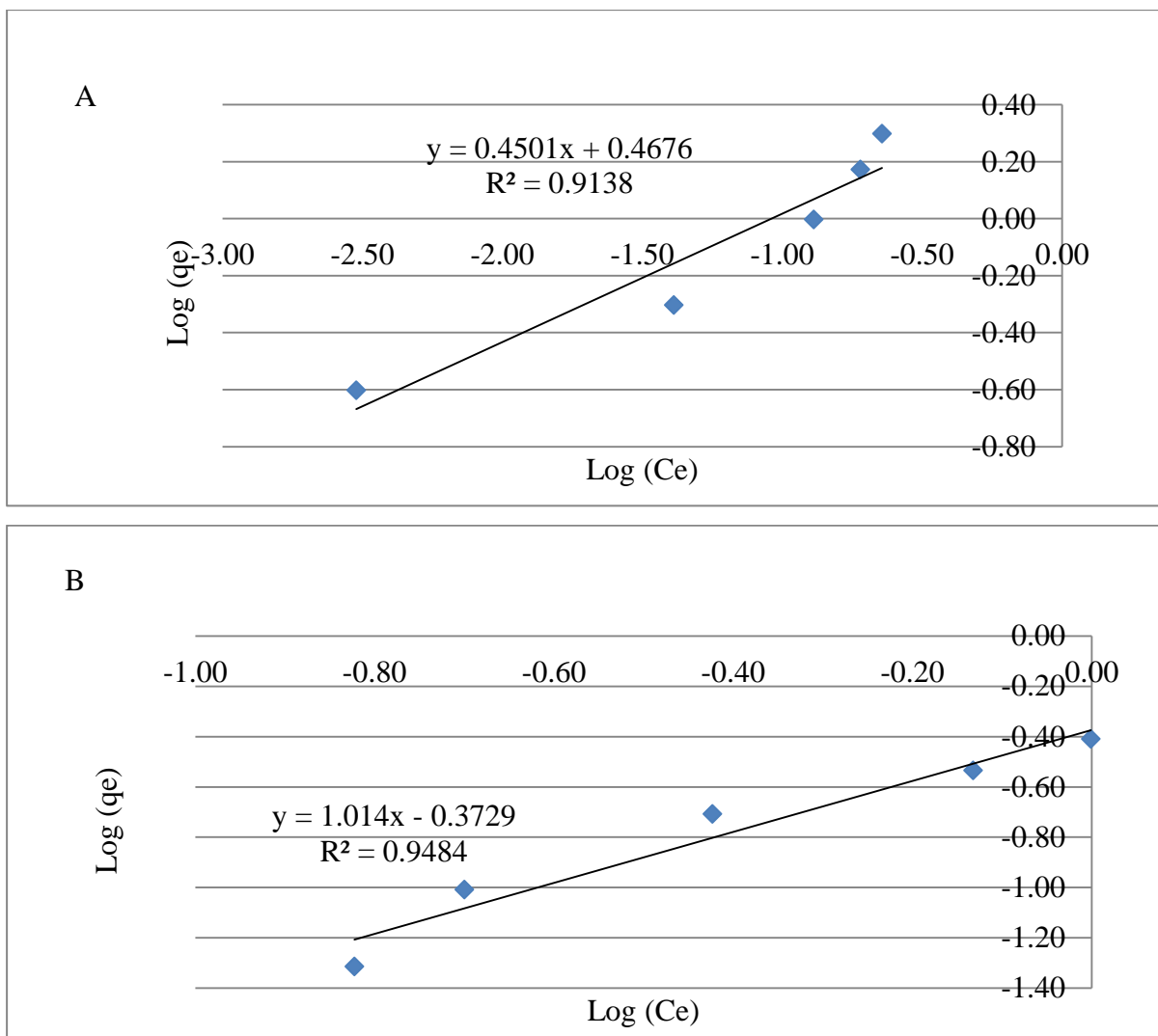


Figure 4.13: Freundlich isotherm analysis for phenanthrene adsorption with PAC (A) and GAC (B)

Table 4.3: Langmuir and Freundlich parameters for phenanthrene adsorption with PAC and GAC at equilibrium

Adsorbents	Langmuir isotherm model			Freundlich isotherm model	
	q_{\max} ($\mu\text{g}/\text{mg}$)	K_L ($\text{L}/\mu\text{g}$)	R_L	K_f ($\mu\text{g}/\text{mg}$)/($\mu\text{g}/\text{L}$) ⁿ	n
PAC	2.37	9.722	0.042	2.93	2.22
GAC	17.86	0.023	0.706	0.42	0.99

The maximum capacity, q_{\max} , defines the total capacity of the phenanthrene on adsorbents.

The greater q_{\max} value would be expected for PAC, if the adsorption data were well fitted with Langmuir isotherm. This is because of higher specific surface area of PAC when compared to specific surface area of GAC. The adsorption data obtained from laboratory experiments were not fitted in Langmuir isotherm model and higher q_{\max} (17.86 $\mu\text{g}/\text{mg}$) was obtained for GAC in comparison to q_{\max} (2.37 $\mu\text{g}/\text{mg}$) of PAC. However, from the calculation of R_L value, the adsorption process was found to be favourable for both types of adsorbents (Table 4.3).

K_f and n values showed the tendency of phenanthrene uptake was higher for GAC when compared to PAC. The K_f value was obtained as 2.93 for PAC and 0.42 for GAC and the K_f value for anthracene (three rings structure PAH as phenanthrene) adsorption with AC was found in similar range as 1.37 (Saad et al., 2014). The values of Freundlich nonlinearity coefficient n were also obtained near to unity or above indicating favourable sorption of phenanthrene on ACs. Similarly, n values for PAH (pyrene) adsorption with activated carbon was reported in the range of 0.9 to 1.05 in a study by Hale et al. (2011). There are many studies which fitted PAHs adsorption data with Freundlich isotherm model (Valderrama et al. 2008, Amstaetter et al. 2012, Oleszczuk et al. 2012, Hale et al. 2011, Rad et al. 2014).

The data and results obtained from detail study of PAH adsorption characteristics of activated carbon provided opportunity to select effective PAH adsorption media to be used in constructed wetlands to remove stormwater PAHs.

4.4 Conclusion

The equilibrium condition was reached within 5 h for PAC and within 48 h for GAC. Second-order kinetic was fitted well when compared to first-order kinetic with correlation coefficient value of 1 for both adsorbents. Furthermore, effect of mass of adsorbents on phenanthrene was analysed and higher removal efficiency of phenanthrene was observed at higher concentration of adsorbents for both types of adsorbents. Freundlich isotherm model was well fitted for PAC and GAC when compared to Langmuir isotherm model with higher correlation coefficients as 0.91 and 0.95 for PAC and GAC respectively. The maximum adsorption capacity of GAC (17.86 μg) was observed greater than maximum adsorption capacity of PAC (2.37 $\mu\text{g}/\text{mg}$) from Langmuir isotherm model which might be due to obtaining less value of correlation

coefficient while fitting adsorption data into Langmuir isotherm model. However, from the calculation of R_L value, the adsorption process was found to be favourable for both types of adsorbents.

To completely eliminate the urban stormwater PAHs, it is important to remediate PAHs adsorbed into the soils and sediments of bank of water bodies. PAHs extraction with organic solvents is one of effective methods to remediate PAHs from solid media. PAHs solubilisation is main mechanism in PAHs extraction. Therefore, PAH solubilisation with various organic solvents has been considered and presented in chapter 5.

Chapter 5

Solubility of PAHs by using organic solvents

5.1 Introduction

The PAHs deposited in urban surfaces are transferred into the water sources with stormwater runoff and pollute the nearby water sources as well as soil and sediment of bank of water bodies (Bathi et al. 2012). Therefore, PAHs remediation from soil and sediment become of particular concern. The PAHs from contaminated soil and sediment could be removed by extraction technique by using various types of solvents (Haleyur et al. 2016; Khanjari et al. 2016). Among the PAHs extraction solvents, organic solvents were the earliest reagents used in laboratory-scale as well as in field scale studies (Lau et al., 2014). Solubility of PAHs in the organic solvents is the main factor in the PAHs remediation by extraction technique, (Lau et al., 2014). Thus solubility data of PAHs in organic solvents is essential to determine their potential applications in remediation of contaminated soil and sediment.

Numerous studies (Haleyur et al. 2016; Chen et al. 2015; Gong et al. 2007; Viglianti et al. 2006) have been carried out on PAHs remediation from contaminated soil by using organic solvents such as ethanol, methanol, dichloromethane, pentanol, acetone, ethyle acetate, propane, butane, n-hexane, toluene, benzene and dimethyl ether. These studies have only focused on PAHs extraction process and PAHs extraction capacity of organic solvents. Only little has been done on PAHs solubilisation analysis with organic solvents. Thus the main aim of this present study is to evaluate solubilisation capacity of phenanthrene, one of the most commonly available PAHs in the environment (Pazos et al., 2010) with various types of organic solvents as acetone, hexane and methanol. Solubilisation of PAHs with single and mixed solvent systems are considered in this study along with effect of initial concentration of PAH and mixing time in phenanthrene solubilisation with organic solvents.

5.2 Material and Methods

Solid phenanthrene ($\geq 99.5\%$ pure), acetone ($\geq 99.9\%$ pure) and hexane (95% pure) were purchased from Sigma Aldrich. Liquid phenanthrene (99% pure) was obtained from Supelco and methanol ($\geq 99.9\%$ pure) was obtained from Fluka. Digital weighing machine from

Sartorius, Innova 2100 platform shaker from Brunswick Scientific and GC-FID from Thermo Scientific were used for solubility experiments and PAH analysis.

5.2.1 Phenanthrene solubilisation with organic solvents in single system

Three types of organic solvents as acetone, hexane and methanol were chosen to perform laboratory experiments on phenanthrene solubility. The reason of this experiment is to evaluate performance of various organic solvents in PAH solubilisation. 1, 1.5 and 2 mg of solid phenanthrene was mixed with 40 ml of each organic solvent in separate conical flasks. To eliminate the error during transferring solid phenanthrene to prepare PAH solution, phenanthrene was measured in conical flask after setting zero to weighing machine with empty conical flask. Duplicate samples were prepared for further verification of results for each type of sample. The conical flasks containing the mixture were sealed with parafilm in order to prevent solvents evaporation and then placed on platform shaker to mix at speed of 100 rpm for 24 h. The sample of batch solubilisation test is presented in Figure 5.1. The supernatant from each sample was collected in 2ml glass vials and analysed with GC-FID.



Figure 5.1: Batch experimental setup for PAH solubilisation with organic solvent

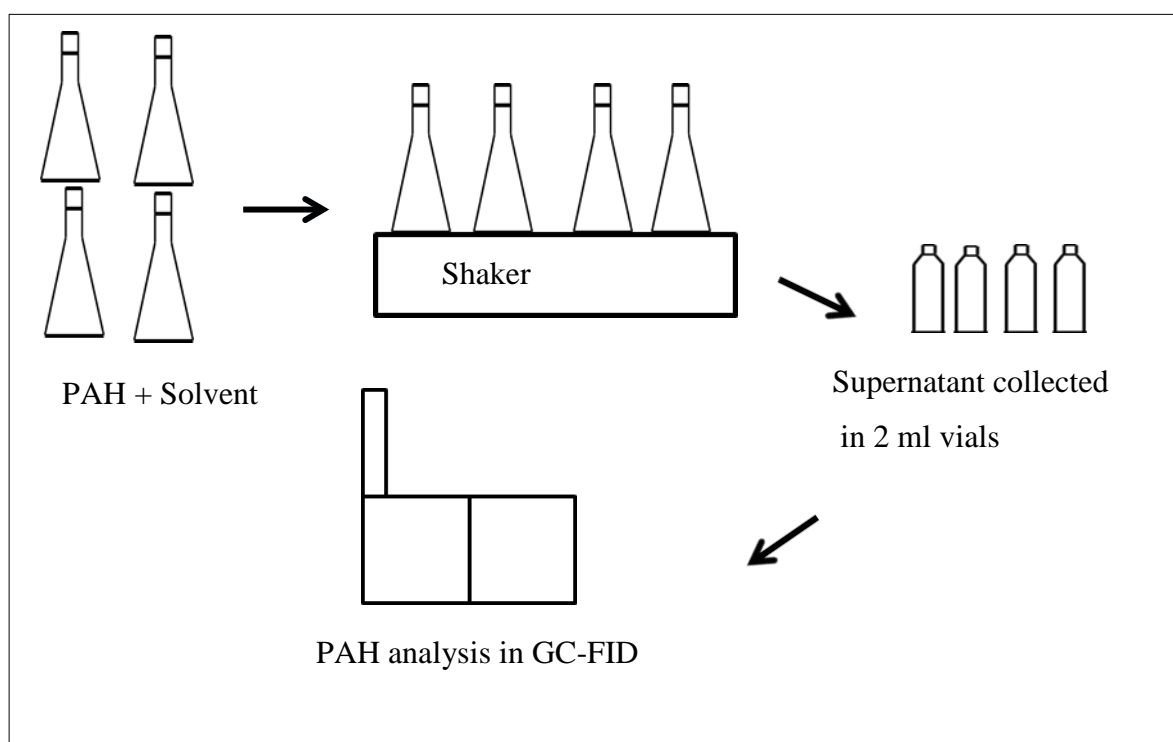


Figure 5.2: Schematic diagram for PAH solubilisation test

5.2.2 Phenanthrene solubilisation with mixed organic solvents

Phenanthrene solubilisation test was performed with different proportions of acetone and hexane as 1:1, 1:3 and 3:1. Different proportions were tested to evaluate the best proportion of organic solvents in phenanthrene solubility by comparing the outcomes of experimental results. The batch solubility tests were carried out with same amount of phenanthrene as described in section 5.2.1 with total solution volume of 40 ml in each flask. Phenanthrene solubility was analysed after 24 h shaking at 100 rpm. The purpose of this set of experiment is to compare PAH solubilisation capacity of different proportion of mixed organic solvents. Furthermore, from this set of experiment we can compare PAH solubilisation capacity of single and mixed systems of organic solvents.

5.2.3 Effect of mixing time in phenanthrene solubilisation with organic solvents

Methanol was considered to study the mixing effect in phenanthrene solubility. The method for solubility batch test was similar to method described in above sections (5.2.1 and 5.2.2). The samples (supernatant from each flask) were collected at 24h, 72 h and 120 h to see the effect of mixing time in phenanthrene solubility with methanol.

5.2.4 Method development for PAH analysis

5.2.4.1 GC-FID set up

The model PAH, phenanthrene was analyzed using gas chromatography Trace 1300 GC from Thermo Scientific equipped with a TG-5 MS 30 m × 0.25 mm × 0.25 μm capillary column. The carrier gas was high-purity helium (He). The injection port temperature was maintained at 300 °C. The GC temperature program started at 90 °C for 1 min and then increased at a rate of 25 °C per minute to 215 °C and held for 0.5 minute. The temperature was then increased at a rate of 15 °C per minute to 280 °C. Further, temperature was increased to 310 °C with a rate of 4 °C per minute and held at 310 °C for 20 min. The injection mode was splitless. Phenanthrene was detected by flame ionization detector (FID) system. The FID temperature was maintained as 300 °C.

5.2.4.2 Development of standard calibration curve

The calibration curve was established by running standard phenanthrene samples with concentrations range from 31.25 to 1000 μg/L. The samples were diluted serially by half from 1000 μg/L to 31.25 μg/L and analysed with GC-FID. The standard phenanthrene solutions were prepared in acetone. The data observed for phenanthrene concentration 31.25 μg/L was not applicable due to detection limit of GE-FID. The results observed for other 5 concentrations of standard phenanthrene have been presented in Table B1 in Appendix.

The retention times for phenanthrene peak were only varied from 8.14 to 8.16 minutes indicating a good accuracy of GC-FID in phenanthrene detection. Some data for phenanthrene concentrations were increased and some data were decreased from targeted concentrations (Table B1 in Appendix). Calibration curve has been developed based on standard phenanthrene concentrations and peak areas (Figure 5.3).

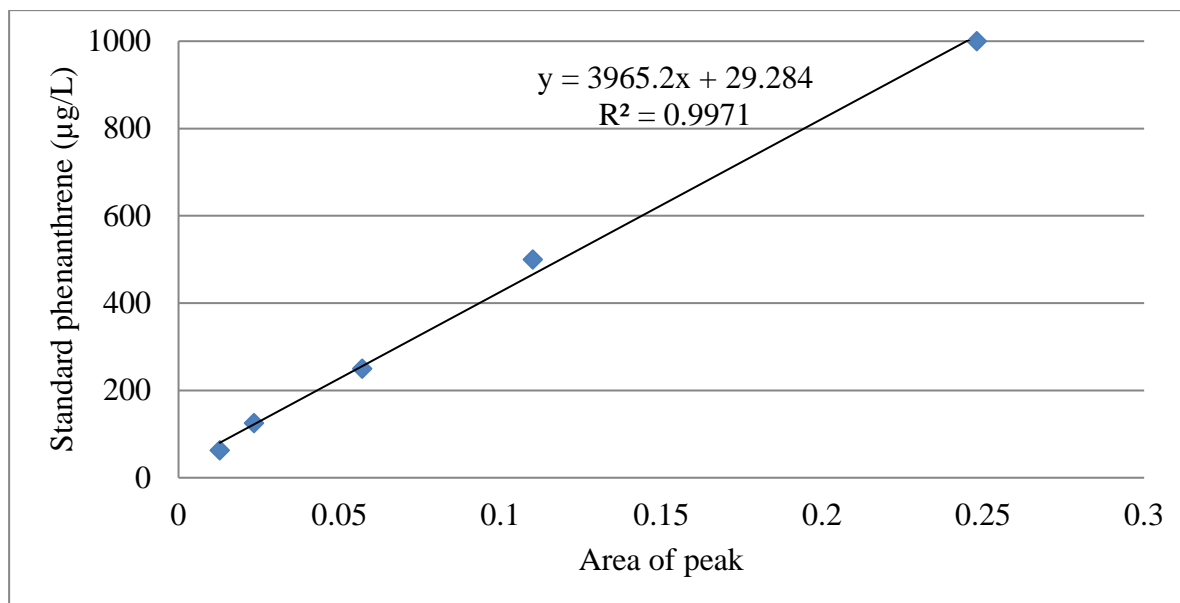


Figure 5.3: Standard calibration curve for standard phenanthrene analysis with GC-FID

When observed data were analysed, high value (0.997) of correlation coefficient was observed with linear equation. All the other samples prepared from laboratory experiments were measured based on this standard calibration graph.

5.3 Results and discussions

5.3.1 Phenanthrene solubilisation with organic solvents in single system

From the solubility result obtained from laboratory experiments, methanol was found to be best solvent in phenanthrene solubility for all varying concentration of phenanthrene (Figure 5.3). For instant, initial phenanthrene 25 mg/L, the solubility of phenanthrene observed was 501.01 µg/L with methanol whereas 178.24 µg/L with acetone and 197.57 µg/L with hexane. Similarly, methanol was found the best solvent (among acetone, cyclohexane, 2- propanol, methanol, acetonitrile, dichloromethane and hexane) in phenanthrene solubilisation and extraction from contaminated soil (Oluseyi 2011).

Greater amount of phenanthrene solubility was found with hexane when compared to acetone for initial phenanthrene 25 mg/L and 50 mg/L (Figure 5.4). However, for initial concentration 37.5 mg/L the trend was opposite between acetone and hexane. Moreover, as expected, the phenanthrene solubility was increased with increased of initial phenanthrene amounts for all cases except 37.5 mg/L phenanthrene with acetone. Thus, maximum solubility of

phenanthrene was obtained for initial phenanthrene concentration 50 mg/L. For initial phenanthrene concentration 50 mg/L, the phenanthrene solubilisation capacity of hexane was 330.33 μ g/L and phenanthrene solubilisation capacity of methanol was 901.28 μ g/L.

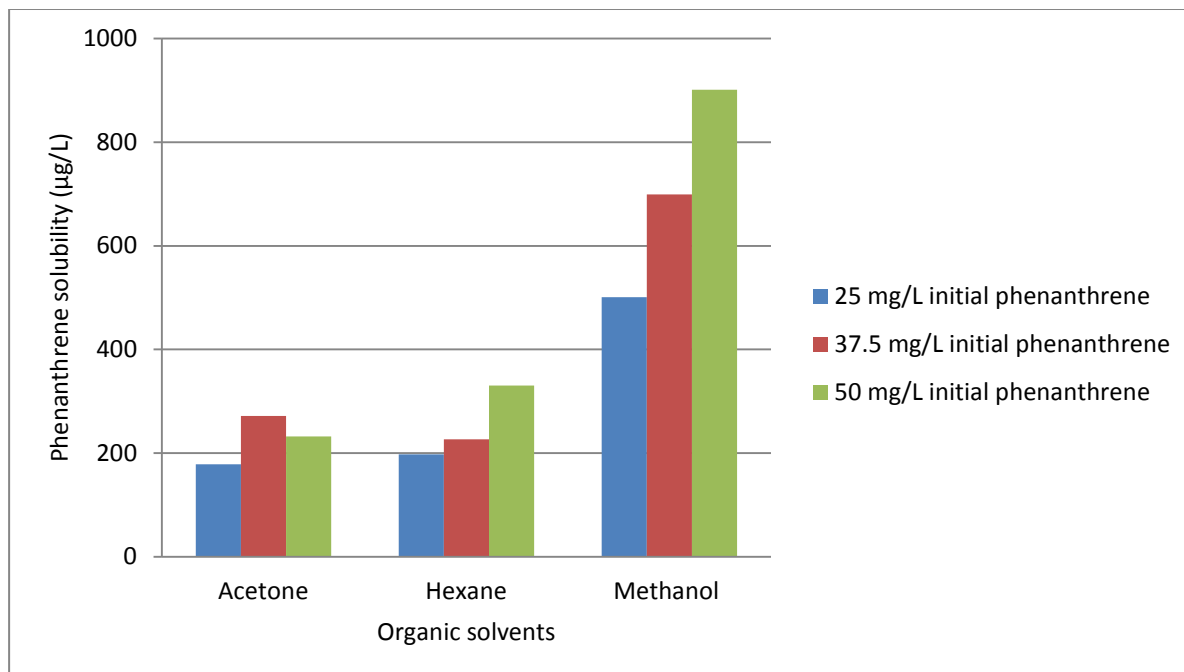


Figure 5.4: Phenanthrene solubility with different types of organic solvents

From the trend of graph, we could see that there might be some error at phenanthrene solubility with acetone for initial phenanthrene 37.5 mg/L. The phenanthrene solubility result at initial concentration 37.5 mg/L was observed higher than that with initial phenanthrene 50 mg/L, however, solubility of phenanthrene was increased with increase of initial phenanthrene concentration in all other cases. The possible error for this result might be due to different crystal size (while weighing) of phenanthrene placed in conical flasks.

5.3.2 Phenanthrene solubilisation with mixed organic solvents

The graphical presentation for analysed data (Table B3 in Appendix B) is displayed in Figure 5.5.

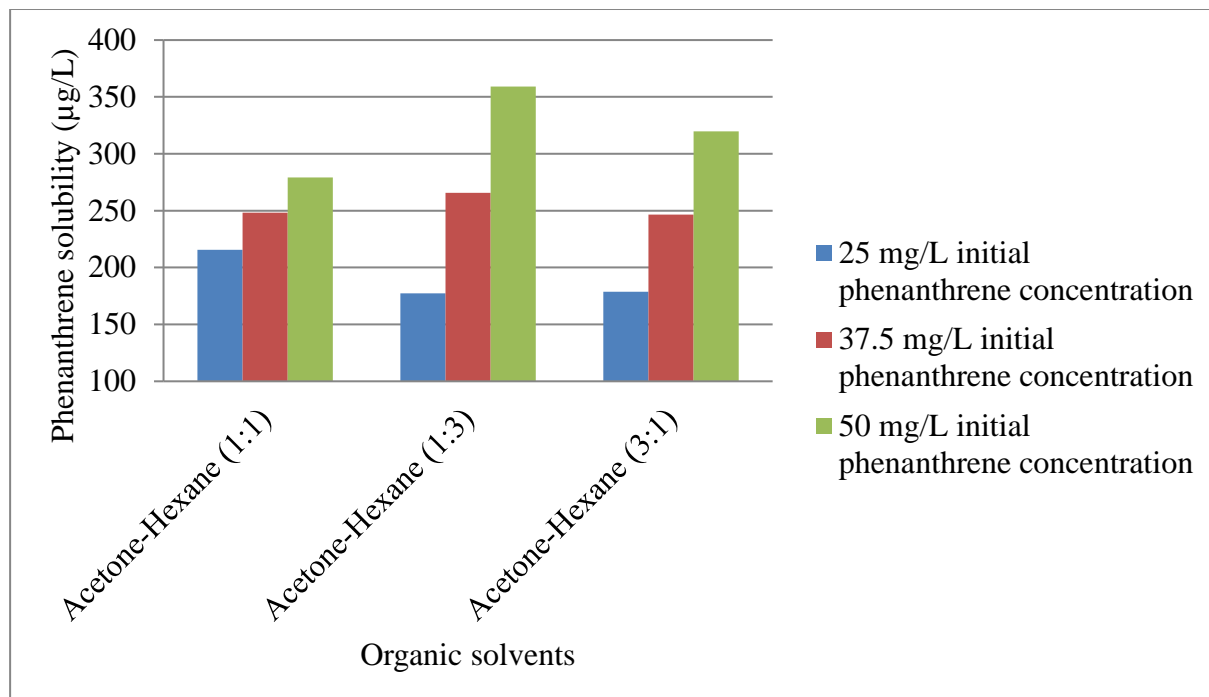


Figure 5.5: phenanthrene solubility with mixed organic solvents

Phenanthrene solubilisation capacities of mixed solvents have been found in different orders for different amounts of initial phenanthrene used (Figure 5.5). For initial phenanthrene 25 mg/L, the order of acetone to hexane ratio was found as 1:1 > 3:1 > 1:3, for initial phenanthrene 37.5 mg/L, the solvent proportion order found was 1:3 > 1:1 > 3:1 and for initial phenanthrene 50 mg/L, the corresponding solvent proportion order was obtained as 1:3 > 3:1 > 1:1 (Figure 5.5).

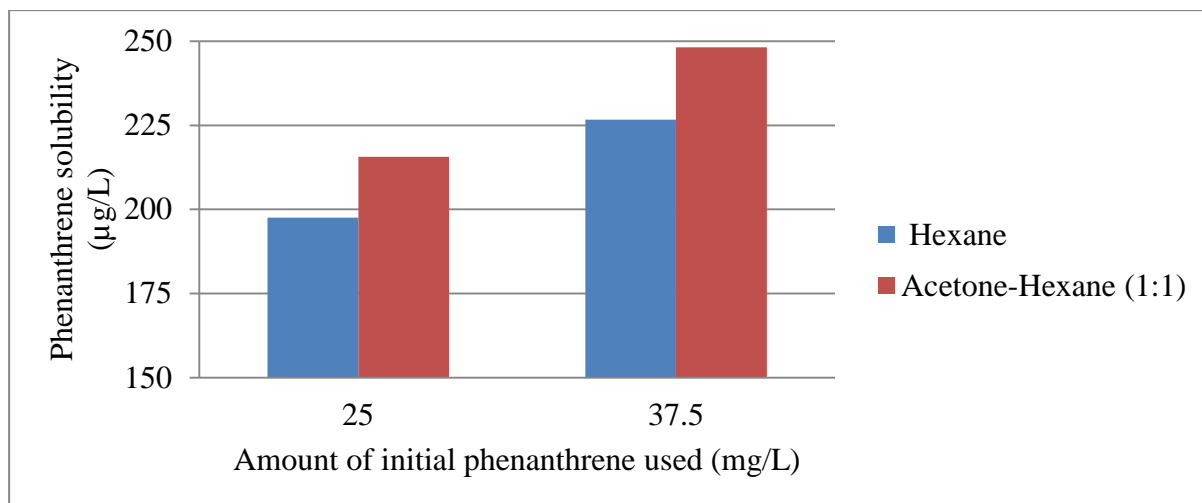


Figure 5.6: Comparison of phenanthrene solubility with Acetone-Hexane (1:1) and Hexane

Phenanthrene solubility with acetone to hexane ratio 1:1 was greater than phenanthrene solubility with only hexane for initial phenanthrene used 25 mg/L and 37.5 mg/L (Figure 5.6). Thus mixed solvents system was found effective in PAHs solubilisation when compared to single solvent revealing mixed solvents are better in PAHs extraction and remediation. Similar result was obtained in a study by Haleyur et al. (2016) where acetone: hexane (1:1) mixed system was found effective than only hexane and dichloromethane:acetone (1:1) mixed system was found more effective than only dichloromethane in extraction of 16 USEPA PAHs. Moreover, the extraction of 16 USEPA PAHs was greater with mixed organic solvents acetone:cyclohexane (1:1) when compare to extraction with only cyclohexane (Chen et al. 2015). A recent study by Hollender et al. (2018) also reported that acetone: toluene (1:1) mixed solvents system was effective in PAHs extraction compare to single solvent. However, a detail further study is required to evaluate the optimum ratio of solvents for solubilising of PAHs as there was not observed consistent order of phenanthrene solubilisation for different proportions of organic solvents considered in the laboratory experiment.

Furthermore, as expected, the phenanthrene solubility was increased with amount of initial phenanthrene used for all proportions of acetone and hexane tested in the laboratory experiments with observing highest solubility for initial phenanthrene 50 mg/L and lowest solubility for initial phenanthrene 25 mg/L (Figure 5.5). The enhancement in phenanthrene solubility with increasing amount of initial phenanthrene could be seen more significant in

case of acetone to hexane ratio 1:3 and 3:1 when compared to acetone to hexane ratio 1:1 (Figure 5.5).

5.3.3 Effect of mixing time in phenanthrene solubilisation with methanol

The phenanthrene solubility was observed increasing with mixing time of phenanthrene and methanol with the order of 120 h > 72 h > 24 h (Figure 5.7). For instant, for 25 mg/L initial phenanthrene, the solubility found was 20278.34 $\mu\text{g/L}$ at 120 h, 18621.13 $\mu\text{g/L}$ at 72 h and 501.01 $\mu\text{g/L}$ at 24 h (Figure 5.7)

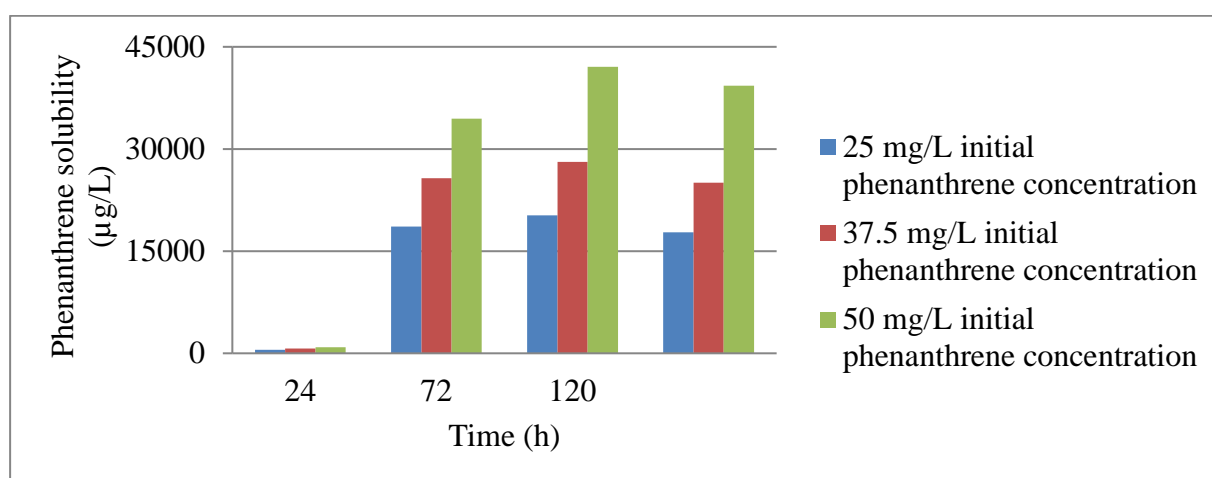


Figure 5.7: Phenanthrene solubilisation with methanol at different interval of time for various initial phenanthrene concentrations

Moreover, phenanthrene solubilisation with methanol was increased with higher concentration of initial phenanthrene concentration. For example, the solubility of phenanthrene at 120 h was found 42080.56 $\mu\text{g/L}$ for initial phenanthrene 50 mg/L; 28089.14 $\mu\text{g/L}$ for initial phenanthrene 37.5 mg/L and 20278.34 $\mu\text{g/L}$ for initial phenanthrene 25 mg/L (Figure 5.7).

5.4 Conclusions

From the analysis of experimental results, organic solvents are found to be effective in phenanthrene solubility which is the main mechanism of PAHs extraction from contaminated soil and sediment. In single solvent system, methanol was observed as most effective to solubilise phenanthrene. However, there was not observed consistent order of phenanthrene solubilisation with different proportion of organic solvents in mixed solvents systems. Furthermore, phenanthrene solubility was found proportional to the amount of phenanthrene

used initially for all different types of tests performed in this study except one outlier. In addition to this, there is positive effect of duration of mixing in phenanthrene solubility with result up to 84.16% solubility with methanol at 120 h. A detail further study is necessary to optimize the proportion of mixed solvent systems in enhancement of PAHs solubilisation.

Furthermore, PAHs solubility could be enhanced by using surface active compound called surfactants. Surfactants enhanced PAHs remediation is reviewed in detail in chapter 6.

Chapter 6

A review of Surfactant enhanced remediation of polycyclic aromatic hydrocarbons (PAHs)

Note: Content of this chapter has been published as a journal paper

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6.1 Introduction

Polycyclic aromatic hydrocarbons (PAHs) are persistent organic compounds that are ubiquitous in the environment. They occur in the environment by natural and anthropogenic means, such as the pyrolysis of organic matter, fossil fuel use and industrial activities (Gallego et al. 2008; Manoli and Samara 1999; Ravindra et al. 2008). PAHs are toxic, mutagenic and carcinogenic organic compounds, and their toxicity increases with increases in their molecular weight (Liu et al. 2016).

Given the toxic, mutagenic and carcinogenic properties of PAHs, there has been significant interest in developing various methods to remove them from contaminated soils, sediments and waters, such as physical, chemical, thermal or biological remediation, surfactant-enhanced remediation (SER), phytoremediation and hybrid technology (e.g. constructed wetland) (Zhou et al. 2013; Wang et al. 2014; Li, Wong, et al. 2015; Sun, Liu, et al. 2014; Peng et al. 2014; Li et al. 2014; Hu et al. 2014; Yi et al. 2016; Xu et al. 2016; Al-Sbani et al. 2016). Among these methods, biological treatment is an environmentally friendly and economical technique (Bisht et al. 2015), which uses the metabolic processes of naturally occurring bacteria, fungi and algae to degrade PAHs (Mesbaiah et al. 2014). Owing to the benefits of the biological process over other methods, extensive research has recently been conducted (Li, Wong, et al. 2015;

Sun, Ye, et al. 2014; Jiao et al. 2014; Tejeda-Agredano et al. 2013; Abd-Elsalam et al. 2009) employing various microbial species that utilise PAHs as an energy source.

However, the bioavailability of PAHs is often limited by their low solubility and strong sorption to the adsorbents due to their complex chemical structures (Seo and Bishop 2007; Alcantara et al. 2009). The solubility of PAHs decreases linearly with the increase of molecular mass (Heitkamp and Cerniglia 1989). Accordingly, the biodegradability of PAHs decreases with their increased molecular mass, demonstrating that the molecular weight of PAHs influences their biological treatability (Wammer and Peters 2005).

The solubility and biodegradability of PAHs can be enhanced using surfactants, or surface active compounds. Surfactants comprise both hydrophobic and hydrophilic moieties and can accumulate along air-liquid and liquid-liquid interfaces. Surfactants reduce both surface and interfacial tension and at the same time enhance the mixing capacity. Surfactant micelles have a hydrophobic core, which helps to accumulate PAHs and increase the aqueous solubility (Li and Chen 2009). Therefore, SER is becoming a promising technique in removing PAHs from various media (e.g. soil and aqueous) and numerous studies have been conducted (Bezza and Nkhalambayausi-Chirwa 2015; Yu et al. 2014; Swaathy et al. 2014; Ni et al. 2014; Shi et al. 2015; Liang et al. 2016; Bustamante et al. 2012; Jia 2013; Yang et al. 2015; Wei et al. 2015; Pan et al. 2016; Long et al. 2016; Ghosh and Mukherji 2016; Singleton et al. 2016; Cheema et al. 2016). These studies have largely focused on the use of different types of surfactants, their combination, factors affecting the SER process, and the optimum conditions required to remove PAHs from different media. It is essential to summarise their findings to determine their practical implications and to direct further research into the removal of PAHs.

Several reviews have already highlighted different aspects of PAH removal techniques, such as comparisons of different types of surfactants in the biodegradation of PAHs (Makkar and Rocken, 2003), various PAH removal methods from contaminated soil (Gan et al. 2009), different extraction techniques for washing PAH from soil (Lau et al. 2014), remediation of soil contamination using surfactants (Mao et al. 2015), the sorption method for PAH treatment (Lamichhane et al. 2016), constraints in removing PAHs, future directions for the treatment process (Kuppusamy et al. 2017) and bioremediation of PAHs and heavy metals (Liu et al. 2017). However, there is limited information about the SER of PAHs in these reviews.

Therefore, the main objective of this review is to fill this knowledge gap by summarising the literature on different aspects of the SER of PAHs. This review is organised in the following order: a) types of surfactants, b) the synergistic effect of mixed micelles on PAH removal, c) the impact of surfactants on the PAH biodegradation process, d) factors affecting the SER of PAHs, and e) the mechanisms of surfactant-enhanced solubilisation of PAHs. This review paper would assist in optimising and designing the SER process of PAHs from various media.

6.2 Types of surfactants and their effect on PAH biodegradation

Surfactants are categorised as chemical (synthetic) or natural (bio) based on the sources, and they can also be categorised as nonionic, cationic, anionic or zwitterionic based on the ionic charge of the hydrophilic group (Table 6.1) (Paria 2008). Those within two or more hydrophilic or hydrophobic groups are called gemini surfactants.

Table 6.1: Types and physicochemical properties of surfactants

Surfactant	Name/Components	Chemical formula	Molecular weight (gm/mole)	Density (g/ml)	CMC (mM)	Charge types	References
Tween20	Poly oxyethylene sorbitan monolaurate	$C_{58}H_{114}O_{26}$	1227.54	1.1	0.12	Nonionic	Rodrigues et al. (2013)
Tween80	Polyoxyethylene sorbitan monooleate	$C_{17}H_{35}COOS_6(OCH_2CH_2)_{20}OH$	1309	1.075	0.027		Zhao et al. (2005)
Triton X-100 (TX100)	P-tertiary octyl phenoxy polyethyl alcohol	$C_8H_{17}C_6H_4O(OCH_2CH_2)_{9.5}OH$	625	1.07	0.19		Zhao et al. (2005)
Triton X-305 (TX305)	Octylphenol Ethoxylate	$C_8H_{17}C_6H_4O(CH_2CH_2O)_{30}H,$	1526	1.092	0.7		Zhu and Feng, (2003)
TritonX- 405 (TX405)	Polyoxy ethylene (40) isoctyl phenyl ether	$C_8H_{17}C_6H_4O(OCH_2CH_2)_{40}H$	1966	1.096	0.904		Zhou and Zhu, (2004)
Triton X-114 (TX114)	Polyethylene glycol tert-octyl phenyl ether	$(C_2H_4O)_{7.5} C_{14}H_{22}O$	537	1.058	0.21	Nonionic	Egan (1976)

Brij35	Poly(oxyethylene) 23 dodecyl ether	$C_{12}H_{25}(OC_2CH_2)_{23}OH$	1200	1.05	0.055		Zhao et al. (2005)
Brij56	Polyoxyethylene (10) cetyl ether	$C_{16}H_{33}(-OCH_2-CH_2)_{10}OH$	682	0.977	0.036		Masrat et al. (2013)
Brij58	Polyoxyethylene (20) cetyl ether	$C_{16}H_{33}(OCH_2CH_2)_{20}OH$	1123.5	1	0.0081		Zhou and Zhu, (2004)
Brij98	Polyoxy ethylene (20) oleyl ether	$C_{18}H_{35}(OCH_2CH_2)_{20}OH$	1149.56	1.07	0.252		
Sophorolipid	Sophoro lipid	-	647-650	1.097	0.0916		Thaniyavarn et al. (2008); Baccile et al. (2013)
Saponin	Pentacyclic triterpene saponin	$C_{27}H_{42}O_3$	1650	1.02	0.0606		Seyed Razavi et al. (2012)
Guar gam	Galactomannan	$C_{18}H_{32}O_{16}$	504.438	-	-		
	Alfonic 810-60	-	-	0.993	-		
Tergitol NP-10	Polyoxy ethylene nonyl phenyl ether	$C_{15}-H_{24}-O(C_2-H_4-O)_n$	642	1.06	0.12	Rodrigues et al. (2013)	
CTAB	Cetyltrialkyl ammonium bromide	$CH_3(CH_2)_{15}NBr(CH_3)_3$	364.45	-	0.784	Cationic	Yang et al. (2015)

DDEAB	Dodecyl ethyl dimethyl ammonium bromide	$(\text{CH}_3(\text{CH}_2)_{11}\text{N}^+(\text{CH}_3)_2\text{C}_2\text{H}_5)\text{Br}$	322.37	-	14		Masrat et al. (2013); Abe et al. (1987)
DPC	1-dodecylpyridinium chloride	$\text{C}_{17}\text{H}_{30}\text{ClN}$	283.884	-	-		
DDAC	Didecyl dimethyl ammonium chloride	$\text{C}_{22}\text{H}_{48}\text{ClN}$	362.083	1.29	-		
HTMAB	Hexadecyl trimethyl ammonium bromide	$\text{C}_{16}\text{H}_{33}\text{N}(\text{CH}_3)_3\text{Br}$	364.45	0.39	-		
AOT	Sodium bis(2-ethylhexyl) sulfosuccinate	$\text{C}_{20}\text{H}_{37}\text{NaO}_7\text{S}$	444.56	1.1	0.638	Anionic	Panda and Kabir-ud-Din, (2011)
JBR425	Rhamnolipids	$\text{C}_{32}\text{H}_{58}\text{O}_{13}$	504.6	-	-		Mao et al. (2015)

PFOA	Perfluoro octanoic acid	$C_7F_{15}COOH$	414.07	-	-		
SDBS	Sodium dodecyl benzene sulfonate	$C_{12}H_{25}C_6H_4SO_3Na$	348.48	-	2.66		Yang et al. (2015)
SDS	Sodium dodecyl sulfate	$C_{12}H_{25}OSO_3Na$	288.38	1.01	5.5		Zhao et al. (2005)
Lecithin	Lecithin	$C_{35}H_{66}NO_7P$	643.887	1.06			Yeap et al. (2012)
Cyclodextrin (Mod-b-CD)	β -Cyclodextrin	$C_{42}H_{70}O_{35}$	1135	-	-	Zwitterionic	Loft and Brewster (1996)
CAS	Cocamy dopropyl hydroxyl sultaine	$CH_3(CH_2)_{13}N(OH)(CH_2)N(CH_3)_2(CH_2)(CHOH)(CH_2SO_3)$	452.69	-	-		Mao et al. (2015)
Alkyl polyglucoside	Triton CG-425 Alkyl Polyglucoside	$C_{16}H_{32}O_6$	320.426	1.1		Gemini nonionic	-

Alkanediyl- α,ω -type	butanediyl 1,4- bis(dimethyl cetylammonium bromide)	$2N(CH_2)_{34}(CH_3)_6 2Br$	-	-	-		Mobin and Masroor (2012)
	pentanediyl 1,5 - bis (dimethyl cetylammonium bromide) and	$2N(CH_2)_{35}(CH_3)_6 2Br$	-	-	-	Gemini cationic	Mobin and Masroor (2012)
	Hexanediyl-1,6- bis(dimethyl cetyl ammonium bromide)	$2N(CH_2)_{36}(CH_3)_6 2Br$	-	-	-		Mobin and Masroor (2012)

6.2.1 Synthetic surfactants

Ionic and nonionic synthetic surfactants have been extensively used in the remediation of PAHs from soil and aqueous media (Mulligan et al. 2001). The solubilisation order of surfactants was found to be nonionic > cationic > anionic with logarithmic scale values of the micelle-water partition coefficient (K_m) of 4.79, 4.66 and 4.32, respectively, for naphthalene, and 6.91, 6.64 and 6.44, respectively, for pyrene in one study (Masrat et al. 2013). The surfactants used were nonionic (Brij30 and Brij56), cationic (dodecyl ethyl dimethyl ammonium bromide, cetyl trimethyl ammonium bromide (CTAB) and anionic (sodium dodecyl sulfate (SDS)). A similar order was observed for anionic and non-ionic surfactants in naphthalene and phenanthrene solubilisation (Sales, de Rossi, and Fernandez 2011). When various PAHs (naphthalene, acenaphthylene, anthracene, phenanthrene and pyrene) were solubilised using the nonionic surfactants, the sequence of solubility above their critical micelle concentration (CMC) was Triton X-100 (TX100) > Brij35 > Triton X-305 (TX305), with maximum $\text{Log}K_m$ values of 5.90, 5.86 and 5.65 for TX100, Brij35 and TX305, respectively (Zhu and Feng 2003). Moreover, Tween80 was observed to be better than other nonionic surfactants (Brij35 and TX100) in solubilising phenanthrene (Iglesias et al. 2014).

As a nonionic synthetic surfactant, Tween80 is more biodegradable and less toxic than anionic and cationic surfactants, and it has been widely used in the bioremediation of PAHs (Collina et al. 2007; Zhang and Zhu 2012). In the presence of Tween80 (500 mg/L), the biodegradation of pyrene (100 mg/L) by *Burkholderia cepacia* could be achieved by up to 50% within 80 h, indicating that microorganisms can tolerate a high concentration of Tween80 (Chen et al. 2013). Similarly, phenanthrene removal efficiency of up to 99% was achieved in the presence of Tween80 (5000 mg/L) from the bioremediation effluent solution (Gharibzadeh et al. 2016). Use of nonionic surfactants (Brij30, Brij35, Tween80 and TX100) increased the PAH concentration in the aqueous phase of soils, soil slurry and sediment, which enhanced PAH biodegradation (Kim et al. 2001; Hussein and Ismail 2013; Iglesias et al. 2014). Similarly, other studies (Aryal and Liakopoulou-Kyriakides 2013; Rodrigues et al. 2013; Li and Zhu 2012) reported that the improved solubility of PAHs with synthetic surfactants further increases their biodegradability.

6.2.2 Biosurfactants

Similar to the synthetic surfactants, biosurfactants are reported to increase the apparent solubility of PAHs, which facilitates their mobility and biodegradability (Kobayashi et al. 2009; Tecon and van der Meer 2010). In general, there are two different types of biosurfactants: a) microbial-based surfactants such as glycolipids (rhamnolipids, trehalolipids and sorphorolipids), lipopeptides, surfactins, lichenysin and phospholipids (Gudina et al. 2016; Vijayakumar and Saravanan, 2015) and b) plant-based surfactants such as saponin, sapindus saponin and sapindus mukurossi (Blyth et al. 2015; Iglesias et al. 2014; Kommalapati et al. 1996; Zhou et al. 2013). Biosurfactants offer many potential advantages (e.g. cost-effective production, biodegradability, low toxicity and a wide range of environmental resilience) compared to synthetic surfactants (Swaathy et al. 2014; Madsen et al. 2015; Uzoigwe et al. 2015; Lang and Wullbrandt 1999; Banat et al. 2014).

The less toxic effect of biosurfactants is due to their good biocompatibility with the cell membrane of microbes (Sotirova et al. 2008). For example, the biodegradation of PAHs was 95% with the biosurfactant rhamnolipids (10 mg/kg), but only 92% with Tween80 (50 mg/kg) and 90% with SDBS (50 mg/kg) (Wang et al. 2016). Furthermore, the phenanthrene solubilising capacity of saponin was found to be higher than that of Tween80, Brij58 and TX100 (Zhou et al. 2011), which demonstrates that biosurfactants are more effective than synthetic surfactants, especially for phenanthrene solubilisation.

Biosurfactants enhance the growth of microorganisms on a hydrophobic surface by overcoming the poor bioavailability of PAHs and increasing the nutrient uptake rates (Sotirova et al. 2009; Bezza and Nkhalambayausi-Chirwa 2015; Tecon and van der Meer 2010). The use of a biosurfactant was found to have increased the bioremediation of PAHs from 57% to 86.5% (Bezza and Nkhalambayausi-Chirwa 2015). Similarly, biosurfactants (400 mg/L lipopeptide) increased the aqueous solubility of phenanthrene, fluoranthene and pyrene by 19, 33 and 45 times, respectively, and enhanced the substrate utilisation rate up to three-fold (Bezza and Nkhalambayausi-Chirwa 2016). Moreover, 0.2% and 0.6% of biosurfactant enhanced the degradation fraction to 34.2% and 63%, respectively, from only 6% without surfactant (Bezza and Nkhalambayausi-Chirwa 2017).

Among the biosurfactants, rhamnolipids are effective in terms of production, metabolic pathways, gene regulation and microbial species diversity (Muller et al. 2012). Phenanthrene

desorption from contaminated soil increased with an increase in rhamnolipid concentrations (An et al. 2011). The degradation rate of anthracene increased by 37.52% with 0.065 mM rhamnolipids and that of pyrene by 25.58% with 0.075 mM rhamnolipids (Peng et al. 2015). Furthermore, a high (99.5%) degradation of phenanthrene was observed with *Sphingomonas* species GF2B in the presence of rhamnolipids (Ortega Calvo 2016; Pei et al. 2010). The solubilities of naphthalene, phenanthrene and pyrene increased linearly with increased concentrations of rhamnolipids above the CMC, where the molar solubilisation ratio (MSR) of PAHs were in the order of naphthalene (7.44) > phenanthrene (2.83) > pyrene (1.34) (Li, Pi, et al. 2015), demonstrating that PAH solubility decreased as PAH ring numbers increased.

6.2.3 Gemini surfactants

Gemini surfactants comprise more than one hydrophobic and hydrophilic groups (anionic, cationic, nonionic, zwitterionic) (Figure 1A), which are joined by an alkyl spacer (Esumi, Goino, and Koide 1996). The hydrophilic portions of gemini surfactants can be anionic sulfates, carboxylates, phosphates, cationic quaternary ammoniums, nonionic polyethers, polysaccharides and complicated hydrophilic oligomers, while the hydrophobic portions are hydrocarbon chains (Wang et al. 2013). In general, the surfactant molecules are similar, but the spacer group that connects two surfactant moieties at or near the head group could be hydrophilic or hydrophobic, flexible or rigid (Atkin et al. 2003). Moreover, the length of the spacer group largely influences the properties of the gemini surfactants (Wei et al. 2013). For example, gemini surfactants with short spacers and a long alkyl chain possess a stronger ability to form larger assemblies (Siddiqui et al. 2013). The CMC values of gemini surfactants are 10 to 100 times less than those of monomeric surfactants, which minimises the number of surfactants required to solubilise PAHs (Chorro et al. 1998).

Moreover, gemini surfactants are different from zwitterionic surfactants, which possess both positive and negative charges in the head group (Varade and Ghosh, 2017). Zwitterionic surfactants can be absorbed on both negative and positive charge surfaces without changing their charge by a significant amount (Rosen, 2004). The cationic fraction of zwitterionic surfactants is preferably based on the ammonium group, while the anionic fraction may include carboxylic and sulfonic acids, and sulfuric acid esters (Rosen, 2004).

Gemini surfactants enhance the remediation of PAHs (Zhao et al. 2015; Yadav et al. 2015; Wei, Li, et al. 2016; Serdyuk et al. 2016; Panda et al. 2016). A positive effect in naphthalene, phenanthrene and acenaphthene remediation in a soil-water system with cationic gemini surfactant C12-3-12 has been observed by (Wei, Huang, et al. 2016) (Table 6.2). A linear increment of PAH (naphthalene, anthracene, pyrene) solubility at surfactant concentrations above the CMC was observed with mixed micelles of cationic gemini surfactant and conventional surfactants (Panda and Kabir-ud-Din 2013). Moreover, equimolar gemini cationic and nonionic surfactants can dramatically improve the solubility of naphthalene and pyrene (Wei et al. 2012), as detailed in Table 6.2. The solubility of naphthalene and pyrene by cationic gemini surfactants and their equimolar bi and ternary gemini surfactants systems significantly enhanced linearly above the CMC (Wei et al. 2013). Thus the PAH solubilisation capacity of gemini surfactants could be further enhanced by the formation of mixed micelles with monomeric surfactants.

Table 6.2: Gemini surfactants and combinations of them in solubilisation of PAH

Surfactants	PAHs	LogKm			Reference
		Single gemini	Binary system	Tertiary system	
Cationic gemini (C12–3–12)	naphthalene	2.9304	-	-	Wei et al. (2016)
	acenaphthene	3.4982			
	phenanthrene	4.2233			
Gemini: C16-10-C16, C16-12-C16 Monomeric: CPB, CTPB, CDEEAB, TDEEAB	naphthalene	4.4724-4.6027	4.6461-5.7751	-	Lakra et al. (2014)
	anthracene	4.6461-4.9935	4.9935-6.5567	-	
	pyrene	4.6461-4.9935	5.4277-5.7317	-	
Cationic cetyltrimethyl ammonium bromide (CTAB) , anionic sodium dodecyl sulfate (SDS), nonioinic polyethylene glycol dodecyl ether (Brij35) and a cationic gemini bis (hexadecyl dimethyl ammonium) pentane dibromide	fluorene	2.9064	2.0174-3.0652	-	Kamil and Siddiqui (2013)
Alkanediyl- α,ω -bis (dodecyl dimethyl ammonium bromide) and their bi and tertiary mixture	naphthalene	5.347-5.514	5.410-5.449	5.334	Wei et al. (2013)

	pyrene	5.786-6.265	5.934-6.223	5.913	
Pentanediy1-1,5-bis(dimethylcetylammoniumbromide) (G5), cetyltrimethylammonium bromide (CTAB), sodium bis (2-ethylhexyl) sulfosuccinate (AOT) and polyoxy ethylene (20) cetyl ether (Brij58)	naphthalene	4.6678	4.5332-4.8328	-	Panda and Kabir-ud-Din (2013)
	anthracene	6.6782	3.1220-6.7434	-	
	pyrene	6.6739	3.3304-6.9648	-	
Gemini cationic: C12-2-12, C12-2-16, Monomeric: C12E23	naphthalene	5.997-6.193	5.937-6.284	6.208	Wei et al. (2012)
	pyrene	4.651-5.083	5.097-5.300	5.231	
Gemini surfactant, C16H33N+(CH3)2 (CH2)5 N+(CH3)2 C16H33 2Br ⁻ Monomeric: cetyl pyridinium chloride (CPC), sodiumbis(2-ethylhexyl) sulfosuccinate (AOT), Brij56	anthracene	6.03	6.09-6.36	-	Kabir-ud-Din et al. (2009)
	pyrene	6.39	6.45-6.86	-	

K_m = micelle-water partitioning coefficient

6.2.4 Use of surfactants in the form of colloidal gas aphrons

Surfactants can also be used in the form of colloidal gas aphrons (CGAs) to remove PAHs. CGAs consist of a system of spherical microbubbles known as ball foam, which possesses some colloidal properties. The ball foam is small in size and possesses thick surfactant shells that result in its high stability (Hashim et al. 2012). In a study by Roy et al. (1995), the CGA generated using a nonionic surfactant, Tergitol, showed a similar trend to that of conventional surfactants, with the higher the surfactant concentration the larger the removal of naphthalene from the soil matrix. When the overall performance of the conventional surfactant solutions and the CGA suspensions was compared, it was observed that the percentage of removal of naphthalene with CGA was lower than that removed by surfactant solutions (Roy et al. 1995). The low removal is believed to be due to the channelling and pore clogging caused by the dispersion of soil colloids by CGAs.

Kommalapati et al. (1996) studied the removal of hexachlorobenzene from soil by CGAs produced from soapnut (*Sapindus mukurossi*), a biosurfactant prepared from the fruit pericarp. The study showed that, for soil contaminated with a small amount of hexachlorobenzene (2 mg/kg), the CGA suspensions generated with soapnut performed better than conventional solutions. However, at a higher level of contamination (9-110 mg/kg), a CGA suspension of 1% strength natural surfactant, soapnut in the form of conventional solutions, outperformed the CGA suspensions in the removal of hexachlorobenzene.

6.3 Synergistic effect of mixed micelles

Anionic surfactants are likely to precipitate in the soil and nonionic surfactants are more likely to adsorb onto the soil fractions (Tsomides et al. 1995), which results in a high remediation cost due to the need for more surfactants (Kim et al. 2001). It further pollutes the environment. Sorption of nonionic surfactants could be prevented using a combination of nonionic and anionic surfactants (Yu et al. 2007). Therefore, many recent studies (Sales and Fernandez 2016; Li and Zhu 2012; Azum et al. 2014) have investigated how to improve the solubility of PAHs using various combinations of surfactants (Table 6.3). The mixed surfactants have synergistic advantages in PAH solubilisation by reducing the CMC value more than either individual anionic or nonionic surfactants (Zhu and Feng 2003; Shen et al. 2007). For example, Shi et al. (2015) found the solubility of phenanthrene, fluoranthene and benzo(a)pyrene with anionic and nonionic surfactants to be in the order of SDS-TX100 >

SDBS-TX100 > TX100 > SDBS > SDS, with the highest solubility being 265.88 mg/L at 1:9 SDS-TX100 (Table 6.3). Using the surfactants SDS and TX100 at a ratio of 1:4, Liang et al. (2014) found the solubility of naphthalene, phenanthrene and fluorene to be significantly increased compared to their solubility with SDS. Similarly, Sales et al. (2011) found the solubility of naphthalene in a Tween80-fatty acid mixed micelle system to be higher than in the single micelle. Holland and Rubingh (1983) found that mixed surfactants could be employed over a wider range of temperature, salinity and hardness conditions than an individual surfactant.

Table 6.3: PAHs solubilisation with mixed micelle

Surfactants	PAHs	Solubility parameters/ PAH removal	References
Tween80, Sodium Laurate (SL)	naphthalene, phenanthrene	3 mM Tween80 mixed with 20 mM SL reduced SL precipitation and Tween80 adsorption which result in enhancement of naphthalene and phenanthrene solubilisation. The ratio between experimental and theoretical recovery for naphthalene and phenanthrene were 1.4 and 1.2, respectively.	Sales and Fernandez (2016)
4-butylazobenzene-4-(oxyethyl) trimethylammonium bromide (AZTMA), Tween80	phenanthrene, pyrene, acenaphthene	MSR and Km for PAHs were in the order of pyrene > phenanthrene > acenaphthene which is much higher than that of single surfactants.	Long et al. (2016)
Brij30, Tergitol TMN-3,	phenanthrene	Phenanthrene concentration dropped to < 0.001mg/L from 400 mg/L due to biodegradation in the presence of 40 g/L equimolar Brij30 and Tergitol TMN-3. The bacterial genus used in this study was <i>Sphingomonas polyaromaticivorans</i>	Pan et al. (2016)
SDS, SDBS, TX100	phenanthrene, fluoranthene, benzo(a)pyrene	The synergic effect of surfactants in PAHs treatment of contaminated soil was in the order of TX100-SDS (9:1) > TX100-SDS (8:2) > TX100-SDS (7:3) > TX100-SDBS (7:3) > TX100 > SDBS > SDS. The highest PAH removal was 33.47% at TX100-SDS (9:1).	Shi et al. (2015)
SDBS, TX100	pyrene	LogKm for SDBS was 5.0604, LogKm at1:9 of SDBS and TX100 was 5.8215	Wei et al. (2015)

SDS, TX100	naphthalene, phenanthrene, fluoranthene	LogKm values for naphthalene, phenanthrene, and fluorene in the presence of SDS were 5.243, 5.401 and 5.017, respectively, and at 1:4 of SDS and TX100 the respective values were 5.529, 5.823 and 5.427.	Liang et al. (2014)
Tween80, Saponin	phenanthrene	The highest solubility of phenanthrene (0.9 mM) was observed at saponin and Tween80 molar ratio of 1:1.2.	Iglesias et al. (2014)
SDBS, Tween80	phenanthrene, pyrene	Phenanthrene and pyrene residuals in the soil were 0.856 and 2.32 mg/kg, respectively, after treatment with mixed surfactants (SDBS and Tween80, at mass ratio 2:3 with the total concentration of 100 mg/kg) whereas phenanthrene and pyrene residuals without surfactants were 3.79 and 8.56 mg/kg, respectively. The mixed surfactants required were only 1/15 by mass in comparison to Tween80 alone to remove an equal amount of PAHs in both planted and unplanted soils.	Ni et al. (2014)
Tween80, fatty acids	naphthalene,	Fatty acid and Tween80 mixed micelles increased the solubility of naphthalene than an individual surfactant.	Sales et al. (2011)
SDS-TX100	phenanthrene	Biodegradation of PAH in the presence of mixed surfactants (SDS to TX100 ratio 1:9) was about 165% of that of single TX100 at a concentration of 1.6 mM.	Yu et al. (2007)
SDS, Tween80, Brij35, TX100	phenanthrene	PAHs solubilisation was significantly improved with mixed surfactants (anionic to nonionic ratio of 1:9) at total concentration of 5 mM and found in the order of SDS-Tween80 (163.4 mg/L) > SDS-Brij35 (125.7 mg/L) > SDS-TX100 (84.14 mg/L).	Zhao et al. (2005)
SDS, Brij35, Brij58, TX100, TX 405	pyrene	MSR of pyrene in mix surfactants followed the order of SDS-TX405 > SDS-Brij35 > SDS-Brij58 > SDS-TX100.	Zhou and Zhu (2004)

Brij35, SDS, TX100, TX305	naphthalene, acenaphthylene, anthracene, phenanthrene, and pyrene	PAHs solubility order was SDS-TX305 > SDS-Brij35 > SDS-TX100 with respective LogKm values of PAHs in surfactant solution were 4.78-6.50, 4.65-6.45, 4.64-5.99.	Zhu and Feng (2003)

When increasing the solubility of PAHs, the application of mixed surfactants also increases the bioavailable fraction of PAHs. For example, mixed anionic-nonionic surfactants (SDS and TX100 at 1:9) increased the phenanthrene biodegradation by 165% when compared with TX100 (1.6 mmol/L) alone (Yu et al. 2007). Similarly, the number of mixed surfactants (SDBS to Tween80 ratio: 2:3 and concentration 100 mg/kg-soil) required was only about 1/15 by weight to remove the same amount of phenanthrene and pyrene when compared with Tween80 alone (Ni et al. 2014). Thus, the mixed micelles solubilisation with a selection of a proper combination of surfactants is important for efficient and effective SER of PAHs.

6.4 Impact of surfactants on the biodegradation of PAHs

The positive and negative impacts of surfactants on the biodegradation of PAHs are detailed below.

6.4.1 Positive impact of surfactants on the biodegradation of PAHs

The bioavailable fraction of PAHs can be increased by surfactant micellar solubilisation. Therefore, surfactant-enhanced biodegradation has become an effective technique for PAH remediation. Many studies (Rodrigues et al. 2013; Pansyrnaya et al. 2013; Chen et al. 2013; Li and Zhu 2012) have demonstrated a positive effect of surfactants in PAH biodegradation. Table 6.4 shows the role of various microbial communities in degrading PAHs in the presence of surfactants. The biodegradation of 15 PAHs by *Bacillus* and *Pseudomonas* species increased by 29.5% after the use of biosurfactant (i.e. 57% and 86.5% in the absence and presence of biosurfactant, respectively; Table 6.4) (Bezza and Nkhalambayausi-Chirwa 2015). A similar result, a higher biodegradation efficiency of USEPA 16 PAHs by gram-positive bacteria was noted in the presence of biosurfactant (Table 6.4) (Blyth et al. 2015). *Acinetobacter woffii* RAG-1 could degrade nearly all phenanthrene (99.5%) in the presence of rhamnolipids ((Yu et al. 2014). Similarly, > 95% of anthracene degraded in the presence of CTAB and Tween80 and > 90% of naphthalene degraded in the presence of CTAB by 1C strain (Mesbaiah et al. 2014). The use of biosurfactant facilitated anthracene degradation > 95% within 22 days (Table 6.4) (Swaathy et al. 2014). Moreover, the biodegradation of higher and lower molecular weight PAHs increased by 7.59 times and 2.8 times, respectively, in the presence of TX100 by bacterial species *Achromobacter xylosoxidans* (Dave et al. 2014), demonstrating that surfactants are effective for biological treatment of higher molecular weight PAHs.

Table 6.4: Surfactant enhanced biodegradation of PAHs in the presence of different microbial communities

Surfactants	PAHs	Bacteria/Fungi	Description	References
Brij30, Span20, polyoxyethylene sorbitol hexaoleate	High molecular weight PAHs	<i>DT40 B- lymphocyte</i>	Biodegradation of four rings and five-rings PAHs improved by the use of surfactants and the removal efficiency was 80%.	Adrion et al. (2016)
Tergitol TMN-3, Brij30	phenanthrene	<i>Sphingomonas polyaromaticivorans</i>	Biodegradation in mixed micelles with two equimolar nonionic surfactants (Tergitol TMN-3 and Brij30, total concentration of 40 g/L) was found to be effective. Phenanthrene concentration decreased from 400 mg/L to 0.001 mg/L.	Pan et al. (2016)
Tween80	pyrene	<i>Pseudomonas aeruginosa</i> RS1	In the presence of Tween80 and <i>Pseudomonas aeruginosa</i> RS1, pyrene concentration dropped to 1.11 mg/L from 100 mg/L.	Ghosh and Mukherji, (2016)
Lipopeptide	15 PAHs	<i>Bacillus stratospheric,</i> <i>Bacillus subtilis, Bacillus megaterium,</i> <i>Pseudomonas aeruginosa.</i>	Degradation of PAHs (initial concentration 3064.6 mg/kg) from contaminated soil was 86.5% after 45 days in the presence of biosurfactant whereas only 57% in the absence of surfactant.	Bezza and Nkhalambaya usi-Chirwa (2015)
Alphitonia excelsa based biosurfactant	USEPA 16 PAHs	Gram-positive degrading bacteria.	At 12 weeks, 78.7% degradation in the presence of surfactant whereas 62.0% without surfactant. The initial PAHs concentrations were 2525 mg/kg soil.	Blyth et al. (2015)

TX100	11 PAHs	<i>Achromobacter xylooxidans</i>	In the presence of a surfactant, the degradation of lower molecular weight PAHs increased by 2.8 fold and the degradation of higher molecular weight PAHs increased by 7.59 fold. The initial total PAHs concentration in the study was 164.20 mg/kg.	Dave et al. (2014)
Rhamnolipids	phenanthrene,, pyrene	<i>Acinetobacterl woffii</i> RAG-1	Phenanthrene (180-200 mg/kg) and pyrene (190-200 mg/kg) degradation using 500 mg/L surfactant were 99.5% and 77.7%, respectively, after amendment of DOM.	Yu et al. (2014)
Biosurfactant	anthracene	<i>Bacillus licheniformis</i> (MTCC 5514)	Anthracene degradation in the presence of lecithin (10%) with isolate MTCC 5514 was > 95% in the aqueous medium within 22 days.	Swaathy et al. (2014)
Tween80	fluorene, phenanthrene, anthracene, pyrene	Fungi <i>Trametes versicolor</i>	> 90% of PAHs degraded in a surfactant (5000 mg/L) added soil-water system within a week.	Rodríguez-Escales et al. (2013)
Tween20, SDS,	fluoranthene, anthracene	<i>Pseudomonas putida</i> (ATCC 17514)	Tween20 (0.08 mM) increased fluoranthene biodegradation and doubled the maximum specific biodegradation rate of anthracene. SDS (0.35mM) doubled the removal rate of the anthracene.	Rodrigues et al. (2013)
Tween80	pyrene	<i>Bacillus subtilis</i> , <i>Burkholderiacepacia</i>	Biodegradation of pyrene was found high in the presence of Tween80. In the presence of Tween80 (500 mg/L) about 50% of pyrene with an initial concentration of 100 mg/L was degraded within 80 h.	Chen et al. (2013)

Tween20, Tween80	phenanthrene, pyrene	<i>Arthrobacter</i> strain Sphe3	Degradation of phenanthrene was 99.03% and 96.44% in the presence of Tween20 and Tween80, respectively. Degradation of pyrene was 97.39% and 96.61% in the presence of Tween20 and Tween80, respectively. Surfactant concentration was 0.25 g/L for both tests.	Aryal and Liakopoulou-Kyriakides, (2013)
Tween80, SDBS	phenanthrene	<i>Citrobacter</i> species. (Strain SA01)	Phenanthrene biodegradation increased by 8.9% to 17.2% in the presence of both surfactants (50 mg/L).	Li and Zhu, (2012)
Brij30	phenanthrene	<i>Pseudomonas putida</i> (DSMZ 8368)	Absorbance at 600 nm (OD600) with surfactant was 1.67 and OD600 was 1.59 without surfactant.	Pantsyrnaya (et al. 2012)
Rhamnolipids	phenanthrene	<i>Sphingomonas</i> <i>species</i> (GF2B)	In the presence of a surfactant, removal of phenanthrene (initial concentration 1.0 g/L) was 99.5% within 10 days and only 83.6% in absence of surfactant.	Pei et al. (2010)
Rhamnolipids	15 PAHs	Arbuscular mycorrhizal fungi+ microbial consortium of PAH degraders	The average removal efficiency of total PAHs was 61% and fluoranthene, pyrene, benzo(a)pyrene removal efficiency were 89.39, 88.36, 92.31%, respectively, at 90 days of surfactant enhanced treatment. Average total PAHs removal was 17% in the absence of surfactant. The initial PAHs concentration was 12.85 g/kg soil.	Zhang et al. (2010)
Rhamnolipids	anthracene	<i>Pseudomonas</i> species 12B	52% degradation of anthracene (100 mg/L) in the presence of surfactant within 18 days compared to 32% in the absence of a surfactant.	Chang-Zheng (2008)

Tween80	phenanthrene	phenanthrene degrading bacteria.	Overall phenanthrene removal efficiency was 99.9% in the horizontal-vertical flow macrophyte based constructed wetland treatment system.	Machate et al. (1997)

As detailed in Table 6.4, *Arthrobacter* strain Sphe3 could degrade phenanthrene and pyrene up to 99.03% in the existence of nonionic surfactants (Aryal and Liakopoulou-Kyriakides 2013). The phenanthrene degradation rate by *Pseudomonas putida* was higher in the presence of Brij30 (0.5 g/L) (Pantsyrnaya et al. 2012). Other studies (Pei et al. 2010; Zhang et al. 2010; Chang-Zheng 2008) also reported that both bacteria (*Sphingomonas* species, *Pseudomonas* species) and fungi (Arbuscular mycorrhizal) advance the degradation of PAHs in the presence of rhamnolipids (Table 6.4). Moreover, the DT40 *B-lymphocyte* cell line and two of its DNA-repair deficient mutants removed 80% of higher molecular weight PAHs in the company of three surfactants (Brij30, Span20 and polyoxyethylene sorbitol hexaoleate) (Adrion et al. 2016). A significant degradation (from an initial concentration of 400 mg/L to final concentration of 0.001 mg/L) of phenanthrene was observed by *Sphingomonas* Polyaromaticivorans when surfactant (Tergitol TMN-3 and Brij30) concentration was 40 g/L (Table 6.4) (Pan et al. 2016). In the constructed wetland, a high removal efficiency (99.9%) of phenanthrene with the use of Tween80 was observed (Machate et al. 1997), which demonstrates the synergistic role of microbes, plants (*Typha* species and *Scirpus lacustris*) and surfactants in removing PAHs.

6.4.2 Adverse impact of surfactants on the biodegradation of PAHs

Along with positive effects, there is also a toxic effect of surfactants on microbial activities, resulting in an adverse effect on PAH biodegradation (Lladó et al. 2015; Llado et al. 2013; Rodrigues et al. 2013; Ghosh and Mukherji 2016). For example, the degradation rate of naphthalene and phenanthrene by 1 C strain was reduced after the use of Tween80 (Mesbaiah et al. 2014). However, a positive growth rate of bacterial biomass was noted, which could be a result of consumption of PAHs as a carbon source by bacteria.

Moreover, Ghosh and Mukherji (2016) found that TX100 (1.19 g/L) and pyrene (0.1g/L) have a toxic effect on *Pseudomonas aeruginosa*. The inhibited growth of *Pseudomonas aeruginosa* could be due to the toxic metabolites obtained by utilisation of TX100. When the ratio of SDS and TX100 was increased to more than 1:9, the biodegradation of phenanthrene in the mixed solutions completely stopped (Yu et al. 2007). The bacterial cells (*Arthrobacter strain Sphe3*) dropped to 19.27% and 13.25% of initial numbers (Table 6.5) when they were incubated 24 h with TX100 (2 g/L) and SDS (2 g/L) (Aryal and Liakopoulou-Kyriakides 2013), indicating that SDS could be more toxic than TX100.

Table 6.5: Negative effect of surfactant on PAHs biodegradation

Surfactant	PAH	Microorganisms	Description	Reference
TX100, Brij30	phenanthrene	<i>Sphingomonas species</i> GY2B	Both surfactants have a toxic effect on the growth of <i>Sphingomonas species</i> GY2B. The more toxic effect was noted with Brij30 than TX100.	Liu et al. (2016)
TX100	pyrene	<i>Pseudomonas aruginosa</i>	Surfactant (1.19 g/L) in mineral media had a toxic effect on bacteria.	Ghosh and Mukherji (2016)
Tween80	naphthalene	1C strain	Naphthalene degradation was less in the presence of Tween80.	Mesbaiah et al. (2014)
Brij30	Higher molecular weight PAHs	Higher molecular weight PAHs degraders	Brij30 inhibited PAHs degraders.	(Llado et al. 2013)
CTAB, SDS	fluoranthene, anthracene	<i>Pseudomonas putida</i> (ATCC 17514)	CTAB (0.27 mM) had a negative effect on biodegradation of both PAHs. SDS (0.35 mM) reduced 50% biodegradation rate of fluoranthene.	Rodrigues et al. (2013)
SDS, TX100	phenanthrene, pyrene	<i>Arthrobacter</i> (Strain Sphe3)	The bacterial number obtained after 24 h in the presence of SDS and TX100 were 13.25% and 19.27%, respectively. The initial surfactant concentration was 2.0 g/L.	Aryal and Liakopoulou-Kyriakides (2013)
Brij30	phenanthrene	Pyr01 consortium	0.5 g/L of surfactant had a negative effect on PAH degradation.	Pantsyrnaya et al. (2012)

Tween80	phenanthrene	<i>Sphignomonas species</i> (GF2B)	PAH degradation in the presence and absence of Tween80 were 33.5% and 83.6%, respectively, at 10 days.	Pei et al. (2010)
SDS, TX100	phenanthrene	Phenanthrene degrading microbes	SDS to TX100 ratio at > 2:8 in solution had a negative effect on phenanthrene biodegradation.	Yu et al. (2007)

A negative effect of Brij30 on PAHs of higher molecular weight degrading bacteria was also observed (Llado et al. 2013). Similarly, Brij30 hindered the proliferation of *Actinobacteria* and *Bacteroidetes* in PAH-contaminated soil (Lladó et al. 2015). CTAB (0.27 mM) had a negative effect on the biodegradation of fluoranthene and anthracene, and the use of SDS (0.35 mM) reduced the biodegradation of fluoranthene with *Pseudomonas putida* by 50% (Table 6.5) (Rodrigues et al. 2013). A negative effect on phenanthrene degradation by Pyr01 consortium in the presence of Brij30 (0.5 g/L) was also reported (Pantsyrnaya et al. 2012). The biodegradation of phenanthrene by *Pseudomonas putida* reduced in the presence of Brij35 and Tween80 (Doong and Lei 2003). However, in the presence of Brij30, *Pseudomonas putida* is a good degrader of phenanthrene (Pantsyrnaya et al. 2012). Phenanthrene degradation by *Sphingomonas* species GF2B was only 33.5% in the presence of Tween80 within 10 days, whereas the degradation increased up to 83.6% in the absence of Tween80 (Table 6.5) (Pei et al. 2010). Phenanthrene degradation by *Sphingomonas* species GY2B enhanced in the presence of Tween80, which could be the result of different bacterial species. A toxic effect on *Sphingomonas* species GY2B was noted in the presence of TX100 and Brij30 during phenanthrene degradation (Table 6.5) (Liu et al. 2016). All these observations show that the biodegradation of PAHs not only depends on types of microorganisms but also depends on the types of surfactants used.

6.5 Factors affecting the surfactant-enhanced treatment of PAHs

6.5.1 Surfactant concentration

Generally, the PAH solubilisation capacity of surfactants enhances with an increase in surfactant concentrations (Zhao et al. 2005; Hussein and Ismail 2013; Congiu and Ortega-Calvo 2014). For example, the phenanthrene desorption rate in the soil-water system increased with the increase of rhamnolipid concentrations (An et al. 2011). The apparent solubility of phenanthrene and pyrene increased by 1.71 and 2.31 times, respectively, at 7.5 mg/L Tween80, and by 2.62 and 13.25 times, respectively, at 75 mg/L Tween80 when compared with apparent solubility in the deionised water (Hu et al. 2015). The solubilities of phenanthrene and pyrene were 29.7% and 44.9%, respectively, at a rhamnolipid concentration of 200 mg/L, whereas the respective values increased to 46.7 and 61.7% at a rhamnolipid concentration of 400 mg/L (Congiu and Ortega-Calvo 2014). Phenanthrene solubilisation was compared at different concentrations of saponin (1.0 and 1.2 mmol/L) and Tween80 (0 - 1.2

mmol/L), and the highest solubility of phenanthrene (0.9 mmol/L) was observed at the highest concentrations of both surfactants (Iglesias et al. 2014). The partitioning of phenanthrene in the coacervate phase increased with increased surfactant concentration (Pan et al. 2016). In comparison to 150 mg/L lipopeptide amended or unamended soil, phenanthrene and pyrene solubilisation increased 3.5 to 4 times when soil was amended by 700 mg/L lipopeptide (Bezza and Nkhalambayausi-Chirwa 2015).

In addition to increased solubilisation, the bioavailable fractions of phenanthrene and pyrene were also found to have increased from 18% to 73% and 6% to 51%, respectively. The anthracene degradation increased up to 37.52% when rhamnolipid concentration changed from 0.04 to 0.065 mM, and pyrene degradation increased up to 25.58% when rhamnolipid concentration increased from 0.04 to 0.075 mM (Peng et al. 2015). Similarly, the solubility of pyrene and anthracene with C₁₆H₃₃N⁺(CH₃)₂(CH₂)₅N⁺(CH₃)₂C₁₆H₃₃ 2Br⁻, cetyl pyridinium chloride, AOT and Brij56 increased linearly with increased surfactant concentrations (Kabir ud et al. 2009).

However, some studies (Peng et al. 2011; Gao et al. 2006) reported that the solubility of PAHs with the help of surfactants could be improved up to a certain level of surfactant concentration. For example, removal of benzo(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene and indeno(1,2,3-cd)pyrene increased rapidly up to surfactant concentrations (TX100 and Tween80) of 5 g/L and removal was not further improved beyond 5 g/L (Peng et al. 2011). Similarly, improvement of phenanthrene degradation was noted by increasing surfactants Brij30 and Tergitol TMN-3 (1:1 w/w) concentrations up to 60 g/L, but the degradation decreased when the surfactant concentration was further increased (Pan et al. 2016). Phenanthrene and pyrene uptake by plant increased up to 74 mg/L of Brij35 and uptake decreased when the Brij35 concentration was \geq 148 mg/L (Gao et al. 2006). Similar observations were noted in the use of *Trametes versicolor* fungus in the biodegradation of PAHs (fluorene, phenanthrene, anthracene and pyrene) (Rodríguez-Escapes et al. 2013).

6.5.2 Temperature

The surfactant assisted solubility of PAHs is proportional to the temperature up to a certain extent. The mineralisation of 2 mg/L anthracene and pyrene in the presence of Tergitol NP-10

(100 mg/L) reduced with a decrease in temperature from 25 °C to 10 °C (Sartoros et al. 2005). Overall, the mineralisation of anthracene and pyrene was 48.8% and 66.1%, respectively, at 25 °C, and 18.5% and 61.5%, respectively, at 10 °C. The solubility of naphthalene, phenanthrene and pyrene increased with temperatures up to 30 °C and the solubility of naphthalene decreased beyond 30 °C due to volatilisation (Li, Pi, et al. 2015). Similarly, when the test was carried out at a temperature range of 15 °C to 50 °C, the optimum temperature was 35 °C for PAH degradation, and anthracene and pyrene degradation were 37.52% and 25.58%, respectively at 35 °C (Peng et al. 2015). In contrast to the previous observation, PAH removal performance with the use of surfactant was not affected by a temperature between 10 °C and 40 °C (Peng et al. 2011). However, further investigation is essential to better understand the effect of temperature on the SER of PAHs.

6.5.3 pH

pH is one of the important parameters for the surfactant-enhanced solubilisation of PAHs. An increase in pH from 2 to 10 has a positive effect on the surface tension of surfactants such as Tween80, Brij35, and Saponin (Iglesias et al. 2014). The CMC decreased when $\text{pH} < 4$ and it remained constant at pH 5 to 10 (Rahman 1983). The MSR of saponin for phenanthrene decreased by 70% with the increase of solution pH from 4 to 8 (Table 6.6) (Zhou et al. 2011). In a test was conducted using rhamnolipids (150 mg/L), the highest phenanthrene solubility was noted at pH 5 (4.7 times greater than that at pH 7), the solubility decreased when pH values increased to 7, and solubilisation was stabilised when pH values further increased from 7 to 8 (Shin et al. 2008). A sharp decrease in phenanthrene solubility at pH 4 in the presence of rhamnolipids could be due to the sorption of surfactant into the soil. Conversely, the solubility of PAHs with the use of biosurfactants increased at a higher pH and obtained the highest solubilisation at pH 11, with solubility values 4.47, 2.43 and 1.6 mg/L of naphthalene, phenanthrene and pyrene, respectively (Li, Pi, et al. 2015). Anthracene and pyrene degradation were tested at pH range 2 to 6 and the optimum pH for both PAHs were 4.5 with 31.85% anthracene and 24.29% pyrene degradation (Peng et al. 2015). The resulting impact of pH on PAH solubilisation is inconsistent in the literature. Therefore, further detailed study is needed to understand the relationship between pH, including various environmental conditions, and the surfactant-enhanced solubilisation of different PAHs.

6.5.4 Salinity

The addition of salt could decrease the solubility of the hydrophilic group and increase the interaction between the lipophilic group and an aqueous solution, which helps to improve the solubility of PAHs (Iglesias et al. 2014). PAH solubility significantly increased when NaCl concentration was increased from 1 to 10 g/L at pH 7. The maximum solubility of naphthalene, phenanthrene and pyrene were 2.27, 1.57, and 0.98 mg/L, respectively, at 8 g/L of NaCl (Li, Pi, et al. 2015). Similarly, phenanthrene solubility with saponin increased with increased concentrations of NaCl (Table 6.6) (Zhou et al. 2011). Pyrene solubility in the saline surfactant solution was greater than in a non-saline solution and maximum solubility was observed at a TX100-to-SDBS ratio of 7:3 (Wei et al. 2015).

Table 6.6: Effect of pH and NaCl concentration variation on phenanthrene solubilisation in the presence of saponin (Zhou et al. 2011)

Effect of pH on phenanthrene solubilisation in the presence of saponin				Effect of NaCl on phenanthrene solubilisation in the presence of saponin			
pH	CMC (µmol/L)	MSR	LogKm	NaCl (M)	CMC (µmol/L)	MSR	LogKm
4	16.5	0.776	6.56	0.01	30.9	0.606	6.50
5	28.1	0.642	6.51	0.05	24.2	0.667	6.52
6	58.6	0.476	6.43	0.10	22.0	0.720	6.54
7	85.3	0.263	6.24	0.50	10.1	1.023	6.63
8	92.5	0.238	6.21	1.00	5.2	1.289	6.67

6.5.5 Dissolved organic matter

When PAHs bind with dissolved organic matter (DOM), there is a reduction in the freely dissolved PAHs and an increase in the apparent solubility of PAHs (Tejeda-Agredano et al. 2014). The degradation of Phenanthrene (180 - 200 mg/kg) in the DOM removed, DOM not removed and DOM (50 mg/L) added soil systems were 94.4, 97.1 and 99.5%, respectively, in the presence of biosurfactants (500 mg/L), and the respective values of pyrene (190 - 200

mg/kg) degradation were 72.3, 74.0 and 77.7% (Yu et al. 2014). Similarly, phenanthrene and pyrene solubility could be enhanced in the Tween80-DOM system (Hu et al. 2015). Moreover, a higher solubility of PAHs was achieved by the Tween80-DOM complex than the summation of PAH solubility by a separate DOM and Tween80 (Cheng and Wong 2006). Humic acid (10 mg/L) significantly enhances the solubility of phenanthrene and pyrene (Tejeda-Agredano et al. 2014). The solubility of ¹⁴C-pyrene in the presence of rhamnolipids (400 mg/L) in soil with 6.1 and 10% organic matter was 61.7 and 52.5%, respectively, at soil-water proportion 800 mg/L (Congiu and Ortega-Calvo 2014). Overall, the solubility of PAHs could be further enhanced by the addition of DOM with surfactants.

6.5.6 Co-solute

The solubility of phenanthrene and pyrene with TX100 increased by 15.38% and 18.19%, respectively, when they were co-solubilised (Liang et al. 2016). Similarly, when co-solubilised, the solubility of naphthalene and phenanthrene with TX100 increased by 20.8 and 38.5%, respectively, whereas the solubility of phenanthrene and fluorene with TX100 decreased by 36.1% and 6.5%, respectively (Liang et al. 2014). A synergistic effect was noted in PAH solubility when naphthalene and pyrene were co-solubilised with Tween80, Brij58, CTAB and SDBS, whereas an adverse effect was observed when Brij78 was used in similar environmental conditions (Yang et al. 2015). Further investigations showed synergisms in the solubility of 4,40-dibromodiphenyl ether and pyrene with Tween80, Brij58, CTAB, SDBS, and Brij78 (Yang et al. 2015). However, the solubility was not increased when 4,40-dibromodiphenyl ether and naphthalene were co-solubilised with Brij58, Brij78 and CTAB surfactants.

Moreover, the biodegradation of lower and higher molecular weight PAHs increased by 2.8 and 7.59 times, respectively, in the presence of TX100 and glucose (Dave et al. 2014). Bioavailable fractions of pyrene in the soil slightly increased from 33.71 to 36.93 mg/kg in the presence of cadmium (Wang et al. 2015). The solubility of phenanthrene and pyrene in co-solubilised form has been found greater than that of single phenanthrene or pyrene with TX100 (Liang et al. 2016).

A study of the solubilisation of PAHs (anthracene, fluorene, and pyrene) with TX100 and Tween80 found that the solubility of more hydrophobic PAHs increased in the presence of

less hydrophobic PAHs (Hussein and Ismail 2013). Similarly, the solubility of phenanthrene greatly improved in the presence of naphthalene, but was reduced in the presence of pyrene (Chun et al. 2002), which could be due to the solubilisation of less hydrophobic compounds at the interfacial region of the hydrophobic core. The solubility of naphthalene was reduced in the presence of phenanthrene and/or pyrene, whereas the solubility of phenanthrene greatly improved in both binary and ternary mixtures (Guha et al. 1998). The solubility of naphthalene-phenanthrene and naphthalene-fluoranthene improved at an SDS-to-TX100 molar ratio of 1:4 compared with naphthalene alone (Liang et al. 2014). The desorption of pyrene with various concentrations (150, 1,000 and 1,150 mg/L) of Tween80 decreased in a co-solubilised system. A similar trend was observed in Gold Crew (16.25 and 32.65 mg/L), whereas a pyrene desorption trend was opposed at higher concentrations (65 and 150 mg/L). Conversely, with the use of BS400, pyrene desorption was enhanced in a co-solubilised system (Rodríguez-Escales et al. 2013). Overall, the results demonstrated that the effect of co-solubilisation depends on both types of surfactants and their concentrations.

6.5.7 Hydrophilic-lipophilic balance of surfactants

The hydrophilic-lipophilic balance (HLB) number and molecular structure are the most important properties of the surfactant for determining its solubilising capacity (Edwards et al. 1991). Surfactants with lower HLB have a greater micellar core volume than that of homolog surfactants with higher HLB and hence possess a greater capacity to solubilise PAHs (Li and Chen 2002; Chun et al. 2002). The naphthalene and phenanthrene solubilising capacity of Brij30, Tween80 and TX100 was in the order of Brij30 > Tween80 > TX100, with an HLB of 9.7, 13.4 and 13.6, respectively (Kim et al. 2001), indicating that surfactants with a lower HLB have better solubility. However, the HLB value alone could not be used to determine the solubilisation capacity of surfactants with different structures (Diallo et al. 1994).

6.5.8 Octanol-water partitioning coefficient of PAHs

Hydrophobicity is the primary property controlling PAH desorption from the soil, as the octanol-water partition coefficient is an important parameter for predicting environmental contaminants (Hussein and Ismail 2013). Hydrophobicity is the primary property that controls PAHs desorption from the soil with surfactants (TX100 and Tween80) to solubilise anthracene, fluorene and pyrene (Hussain 2011). The relative enhancement of an aqueous concentration of ^{14}C -pyrene was higher than that of ^{14}C -phenanthrene caused by the

biosurfactant, which was related to the hydrophobicity of the two PAHs (Congiu and Ortega-Calvo 2014). Similarly, the synergistic effect of a mixed surfactant (SDS-TX305, SDS-Brij35, SDS-TX100) in solubilising naphthalene, acenaphthylene, anthracene, phenanthrene and pyrene has a linear relation to the octanol-water partition coefficient of PAHs (Zhu and Feng 2003). Furthermore, the naphthalene and pyrene solubilisation power of mixed (gemini and conventional nonionic) surfactants increased with an increase in the octanol-water partition coefficient of PAHs (Wei et al. 2012). Solubilisation enhancement of naphthalene and phenanthrene into the micelles formed by SDBS, monoalkylated disulfonated diphenyl oxide (MADS-C12) and dialkylated disulfonated diphenyl oxide (DADS-C12) was found in the order of SDDBS < MADS-C12 < DADS-C12 (Chun et al. 2002), revealing that the hydrophobic chains in the micellar core could play a more important role in PAH solubilisation than benzene rings in the palisade layer.

There was a greater improvement in the solubility of PAHs with a higher octanol-water partition coefficient, but greater inhibition in the solubility of PAHs with a lower octanol-water partition coefficient (Liang et al. 2014). SDS (0.35 mM) led to a reduction of 50% on the biodegradation rate of fluoranthene but doubled the removal rate of the most hydrophobic anthracene (Rodrigues et al. 2013), indicating that the hydrophobicity of PAH is an important parameter in SER. The solubilising capacity of mixed surfactants towards naphthalene and pyrene increases with the increasing octanol-water partition coefficient of PAHs (Wei et al. 2012). Similarly, enhancement in PAH solubilisation by saponin was found to be proportional to the octanol-water partition coefficient of PAHs, with a solubilisation order of pyrene > phenanthrene > acenaphthene > naphthalene (Zhou et al. 2011).

6.6 Mechanisms of surfactant-enhanced solubilisation

As discussed above, surfactants comprise both hydrophobic and hydrophilic moieties and can accumulate along air-liquid and liquid-liquid interfaces. Surfactants reduce both surface and interfacial tension, and at the same time enhance the mixing capacity. The effect of a surfactant on the availability of organic compounds can be explained by three main mechanisms: a) dispersion of non-aqueous phase liquid organics, b) increase of contact area due to reduction in the interfacial tension between the aqueous and non-aqueous phases, and

c) increase of the apparent solubility of pollutants by micellar solubilisation (Edwards et al. 1991).

The critical concentration beyond which the surfactant monomers (Figure 1B) start aggregating to form micelles (Figure 1C) is termed CMC (Edwards et al. 1994).

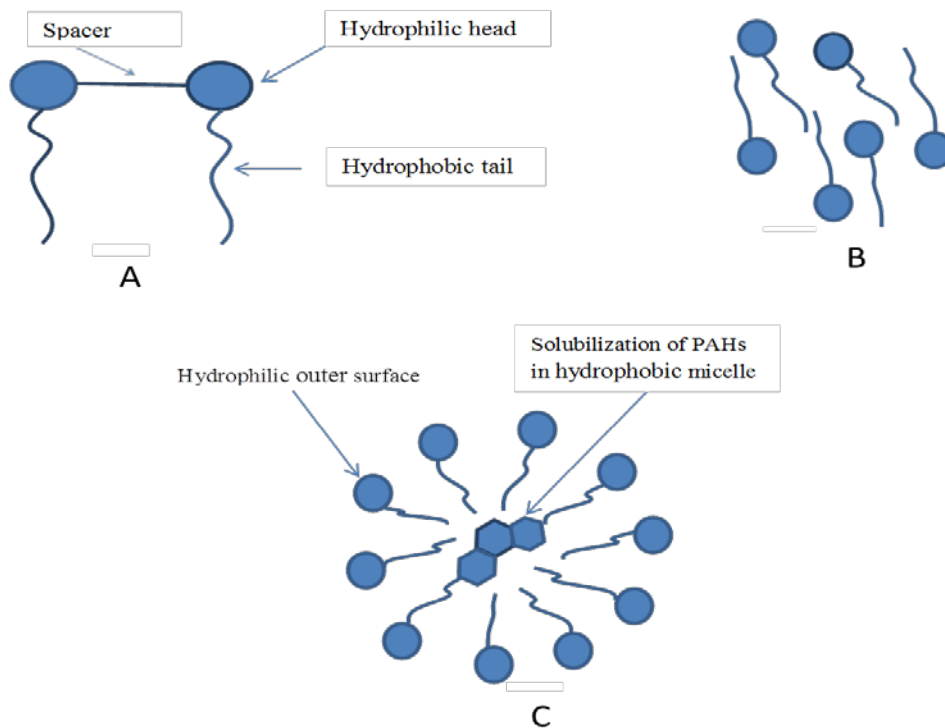


Figure 6.1: Schematic diagram of surfactant monomers and surfactant micelle. A) Gemini surfactant, B) Surfactant monomers, C) Surfactant micelles

As shown in Figure 6.2, the solubility enhancement of PAHs occurs at a surfactant concentration above CMC. The CMC value can be determined by plotting a graph of surface tension and/or interfacial tension with a surfactant concentration of the solution. The CMC is the point from where the trend in the graph changes with a reduction of surface and interfacial tension, whereas substance solubility starts to increase rapidly with an increase in the surfactant concentration (Figure 6.2).

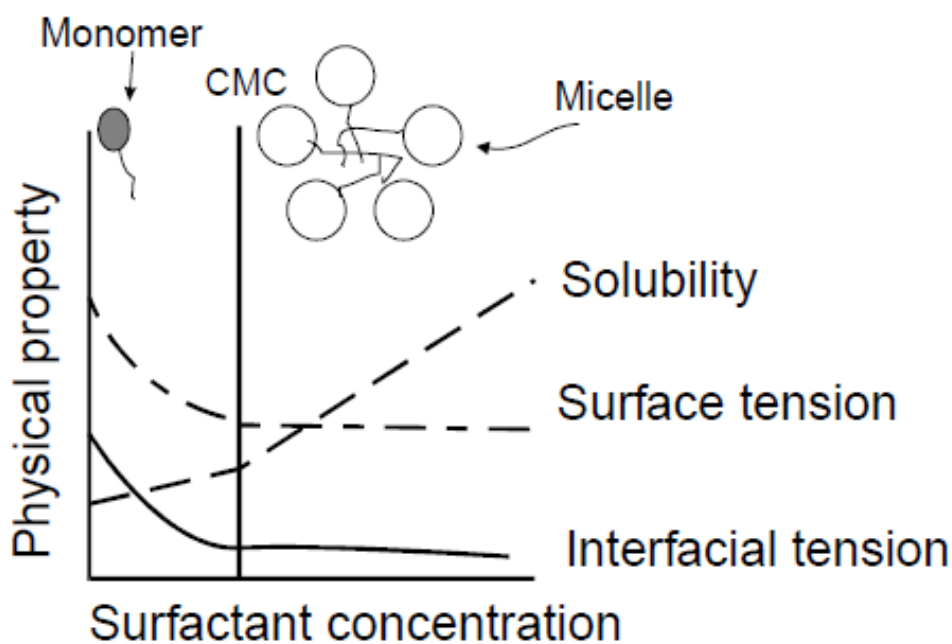


Figure 6.2: A schematic diagram which shows the relation between surface tension, interfacial tension and contaminant solubility with a concentration of surfactant (Mulligan et al. 2001)

At surfactant concentrations above the CMC, the development of micelles results in a sudden variation in the relation between surfactant concentration and physicochemical properties (surface and interfacial tension) of the solution (Makkar and Rocken, 2003, Mulligan et al. 2001). The physicochemical parameters of the surfactant-PAHs systems could be analysed by conductivity and surface tension measurements (Fatma et al. 2015; Panda et al. 2016).

Micelles have a hydrophobic core and hydrophilic outer surface. The hydrophobic core facilitates the accumulation of PAHs in the micelles and dissolves them by increasing the apparent aqueous solubility of PAHs. The effectiveness of a surfactant in solubilising PAHs is quantified by MSR as shown in equation 6.1 (Edwards et al. 1991):

$$MSR = \frac{S_{PAH,MIC} - S_{PAH,CMC}}{C_S - C_{S,CMC}} \quad \text{Eq.6.1}$$

where, $S_{PAH,MIC}$ is total apparent solubility of PAHs (mole/L) at surfactant concentration C_S ($C_S > C_{S,CMC}$), $S_{PAH,CMC}$ is the apparent solubility of PAHs (mole/L) at the CMC and $C_{S,CMC}$ is the concentration of surfactants (mole/L) at the CMC.

The MSR is used to determine the effectiveness of surfactants in solubilising PAHs. For example, 3 to 6 times higher MSR values with the use of biosurfactant (saponin) than with synthetic surfactants (Tween80, Brij58 and TX100) shows that the biosurfactant has a higher phenanthrene solubilising capacity than the synthetic surfactant (Zhou et al. 2011). Similarly, the MSR of fluorene, anthracene and pyrene was found to be greater with cationic surfactants than with anionic surfactants (Yadav et al. 2017). The PAH solubilisation within ionic surfactant micelles also depends on the electrostatic interaction between the ionic charge of surfactant head groups and a π -electron ring of PAHs (Panda et al. 2016).

Furthermore, the micelle-water partition coefficient (K_m) represents the distribution of organic compounds between surfactant micelles and the aqueous phase, as shown in equation 6.2:

$$K_m = \frac{X_m}{X_a} \quad \text{Eq.6.2}$$

where, X_m is the mole fractions of the solute in the micellar phase and X_a is the mole fractions of the solute in the aqueous phase (An et al. 2002).

This can also be expressed in terms of MSR, as shown in equation 6.3 (Zhou and Zhu 2004):

$$K_m = \frac{55.4 * MSR}{S_{PAH,CMC}(1+MSR)} \quad \text{Eq.6.3}$$

During PAH solubilisation in the surfactant micelles, the standard free energy changes from the aqueous phase to a micellar phase, as shown in equation 6.4 (Zana, 2002):

$$\Delta G_S = -RT \ln K_m \quad \text{Eq.6.4}$$

where, ΔG_S (kJ/mol) is the standard free energy change from aqueous phase to micellar phase, R is the gas constant (8.314×10^{-3} kJ/K/mol), and T is the absolute temperature (K)

Biosurfactants enhance the solubilisation of PAHs by increasing the bioavailability of PAHs (Makkar and Rocken, 2003). The use of a biosurfactant helps in growing the number of

microorganisms, resulting in an increase of nutrient uptakes on the hydrophobic surface of surfactants, which means that more PAHs can be degraded (Kuppusamy et al. 2017; Liu et al. 2017). Owing to their amphiphilic nature, surfactants accumulate at surfaces and interfaces, which reduces the surface and interfacial tension, enhancing the solubility and bioavailability of PAHs (Volkering et al. 1995). The main mechanisms of the surfactant-enhanced bioavailability of hydrocarbon are: a) dispersion of nonaqueous-phase liquid hydrocarbon due to a decrease in interfacial tension, b) increased solubility of hydrocarbon in the hydrophobic core of surfactant micelles, and c) facilitation of transport of hydrocarbon from the solid phase to the aqueous phase (Volkering et al. 1995).

In the surfactant micellar system, the hydrocarbon molecules can be either utilised by microorganisms after diffusing into the aqueous phase or can be directly taken by the microorganisms from the micelles (Li and Chen, 2009). The uptake of hydrocarbon from surfactant micelles is carried out by microbes at three different stages, as shown in Figure 6.3.

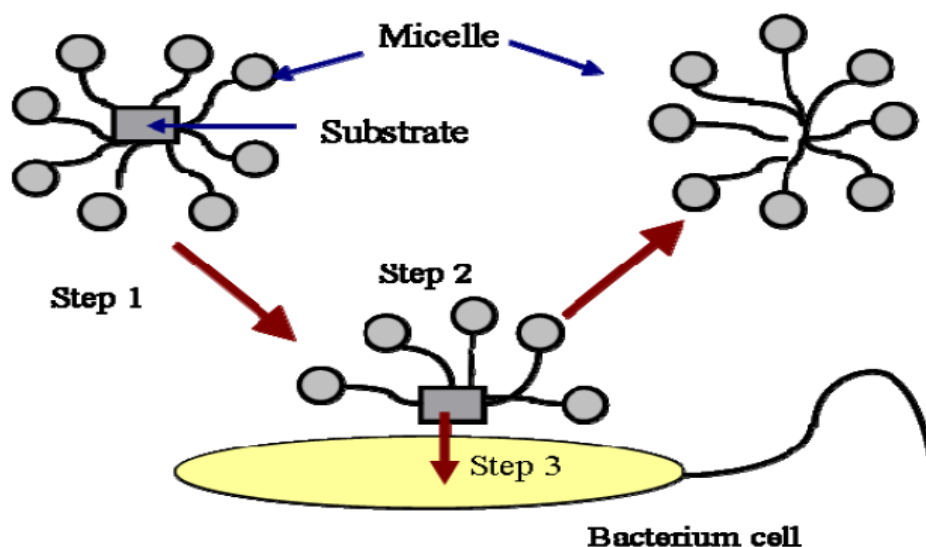


Figure 6.3: Hydrocarbon uptake by bacteria in surfactant micelles (Li and Chen 2009)

In the first step, the substrate-solubilised micelles are transported to the vicinity of the cells, in the second step the substrate-filled micelles exchange with the hemi-micellar layer of surfactant molecules formed around the cells, and in the last step the substrate transfers from the hemi-micelle to the bacterial cell (Li and Chen, 2009).

6.7 Conclusions

SER is a promising technique in removing PAHs from soil and aqueous media with the selection of a proper surfactant(s) and environment for the targeted PAH(s). There are mainly chemical (synthetic) and natural (bio) surfactants, which can be further classified as nonionic, cationic, anionic and zwitterionic surfactants. Surfactants can also be used in the form of CGAs in the treatment of PAHs. Use of a surfactant increases the apparent solubility of PAHs, which assists in the mobility and biodegradability of PAHs. The micellar solubilisations of PAHs are more effective in the mixed system than in the single micellar system because of the reduction of the surfactant quantity and the level of surfactant pollution in the environment. Biosurfactants have many potential advantages such as biodegradability, lower toxicity and a wide range of environmental resilience. However, in some cases, the use of surfactants inhibits the microbial activities. SER of PAHs depends on many parameters such as surfactant concentration, PAH hydrophobicity, temperature, pH, salinity, DOM, co-solute, HLB of surfactant and the octanol-water partitioning coefficient of PAHs. However, further study is needed to understand the relationship between pH and temperature, including various environmental conditions in the surfactant-enhanced PAH solubilisation. Selecting the proper type and quantity of surfactants could improve PAH solubilisation and biodegradation up to 99.99% without an adverse impact on the environment. The findings of this review would be helpful for future research into optimising the SER of PAHs from soil and water media. PAHs solubilisation with surfactants has been studied based on laboratory experiments and discussed in chapter 7.

Chapter 7

PAH solubilisation with anionic and nonionic surfactants in single and mixed micelles

7.1 Introduction

As discussed in chapter 6, surfactant enhanced solubilisation is one of the main mechanisms in surfactant enhanced remediation of PAHs from aqueous and solid media. Thus, surfactant enhanced PAHs solubilisation has become of high concern in removing PAHs from aqueous media and from CW bed media. Biodegradation is one of the main mechanisms to detoxify the PAHs by using varying microorganisms (Li et al. 2015; Sun et al. 2014; Jiao et al. 2014; Tejada-Agredano et al. 2013; Abd-Elsalam et al. 2009), however, this mechanism has been limited due to less aqueous solubility property of PAHs (Alcantara et al., 2009). Use of surfactants could overcome this shortcoming by solubilising PAHs and increasing bioavailability (Makkar and Rocken, 2003) which ultimately enhanced PAHs remediation with environmental friendly techniques.

The study on surfactant enhanced remediation of PAHs has been presented in chapter 6 which has mainly focused on types of surfactants, impact in PAHs biodegradation, factor affecting SER and mechanisms of surfactant enhanced solubilisation. However, detail study on PAHs solubilisation with surfactants in their single and mixed micelle system has been limited. Thus the main aim of this study is to further evaluate PAH solubilisation capacity of anionic and nonionic surfactants based on laboratory experiments which include comparison of single surfactant micelles and mixed surfactants micelles in PAH solubilisation, selection of effective ratio of anionic-nonionic surfactant in PAH solubilisation, comparison of PAHs solubilising capacity of anionic surfactants and nonionic surfactants in their mixed micelles.

7.2 Materials and methods

Tween80 (density 1.08 g/ml) from Acros Organics, acetone (≥ 99.9 pure), Tween20 (density 1.095 g/ml), solid phenanthrene (≥ 99.9 pure), SDS (density 1.03 g/ml), Tetrachloroethylene

(C₂Cl₄) (\leq 100% pure) and SDBS (technical grade) from Sigma Aldrich and liquid phenanthrene (99% pure) from Supelco were obtained to conduct the laboratory experiments.

7.2.1 Comparison of single and mixed micelle systems in phenanthrene solubilisation

Phenanthrene solubilisation tests with two anionic surfactants (SDS and SDBS) and their mixed micelles (anionic to nonionic ratio 1:9) with Tween80 were carried out in batch experiment. Anionic to nonionic ratio was maintained 1:9 based on the past literature (Zhang and Zhu, 2010) which demonstrated the highest desorption of phenanthrene in soil-water system. 40 ml of each single and mixed surfactants solution was prepared in conical flasks (250 ml) with total surfactant concentration of 0.5 mM. Three samples were prepared for each type. 80 mg of solid phenanthrene was added separately in all samples and flasks were sealed with parafilm and aluminium foil to prevent evaporation of solvents. Afterwards, the samples were placed in platform shaker and mixed at 100 rpm for 48 h. Shaking time 48 h was chosen based on literatures (Liang et al. 2016 and Yang et al. 2015) and preliminary experiments conducted in laboratory. The supernatant of each sample was collected in the 10 ml glass conical test tube and PAH was extracted by using dispersive liquid-liquid micro extraction method where (C₂Cl₄) was used as extraction solvent and acetone was used as disperser solvent (Rezaee et al. 2006) and PAH was analysed in gas chromatography connected with flame ionization detector (GC-FID). The experiment was carried out at room temperature (20 °C).

7.2.2 Selection of proportion of anionic and nonionic surfactants in mixed systems

Phenanthrene solubilisation tests were conducted with anionic-nonionic surfactants at different proportions (1:9, 2:8, 4:6, 6:4, 8:2 and 9:1) for total surfactants concentration of 0.5 mM. 100 ml of surfactants solution of each proportion was placed in conical flasks (250 ml). Duplicate samples were prepared for all types of samples. Solid phenanthrene was added separately in all samples with 2 g/L as described in Iglesias et al. (2014). The flasks were then sealed with parafilm and aluminium foil to prevent evaporation of solvent and placed on platform shaker. Mixing was carried out at 100 rpm for 48 h. The experiment was carried out at room temperature (23 °C). At the end of experiment, the supernatants from all conical flasks were collected in 10 ml amber colour glass bottles and were analysed with spectrofluorophotometer. The experimental setup is presented in Figure 7.1.



Figure 7.1: Experimental setup for surfactant enhanced PAH solubilisation

7.2.3 Effect of surfactants concentrations in phenanthrene solubilisation with anionic-nonionic mixed surfactants

Effect of surfactant concentrations was carried out for total surfactant concentrations of 1, 2, 3, 4 and 5 mM. The ratio of anionic and nonionic surfactants was 1:9. Nonionic surfactants considered in laboratory experiment were Tween80 and Tween20. Batch experiment was performed in the laboratory with similar process described at section 7.2.2 and supernatants were analysed with spectrofluorophotometer after 48 h.

7.2.4 Method development for analysis of PAH

7.2.4.1 GC-FID set up for phenanthrene analysis

The phenanthrene was analysed using gas chromatography Trace 1300 GC (Thermo Scientific) with flame ionization detector (FID) system equipped with a TG-5 SilMS 30 m × 0.25 mm × 0.025 μm capillary column. The carrier gas was high-purity helium. The injection port temperature was maintained at 250 °C. The GC temperature program started at 90 °C for 1 min and then increased at a rate of 25 °C per minute to 280 °C. The temperature was then increased to 300 °C with a rate of 4 °C per minute and held at 300 °C for 5 min. The injection

mode was splitless and 1 μl volume was injected. The FID temperature was maintained as 280 $^{\circ}\text{C}$.

7.2.4.2 Standard Calibration curve in GC-FID

Standard calibration curve was plotted for phenanthrene concentrations 31.25 to $\mu\text{g/L}$ (Figure 7.2). Samples were diluted serially by half from 1000 $\mu\text{g/L}$ to 31.25 $\mu\text{g/L}$. The standard phenanthrene solutions were prepared in acetone.

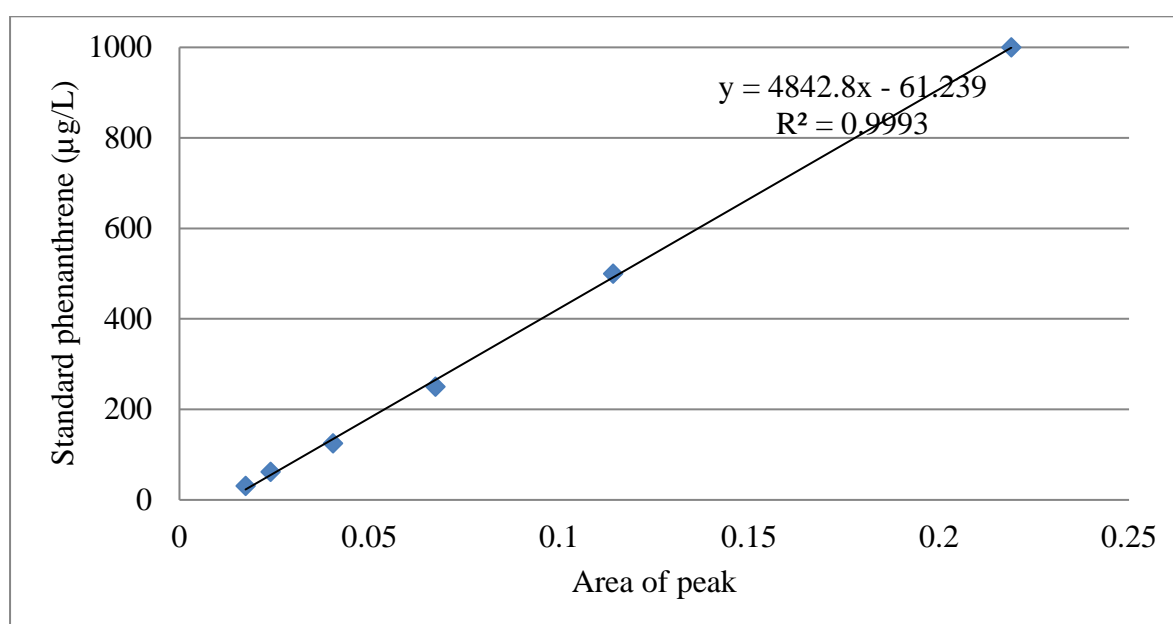


Figure 7.2: Calibration curve for phenanthrene analysis with GC-FID

The retention time to obtain the peak was not significantly shifted which was only varied from 7.782 to 7.805. There were some variations in concentrations of phenanthrene when compared to targeted concentrations (Table C1 in Appendix) which might be due to error during dilution process due to less soluble nature of PAH. With the selected concentrations range, a good linear equation was obtained with correlation coefficient of 0.999.

7.2.4.3 Spectrofluorophotometer set up

To analyse PAH in spectrofluorophotometer, the excitation wavelength of 250nm and emission wavelength 290 to 325 nm was selected at band width of 5nm. The excitation and

emission wavelengths were selected after performing numbers of test to make sure the formation of clean and well located spectrum peak.

7.2.4.4 Standard calibration curve in Spectrofluorophotometer

For standard calibration curve, phenanthrene samples were prepared with concentration range from 0.004 to 1mM. The sample prepared was diluted serially by half from 1 to 0.004 mM. Standard calibration curve was established for intensity and phenanthrene concentration where emission wave length for peak was only varied from 303.8 to 305.8 (Table C2 in Appendix). The linear equation was well fitted with correlation coefficient value of 0.998 (Figure 7.3).

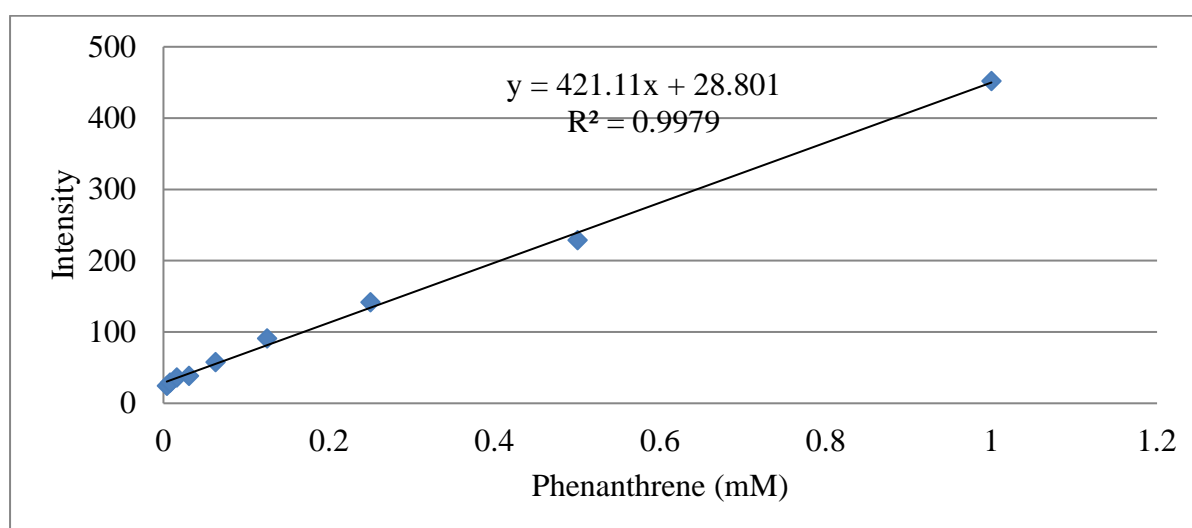


Figure 7.3: Standard curve for phenanthrene concentrations and their corresponding intensity detected by spectrofluorophotometer

7.3 Results and discussion

7.3.1 Comparison of single and mixed micelles in phenanthrene solubilisation

The phenanthrene solubility was 329.39 $\mu\text{g/L}$ with SDS and 492.07 $\mu\text{g/L}$ with SDBS. Furthermore, phenanthrene solubility was obtained as 2680.52 $\mu\text{g/L}$ with SDS-Tween80 and 3064.03 $\mu\text{g/L}$ with SDBS-Tween80 (Figure 7.4). Solubilisation capacity of mixed surfactants was found greater than single surfactant for both types of anionic surfactants. Similarly, 1:9 SDBS-Tween80 was found effective in phenanthrene desorption from soil-water system when

compared to phenanthrene desorption with only SDBS (Zhang and Zhu, 2010). Furthermore, phenanthrene solubilisation capacity of SDBS was observed greater than that of SDS and similar result was also presented by Shi et al. (2015) for PAHs solubility with SDS and SDBS.

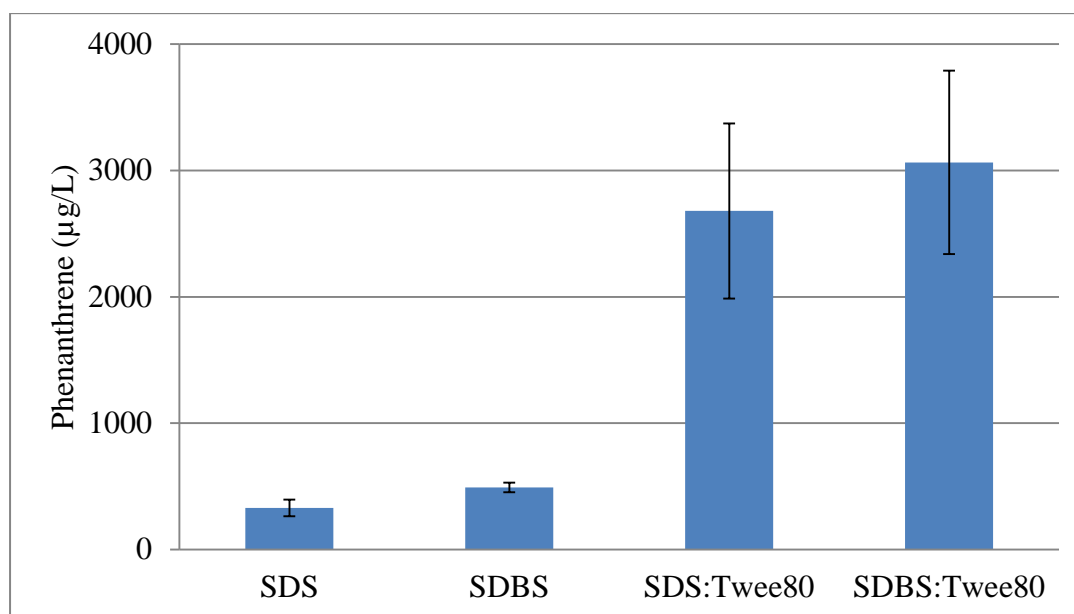


Figure 7.4: Phenanthrene solubilisation with anionic and anionic-nonionic surfactants (0.5mM)

From experimental analysis it was observed that higher amount of phenanthrene was solubilized with anionic-nonionic mixed surfactants when compared with only anionic surfactants. The synergistic effect of mixed micelles has been presented in section 6.3 based on available literature. Furthermore, SDBS was found better than SDS in phenanthrene solubilisation. Therefore, SDS was excluded in further tests and only SDBS was used as anionic surfactant to form mixed micelles with nonionic surfactant Tween80. In addition to Tween80, Tween20 was also tested to compare the performance of two nonionic surfactants in phenanthrene solubilisation. In study by Shi et al. (2015), one nonionic surfactant (TX100) was mixed with two anionic surfactants as SDS and SDBS but further experimental analysis of this study considered one anionic surfactant SDBS and two nonionic surfactants as Tween80 and Tween20. The average value of three samples was considered during plotting graph for each type. The variation of the results in triplicate samples (error bars in Figure 7.4)

might be due to presence of water in the extracted sample which would affect in equal distribution of PAH in the sample due to less aqueous solubility of PAH.

7.3.2 Phenanthrene solubilisation with different proportions of anionic and non-ionic surfactants

To further verify the effective proportions of anioni-nonionic surfactants, different proportions of anionic and non-ionic surfactant were tested. The average values of results from duplicate samples are presented in (Table C4 in Appendix) for SDBS-Tween80 and in (Table C5 in Appendix) for SDBS-Tween20. Phenanthrene solubility with SDBS-Tween80 was less than solubility with SDBS-Tween20 (Figure 7. 5) for all proportions of anionic and nonionic surfactants.

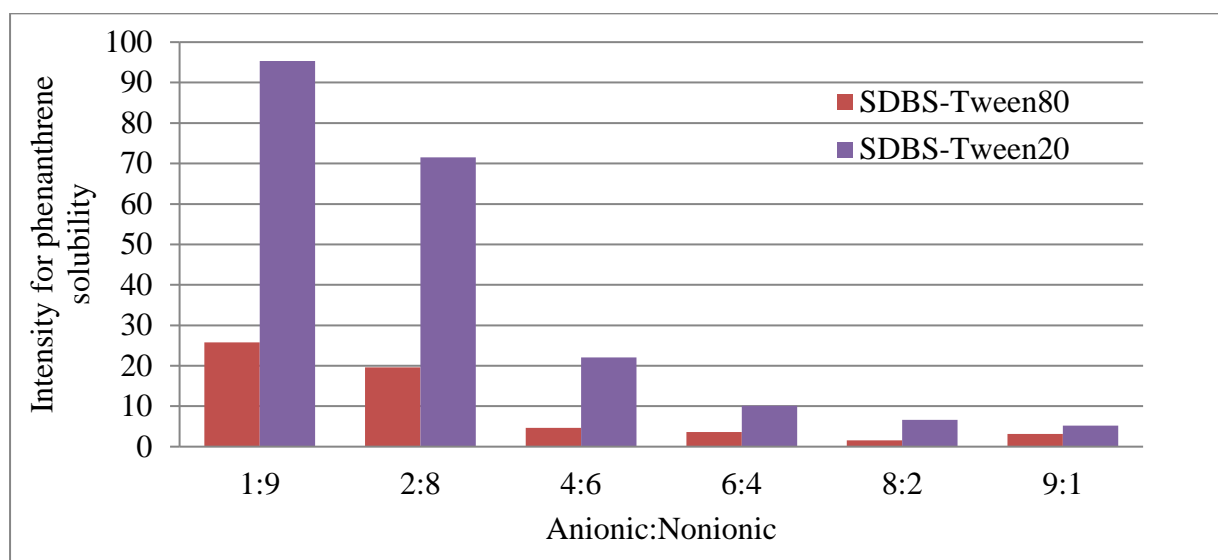


Figure 7.5: Phenanthrene solubility with different proportions of anionic surfactant with Tween80 and Tween20

The highest phenanthrene solubility result was observed for anionic-nonionic surfactant at proportion 1:9 with both nonionic surfactants systems. The phenanthrene solubility was decreased with increasing proportion of anionic surfactant which is in agreement with study by Zhang and Zhu (2010). Similarly, anionic-nonionic mixed surfactants (SDS:TX100) at ratio 1:9 was found effective when compared to 2:8, 3:7, 4:6, 1:1 and 7:3 in PAHs (phenanthrene, fluoranthene and benzo(a)pyrene) solubilisation (Shi et al. 2015).

Moreover, SDBS-Tween20 showed better solubilisation capacity than SDBS-Tween80 for all proportions of anionic-nonionic surfactants systems. Aryal and Liakopoulou-Kyriakides (2013) reported that higher degradation of phenanthrene and pyrene was observed with Tween20 when compared with Tween80 indicating PAHs solubilising capacity of Tween20 greater than PAHs solubilising capacity of Tween80. Furthermore, Shen et al. (2007) reported that SDBS-Tween20 is more effective than only Tween20 in PAH solubilisation. Thus, the mixed micelles formed by 1:9 SDBS-Tween20 would be effective in PAHs solubilisation and PAHs remediation process.

7.3.3 Phenanthrene solubilisation with mixed micelles with varying concentrations of surfactants

The linear relationship was found between surfactant concentrations and PAH solubility as phenanthrene solubility was increased with increased of surfactants concentrations from 1 mM to 5 mM. For instant, phenanthrene solubility was 0.244 mM with 1 mM SDBS-Tween20 and reached up to 0.776 mM with 5 mM SDBS-Tween20. Similarly, phenanthrene solubility was 0.081 mM with 1 mM SDBS-Tween80 and increased to 0.475 mM with 5 mM SDBS-Tween80 (Figure 7.6). The linear relationship of phenanthrene with surfactant concentrations has been reported in many other studies (Liang et al. 2016; Li et al. 2015; Iglesias et al. 2014). Only single surfactant was considered in study by Liang et al. (2016) and Li et al. (2015) as TX100 (nonionic surfactant) and rhamnolipid (biosurfactant) respectively. However, saponin and Tween80 were considered in both single and mixed systems to see the effect of surfactant concentration in phenanthrene solubilisation in Iglesias et al. (2014) where saponin:Tween80 at ratio 1:1.2 found most effective.

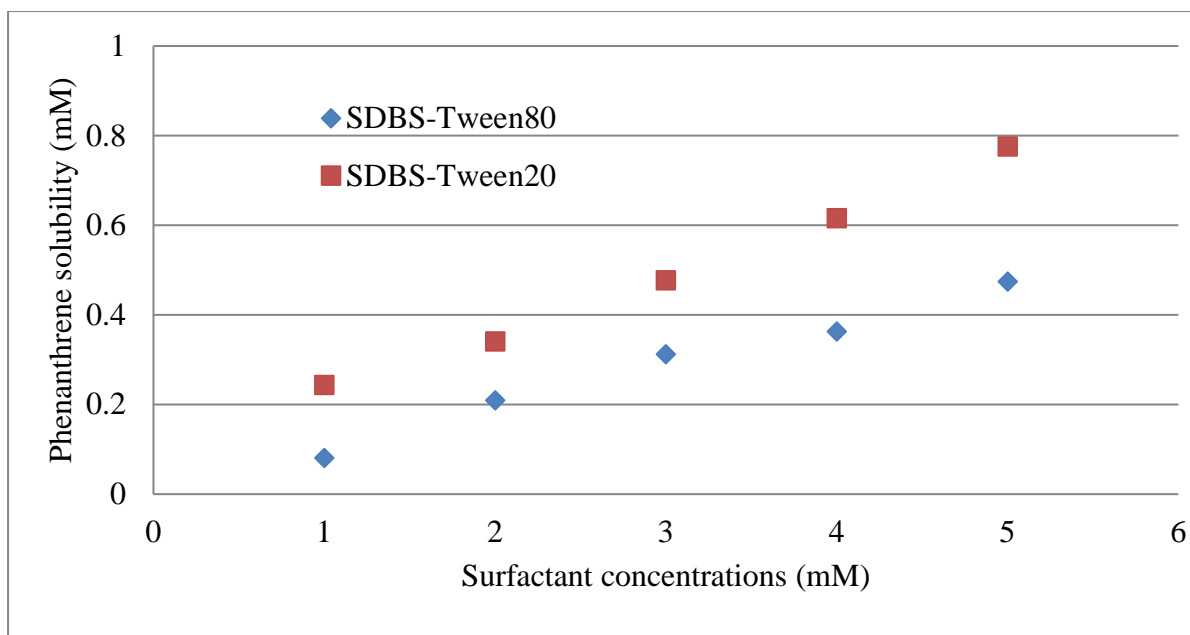


Figure 7.6: solubility of phenanthrene with varying concentrations of surfactants

7.4 Conclusions

From the analysis and discussion of experimental results, it was observed that SDBS was effective in phenanthrene solubility when compared to SDS. Anionic-nonionic mixed surfactants systems were found effective in phenanthrene solubility when compared to single surfactant systems. The highest phenanthrene solubility was obtained at anionic-nonionic surfactants ratio 1:9 among the various proportions considered in the experiments. Furthermore, phenanthrene solubility increased with increase of surfactants concentrations from 1 mM to 5 mM for all systems. Moreover, Tween20 was found effective when compared to Tween80 in phenanthrene solubility for all tested proportions of anionic-nonionic systems for all tested concentrations of surfactants.

After detail study of adsorption (chapter 3 and chapter 4) and solubilisation (chapter 5, chapter 6 and chapter 7) characteristic of PAHs, performance of CWs in PAHs remediation has been studied in chapter 8. It is crucial to understand PAHs adsorption and solubilisation/desorption behaviour of PAH in CWs to design and operate CWs to remediate PAHs in effective and efficient manner.

Chapter 8

Assessment of PAHs removal in constructed wetland

8.1 Introduction

Due to the toxic, mutagenic and carcinogenic properties of PAHs, significant interests in developing appropriate removal process have been raised (Makkar and Rockne 2003; Chen et al. 2008). A number of methods have been investigated to treat PAHs to mitigate the possible risk of PAHs on the environment and human health. Physical, chemical, thermal, biological and phytoremediation processes (which comprise incineration, thermal desorption, radio frequency heating, oxidation, ion exchange, photolysis, adsorption, electrolysis, chemical precipitation, natural attenuation, biostimulation, bioaugmentation, rhizofiltration, phytoextraction, phytostabilisation and phytodegradation techniques) are the major PAHs treatment methods (Zhou et al. 2013; Wang et al. 2014; Li et al. 2015; Sun et al. 2014; Peng et al. 2014; Li et al. 2014; Hu et al. 2014). Among them, PAHs treatment by using constructed wetland (CW) is the effective and efficient method because of a) its less construction and operational cost, b) it provides additional wildlife habitat, c) it is environmental friendly, d) aesthetic and generally well received by the public (Puigagut et al. 2008; Eifert 2000; Fournel et al. 2013).

CW system is hybrid system which possesses multi treatment options (physical, chemical and biological). The physical process comprises sedimentation, filtration, absorption, volatilisation, the chemical process comprises precipitation, adsorption, hydrolysis, oxidation reduction and biological process comprises bacterial metabolisms, plant metabolisms, plant absorption and natural die-off (Eifert 2000). CW technique further provides opportunity of phytoremediation and biodegradation of adsorbed PAHs where plants and microorganisms are involved to break down, remove, absorb and detoxify PAHs. Thus use of CW is considered to be as most effective management practice in removing storm runoff pollutants including PAHs (EPA 2014; Wojciechowska 2013; Kadlec 2008; Tromp et al. 2012; Fountoulakis et al.

2009; Kadlec and Wallace 2009) with no dead-end products to further contaminate the environment.

The basic PAHs removal mechanisms in a constructed wetland are, adsorption, plant uptake, rhizodegradation, biodegradation and volatilization (Fountoulakis et al. 2009; Wojciechowska 2013; Yi et al. 2016; Herrera-Cardenas et al. 2016; Al-Sbani et al. 2016). Among different mechanisms, adsorption is the main mechanisms to remove aqueous PAHs in CW (Wojciechowska 2013), however, phytoremediation and bioremediation are crucial techniques to detoxify the PAHs adsorbed into CW bed media (Tian et al., 2017; Al-Sabani et al., 2016; Meng et al., 2014).

In plant assisted treatment of PAHs in CW, the pollutants either can be taken up directly by plants (Gerhardt et al. 2009) or can be degraded by plant associated enzymes and microorganisms (Liu et al. 2014; Yu et al. 2011). The former process is called phyto-extraction and later one is called rhizo-remediation. Rhizo-remediation is the complex process which includes roots, rhizosphere and microbes resulting effective PAHs treatment (Yu et al. 2011). There are many plants which have potential in removing PAHs from contaminated soil and water. For example, *Echinacea purpurea*, *Festuca arundinacea*, fire phoenix and *Medicago sativa L.* have been studied and found effective in PAH removal from contaminated soil (Liu et al. 2015). Furthermore, *Phragmites australis* and *Arundo donax* removed 16 PAHs from contaminated soil (Fountoulakis et al. 2009). Moreover, arabidopsis and rice has been found effective in phenanthrene removal from soil and water by transforming naphthalene dioxygenase system of *Pseudomonas* into the plants (Peng et al. 2014). The plants assisted bioremediation of PAHs in CW not only depends on the types of plants but also depends on different parts (root system, stems, and leaves) of the plants. For example, accumulation of USEPA categorized 16 PAHs were examined in different parts of *Glyceria maxima* plants and observed that PAHs in root system was 85 µg/kg, in leaves was 143 µg/kg and in stems was 92 µg/kg (Warężak et al. 2015).

There are several studies (Xu et al. 2016; Yi et al. 2016; Al-Sbani et al. 2016; Warężak et al. 2015) in PAHs removal by using constructed wetland which have focus only to limited area such as PAH removal by plants, evaluation of microbial community, temporal and spatial variation of PAH removal, however, the comparative study between various media and plant have been scarcely found. Therefore, the main objective of this study was to evaluate the PAH

removal efficiency with various types of CW bed media and to compare the removal efficiency of PAH with media and plant. This study further includes effect of spatial variation and evaluation of environmental parameters such as dissolved oxygen (DO), pH, oxidation redox potential (ORP) and temperature.

8.2 Material and Methods

White washed sand, *Dianella revoluta* plant, pipes, taps and fitting materials for CWs set up were purchased from Bunnings. PAC (density 0.25-0.6 g/cm³) from Sigma Aldrich, 100% pure ethanol from Westlab, GAC with size 3-4 mm from Rowe Scientific, zeolite (\leq 100% pure) from Sigma Life Science, bentonite ($>$ 95% pure) from Acros Organics and phenanthrene stock solution (99% pure) from Supelco were purchased. A cylindrical drum CR 110LT with 500 mm diameter and 800 mm height was obtained from Ideal System and 280*280*270 mm³ buckets were reused from the laboratory after proper cleaning to set CWs. Aquakem 200 from Thermo Scientific was used to analysed nitrogen and phosphorous and Spectrofluorophotometer RF- 5301PC from Shimadzu was used to analyse PAH.

8.2.1 Plant survivability test

Plant survivability test was carried out to make sure whether plant could grow properly inside the laboratory environment before setting the CWs. This test was performed using *Dianella revoluta* plant for four months from February 2016 to Jun 2016. The plant roots were washed (Figure 8.1A) and place in the sand media into the bucket (280*280*270 mm³) (Figure 8.1B). Tap water was fed by maintaining 3.226 to 3.95 mg/L nitrogen and 0.769 to 0.808 mg/L phosphorus. Water containing nutrients was fed when necessary for proper growth of plant.

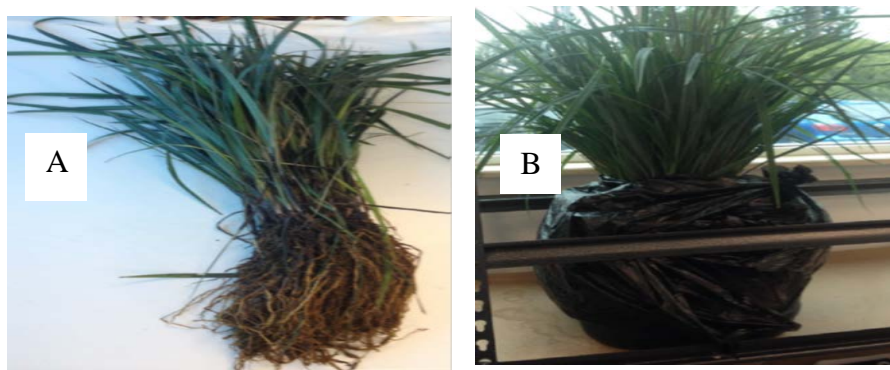


Figure 8.1: (A): Plant with washed roots, (B): Plant grown in sand media

8.2.2 Selection of PAH adsorption bed media of CW

Batch experiment was performed to select best phenanthrene adsorbent media among PAC, GAC, bentonite and zeolite. 500 mg of each adsorbent (PAC, GAC, bentonite and zeolite) was mixed in 50 ml solution containing 40 µg/L phenanthrene in 500 ml conical flasks at room temperature ($20\pm 1^{\circ}\text{C}$). The duplicate samples were prepared for all types of adsorbents. The flasks were sealed with parafilm and then aluminum foil (Figure 8.2A) to prevent evaporation of organic solvent and placed on platform shaker at 175 rpm for 48 h. The concentration of ethanol in all solution was not exceeded 1%. 8 ml supernatant from each flask was transferred into conical test tube (Figure 8.2B) and centrifused at 5000 rpm for 10 minutes to separate solid and liquid (Figure 8.2C). The supernatants from test tube were analysed with Spectrofluorophotometer to measured residual phenanthrene concentration at solution.

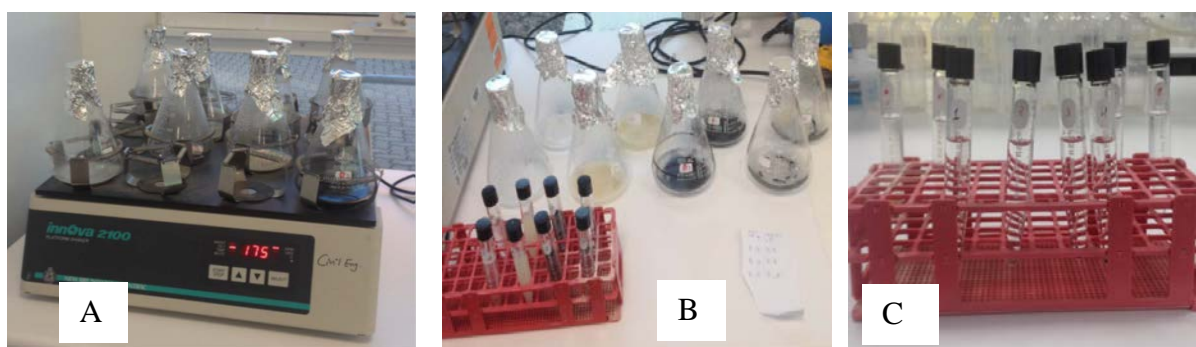


Figure 8.2: (A): Batch test for phenanthrene adsorption with 4 types of adsorbents, (B): Supernatant of adsorption test before centrifugation, (C): sample after centrifugation

Samples placed on shaker for phenanthrene adsorption batch test is presented in Figure 8.2 A. And supernatant placed in conical test tube is shown in Figure 8.2 B, where different colours can be seen for samples with different types of adsorbents.

8.2.3 Constructed wetland setup

To see the effect of different media, plant and spatial variation in phenanthrene removal, altogether six types of CWs were set. White washed sand was naturally dried by leaving on plastic on the bench inside laboratory (Figure 8.3) for one week. Five CWs were set in to $280*280*270\text{ mm}^3$ buckets and one in 500 mm diameter and 800 mm height drum.



Figure 8.3: Drying of washed sand on the bench of laboratory

CW1, CW2 and CW3 were set as detailed in Table 8.1. In all three cases the equal quantity of adsorption media was used. 8 L synthetic storm water containing 40 $\mu\text{g/L}$ phenanthrene and ethanol concentration not exceeded 1% was fed to all CWs and covered with black coloured plastic to prevent the evaporation of water. 2 L of influent sample was also added in all CWs after 2 months of CW set up. In addition to this, 1 L of water containing nutrients was added fortnightly in CW3 for proper growth of plant. The nitrogen concentration used was 3.0 - 3.15 mg/L and phosphorus concentration used was 0.76 to 0.77 mg/L in influent sample used for CWs with plants. The effluent samples were collected from CWs and concentrations of residual phenanthrene was analysed with spectrofluorophotometer.



Figure 8.4: CWs with different media. (A): CW with sand media, (B): CW with sand and PAC, (C): CW with sand, PAC and plant

To observe the effect of spatial variation of CW in PAH removal, 110 L cylindrical drum was used. 530 mm layer of 0.05% PAC by weight of sand was used as adsorption media in CW and the plant used was *Dianella revoluta* (denoted by CW* in Table 8.1). In this CW the effluent collection was maintained at three different levels at 320, 520 and 720 mm from top surface of drum which was 50 mm, 250 mm and 450 mm from surface of upper sand level. The perforated pipes were used to collect the sample throughout the cross section of CW. The taps were fitted at both sides of perforated pipe at three levels. This CW has been presented in Figure 8.5). Synthetic stormwater (40 L) containing 40 µg/L phenanthrene with ethanol concentration < 1% was fed into the system. The residual phenanthrene of effluents from both sides of each level was collected after 5 h of feeding and analysed with spectrofluorometer based on 'Quantitation' function.



Figure 8.5: CW setup to study effect of depth in PAH remediation. (A): Porous pipes fitted at different depth, (B): CW after feeding bed materials

Unfortunately, there was leakage from the bottom of drum in second day and could not take further data. The drum was checked for 1 week by filling tap water but there was no leakage during trial test with only water.

After this incident, another two CWs were set as CW4 and CW5 (Figure 8.6) in the buckets same size as used for CW1, CW2 and CW3. The media used in CW4 were sand and 0.05% PAC by weight of sand. The media used in CW5 were sand, 0.05% PAC by weight of sand and plant.



Figure 8.6: CWs with 0.05% PAC by weight of sand. (A): Without plant, (B): With plant

CW4 and CW5 were set up 5 weeks after setting up of CW1, CW2 and CW3. The feeding of water in CW4 was similar to CW1 and CW2 and feeding of water in CW5 was similar to CW3.

Table 8.1: Summary for different types of CWs setup

CW	CW1	CW2	CW3	CW4	CW5	CW*
Materials used in CW	sand	sand +PAC	sand+PAC+plant	sand +PAC	sand+PAC+plant	sand+PAC+plant
PAC % by weight of sand	0	0.002	0.002	0.05	0.05	0.05
Level of media from bottom of CW (mm)	220	220	220	220	220	530

8.2.4 PAH Analysis of CWs effluent

The PAH analysis method in spectrofluorophotometer was similar to described in section 4.2.4. The PAH of effluent samples were analysed at 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 12, 15, 17 and 20 weeks for CW1, CW2, CW3 and at 1, 2, 3, 4, 5, 6, 7, 8, 10, 12 and 15 weeks for CW4 and CW5. To maintain the quality of Spectrofluorophotometer results, phenanthrene standards were measured regularly.

8.2.5 Monitoring of physicochemical parameters

For physicochemical analysis of DO, ORP, pH, and temperature of CWs effluents were measured at 1, 2, 5, 7, 10, 12 and 15 weeks for CW1, CW2, and CW3 and at 2, 5, 7 and 10 weeks for CW4 and CW5.

8.2.6 Quality control

All analytical operations were conducted under quality control. Commercial liquid phenanthrene stock solution with known concentration was used. The glassware was cleaned with detergent with warm water and then rinsed with pure water and well dried before used. Average of 3 tests was considered the final result in spectrofluorophotometer. Duplicate samples were prepared in batch experiment. Standard phenanthrene was measured at regular interval of time to confirm the used standard template was reliable for PAH analysis. The effluents from all CWs were collected into amber colour glass bottles and immediately analysed by Spectrofluorophotometer. Furthermore, physicochemical parameters were also measured immediately after collecting samples from CWs.

8.3 Result and discussion

The calibration curves were established by running standard samples and other samples were measured based on standard calibration curve. The results obtained were analysed and discussed with presentation of tables and graphs to see whether the desired outcomes were obtained.

8.3.1 Plant surviability test results

The plant was grown with good health. Result of this test evaluated the possibility of CWs set up inside the laboratory. Based on this experiment, the amount of nutrients and water were decided for CWs.

8.3.2 Selection of PAH adsorption media

Four types of adsorbents as PAC, GAC, bentonite and zeolite were tasted for phenanthrene adsorption. After performing the batch adsorption test, the residual phenanthrene concentration of the supernatant was measured to calculate the phenanthrene removal efficiency with different types of adsorbents.

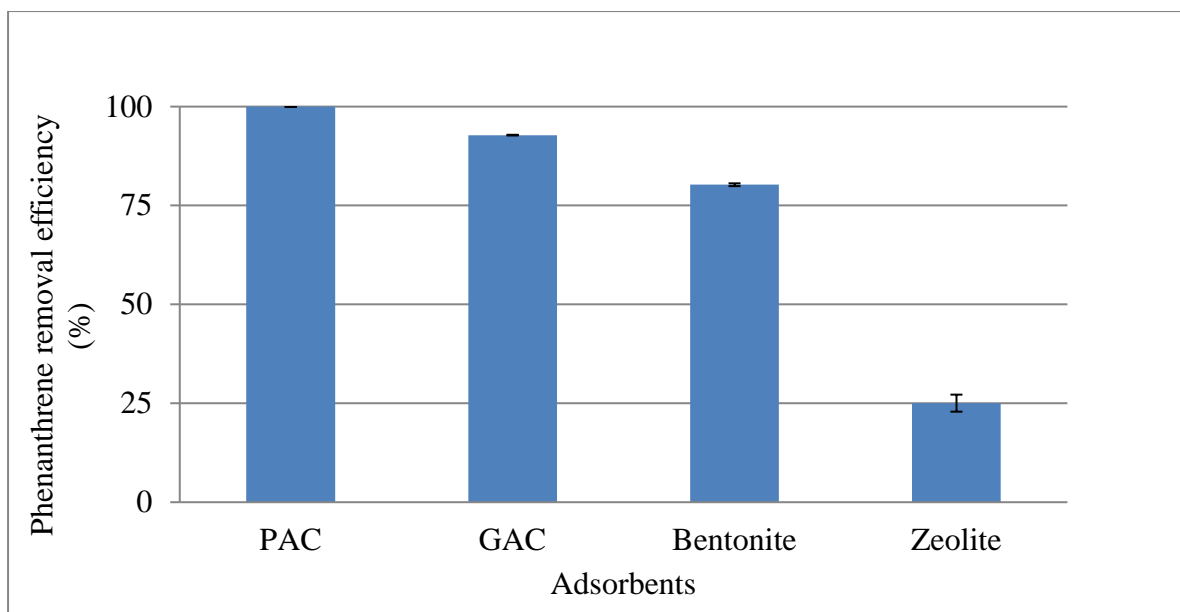


Figure 8.7: Phenanthrene removal capacity of four adsorbents

PAC is the best adsorbent for phenanthrene adsorption with 100% removal (Figure 8.7). Among four media, zeolite has been found less effective in phenanthrene adsorption with removal efficiency of only 25.04%. Phenanthrene removal efficiency of GAC and bentonite were found 92.79 and 80.25% respectively. The aqueous PAHs removal with PAC was obtained as 99% whereas removal with GAC was 64% with 2% (of contaminated soil) AC for PAHs concentration of 38 mg/kg (Brandli et al. 2008). The reason of better adsorption capacity of PAC than GAC is due to smaller particle size of PAC resulting higher specific surface area to adsorb PAHs. Based on result of adsorption test, PAC was selected as PAH adsorption media to mix with sand as CWs bed media.

8.3.3 PAH removal in CWs

8.3.3.1 Comparison between sand and PAC in phenanthrene removal

To evaluate the phenanthrene removal capacity of sand and PAC, data observed for CW1, CW2 and CW4 were considered. The PAH removal efficiency was found higher when PAC was mixed with sand (CW2) when compared to only with sand media (CW1) (Figure 8.6). Furthermore, PAH removal by using CW was increased with increased of PAC proportion which could be seen from results for CW2 and CW4 (Figure 8.8).

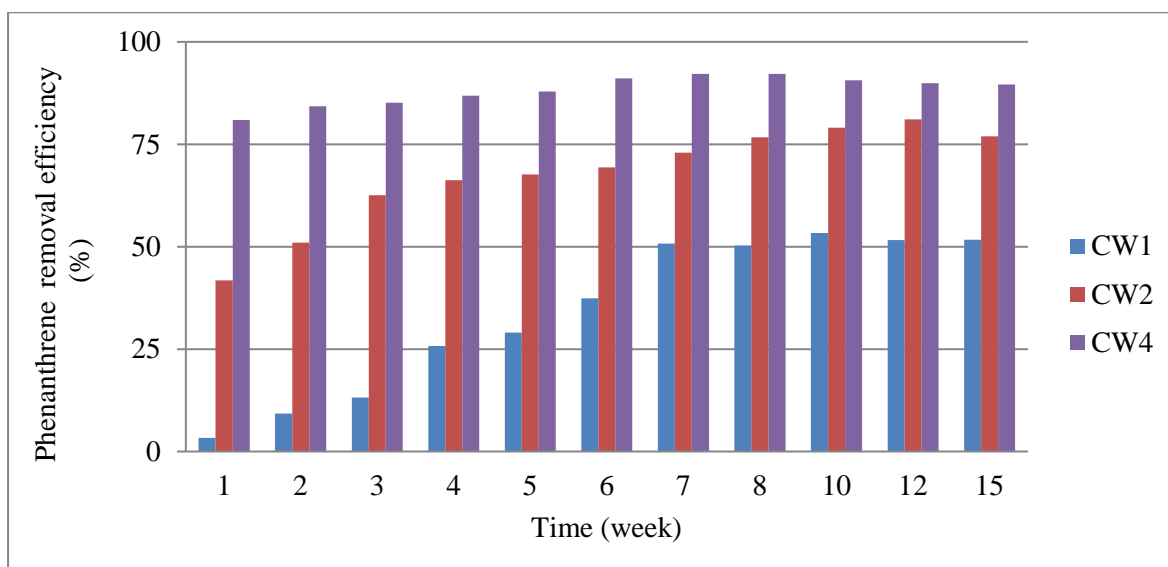


Figure 8.8: Comparison of CW1, CW2 and CW4 in phenanthrene removal

Phenanthrene removal capacity of CWs increased with time until certain period and again started to decrease. For instant, maximum PAH removal efficiency was observed at week 9 for CW1, week 12 for CW2 and week 8 for CW4 (Table 8.6) with corresponding removal efficiency of 53.60, 81.11 and 92.2% respectively. The decrease in phenanthrene removal might be due to desorption of phenanthrene from adsorbed media. 95% phenanthrene was removed with PAC from contaminated sediment (Amstaetter et al. 2012) where 50 mg PAC was used per 5g sediment. An effective result was obtained in this study even with less (0.002%) amount of PAC.

8.3.3.2 Comparison between sand, PAC and plant in phenanthrene removal

From section 8.3.3.1, it is clear that addition of PAC with sand media could enhance the PAH removal capacity. In this section, further evaluation of plant in PAH removal is considered.

The higher removal capacity of CW3 was found when compared to CW2 indicating the positive influence of plant in PAH removal enhancement (Figure 8.9). Thus, the CWs order in phenanthrene removal was found as CW3 > CW2 > CW1 (Figure 8.9) for 20 weeks' time period.

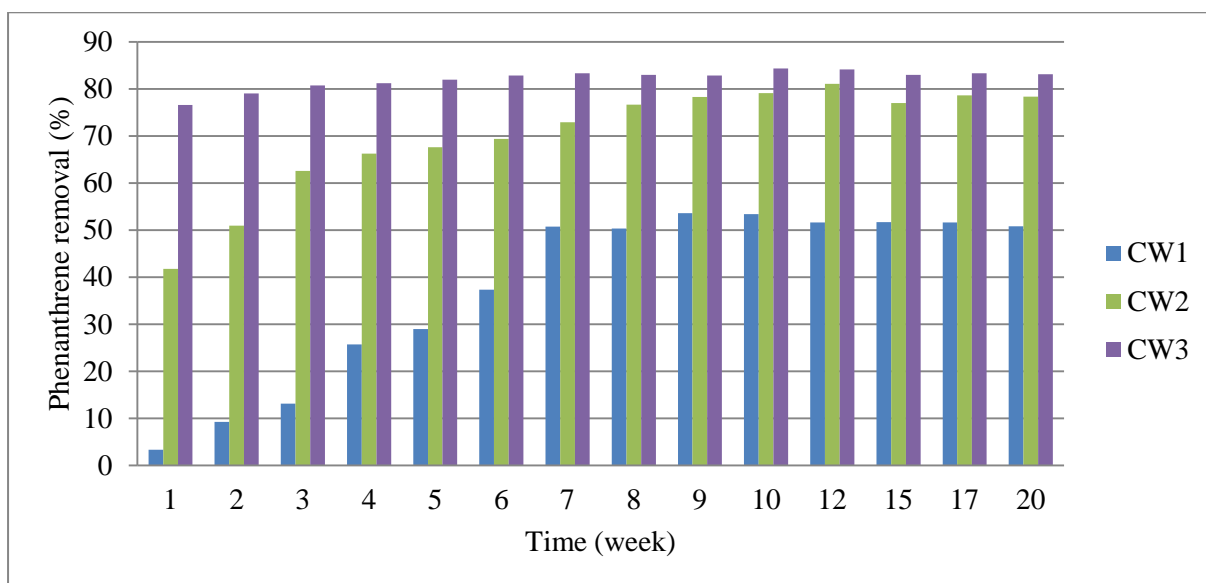


Figure 8.9: Comparison of CW1, CW2 and CW3 in phenanthrene removal

CW5 removed more PAH than CW3 which is due to higher concentration of PAC on CW5 than CW3 until 8th week. However, result observed was in opposite order after 10th week (Figure 8.10) which was due to degradation in health of plant. The phenanthrene removal by CW5 was increased until 4th week and not found further consistent pattern.

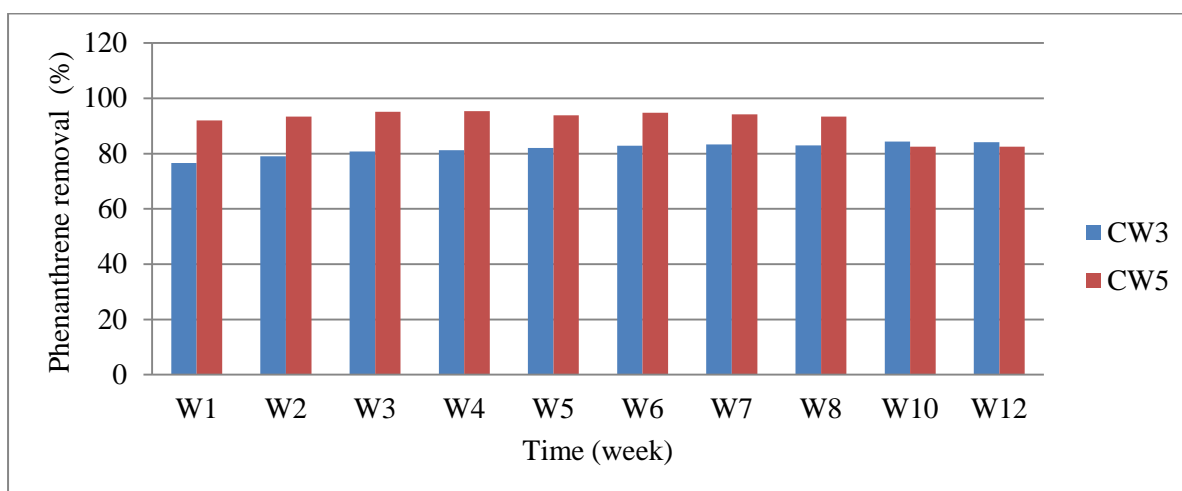


Figure 8.10: Phenanthrene removal by CW3 and CW5 up to 12 weeks

The plant in CW5 was started to dry from 8th week and totally dried after 14th weeks. The reason for not surviving the plant in CW5 might be effect of powder activated carbon at that particular concentration. A study by (Nolan et al. 2014) also reported that there is negative effect of activated carbon on plants. The PAC has more negative effect than GAC on PAH remediation with plant-microorganisms system (Jakob et al. 2012). As the phenanthrene removal efficiency was decreased in CW5 after week 8 due to negative effect of PAC, further detail study is required to optimise PAC concentration in CW bed media to remove PAH efficiently.

8.3.3.3 Effect of depth of CW on phenanthrene removal

To evaluate effect of spatial variation in PAH removal, sample were taken at various depths of CW. After analysing the residual phenanthrene concentrations in the effluents from both sides of all three different levels, the effect of spatial variation was observed. The observed residual phenanthrene concentration was decreased with the depth of adsorbing media indicating PAH removal efficiency was increased with increase of depth of CW bed media (Figure 8.11).

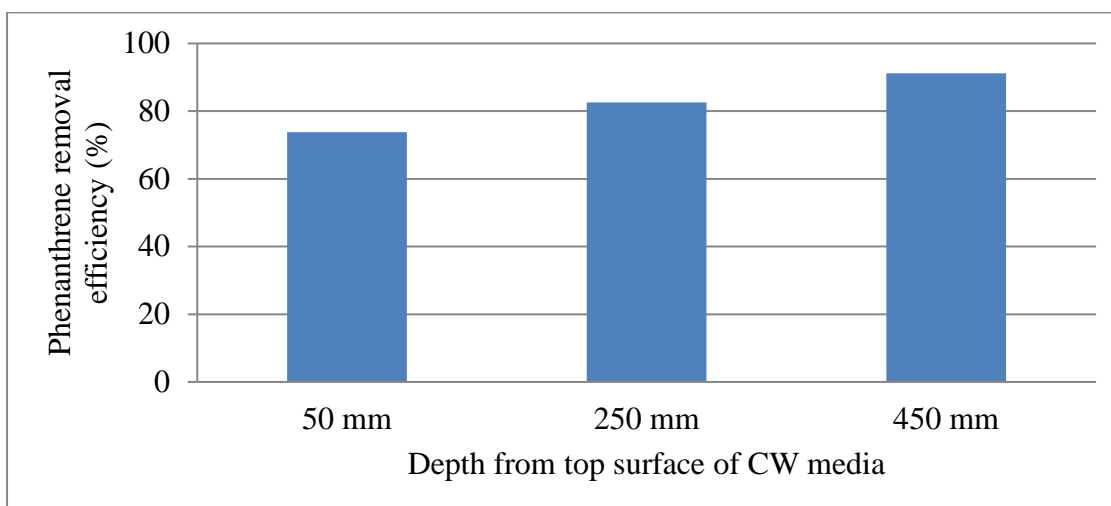


Figure 8.11: Effect of spatial variation in phenanthrene removal

However, the adsorption enhancement rate was decreased with depth of media as 73.82% phenanthrene was removed with 50 mm depth of media and remaining 17.34% was adsorbed

within 400 mm depth of media. Higher amount of PAH could be adsorbed at upper layer than at bottom layer of CW, however, total removal efficiency would increase with thickness of CW bed media. Similar result was observed in other study (Yi et al. 2016). The increase in PAH removal with depth of media is due to availability of more PAH adsorbing sides.

8.3.3.4 Analysis of Environmental parameters in different CWs

Environmental parameters such as DO, ORP, pH and temperature have been monitored in the samples from five CWs. The observed results portrayed for further clarification.

The DO was decreased with time until 12th week for CW1, CW2 and CW3 and increased at 15th week. The DO was also decreased with time in CW4 and CW5 (Figure 8.12). The DO was decreased with addition of PAC when compared to only sand media, however, this pattern was not consistent in CW3 where sand, PAC and plant were used. The higher DO in CW3 might be due to entering of some air as CW was not covered properly as in case of CW1 and CW2 due to presence of plant in CW3.

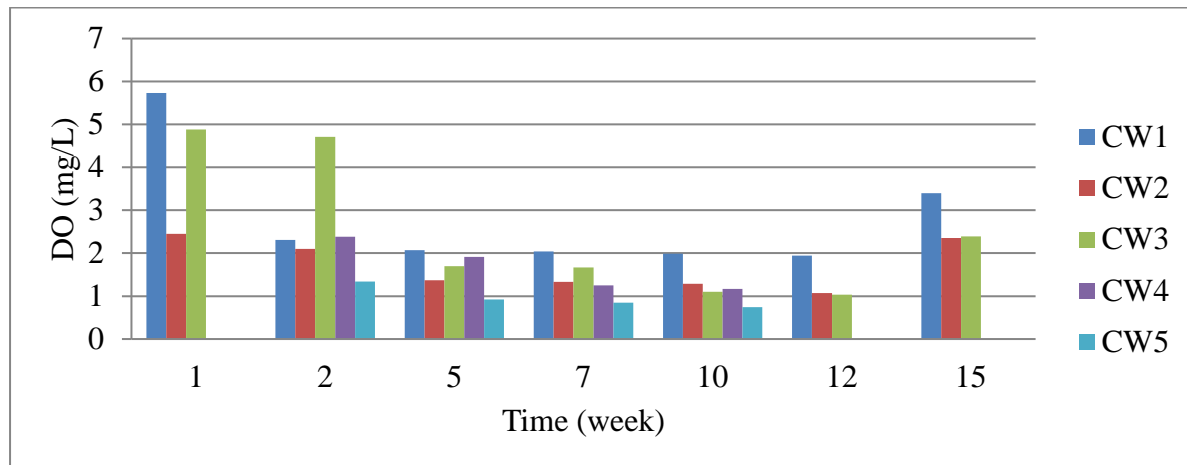


Figure 8.12: DO of effluents from CWs at different interval of time

The recent study by (Al-Sbani et al. 2016) reported similar results for DO of SSF system where in most of the cases, the DO was decreased with time until 84 days and in some cases there was increased DO at 49 days. Furthermore, in the same study it was also reported that DO of the system was independent of presence and absence of plant.

The values of ORP in CWs were observed between 175 to 150 mv where positive results were only obtained at 1st and 2nd weeks for CW1, CW2 and CW3 (Figure 8.13). According to Ong et al. (2009), there would be aerobic environment if ORP is greater than 100 mV and anoxic to anaerobic environment if ORP is less than 100 mv.

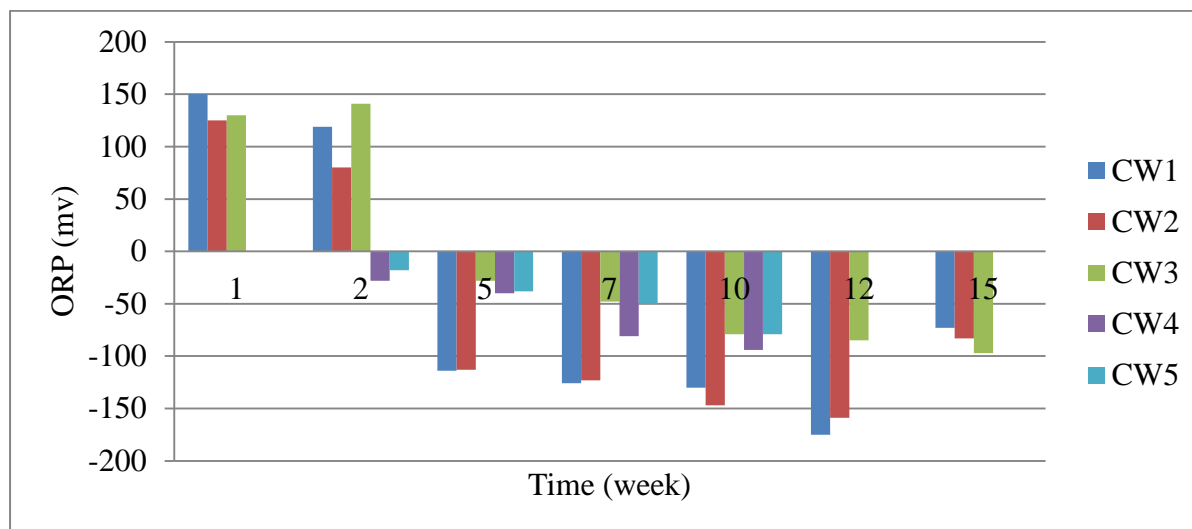


Figure 8.13: ORP of effluents from CWs at different interval of time

Thus, the process in the CWs was under anoxic and anaerobic conditions in most of the cases, however, detail biodegradation process has not been considered in laboratory experiments of this study. The anaerobic condition was due to absence of opportunity to get in enough air into the system because CWs were covered and not supplying the extra air. Similar results were also observed in other studies (Al-Sbani et al. 2016; Yi et al. 2016; Al-Baldawi 2013; Ong et al. 2009).

The pH values were not found in any particular trend with time as well as with types of CWs (Figure 8.14). The pH values were in acidic to neutral range in most of cases. Not regular pattern of effluent pH from CW was reported by Al-Sbani et al. (2016), however, the pH values obtained in that study were in alkaline range in most of the cases .

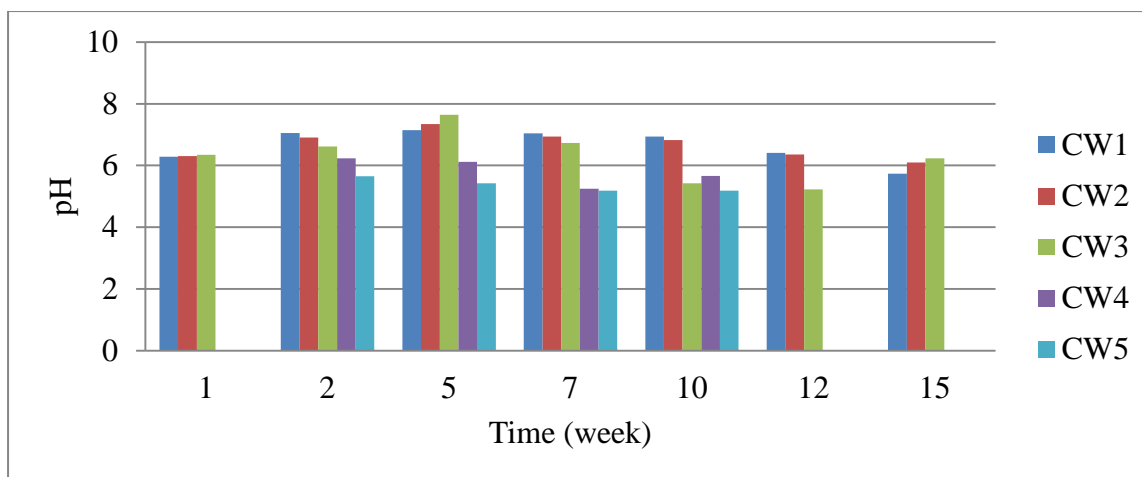


Figure 8.14: pH of effluents from CW1, CW2 and CW3

However, $\text{pH} > 8.5$ found to affect adversely into the components of CWs such as decay of plant assimilation and inhibition of microbiological activities in summer season due to elevated pH (Yin et al. 2016). Other studies also presented that more alkaline condition could affect in DO reduction, intracellular metabolic activities of plant, cell growth, and biomass (Buchanan et al. 2000; Cosgrove 2000; Ranieri et al. 2013 Rorslett et al. 1986). The denitrification and nitrification processes were found hampered at $\text{pH} > 8$ in previous study by Vymazal (2007). Thus, pH values (Figure 8.14) of present study reveal the positive environment in PAH remediation in CWs.

The temperature was found same as room temperature in all samples independent of types of CWs. The Temperature was varied from 20 to 23 °C during the experiment period (Figure 8.15). In the study by Al-Sbani et al. (2016) also mentioned that the temperature obtained in sub surface flow system only depends on weather of sampling time. As CW4 and CW5 were set 5 weeks after CW1, CW2 and CW3, the temperature for 7th week of CW1, CW2 and CW3 is same as that of 2nd week of CW4 and CW5.

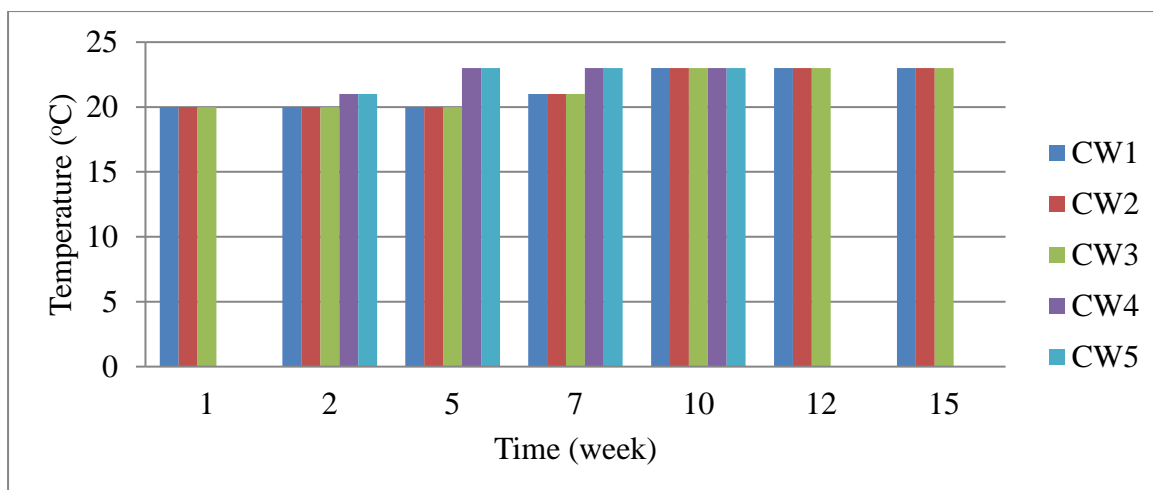


Figure 8.15: Temperature of effluents from CW1, CW2 and CW3

8.3.4 Cost analysis

As discussed in section 2.8, there are different methods to treat PAHs, however, CW is the most effective system because of the excellent ecological properties, less construction and operational costs and easy maintenances (Choi et al.2012). The materials used in laboratory based CW system of present study are black colour plastic containers, sand, *Dianella revoluta* plants, 0.002% to 0.05% PAC, and plastic to cover the container which are cheaper material than installing and operating bulky machinery system. Therefore, the proposed system is cost effective system.

The construction cost of CW is comparable or less than the cost of conventional biological wastewater which provides the similar range of treatment, however, the operation cost is much lower than that of conventional treatment plants (Kadlec 2009). The operation cost of CW was also recorded lower than conventional technology by Gkika et al. (2014) (Table 8.2).

Table 8.2: Cost comparison of CW system of present study with other system

treatment system	Estimated cost	Reference
Biodisc technology	Construction cost €47 per population equivalent (PE) and operational cost €9.75/PE/year for PE 600. (Operational model)	Gkika et al. 2014
CW	Construction cost € 477.1/PE and operation cost € 11.9/PE for PE 600 (Operational model)	Gkika et al. 2014
CW	Construction cost AU\$ 1400 and operational (five months) cost AU\$ 400 for 6 CWs (experimental model)	Present study

8.4 Conclusion

CW is one of the effective techniques in removal of stormwater PAH due to low cost and environmental friendly technique. Laboratory based CW experiment is possible at indoor environment with sunlight from glass window and by providing proper amount of water and nutrients. PAC, GAC and bentonite are very effective in phenanthrene adsorption with PAH adsorption efficiency 100, 92.79 and 80.25% respectively. However, zeolite is less effective in comparison to other 3 types of adsorbents with phenanthrene removal efficiency 25.04%.

Furthermore, *Dianella revoluta* can remove phenanthrene which was revealed by higher removal efficiency of CW3 (84.38%) than CW2 (78.6%). The main mechanism of PAH removal in CW is adsorption process as highest percentage of PAH is adsorbed by CW bed media in comparison to removal by plant only. Furthermore, Positive effect of PAC in CW was found as phenanthrene removal of CW2 (78.6%) was greater than CW1 (53.6%). The

adsorption of phenanthrene was increased with increased amount of PAC which could be observed from phenanthrene removal efficiency of CW2 (78.6%) and CW4 (92.2%), however, there might be negative effect of 0.05% PAC on plant survival. For instance, plant was totally dried after 14 weeks in CW4. In presence of 0.002% PAC by weight of sand there was not any negative effect of PAC on *Dianella revolute* plant as plant was healthy until 5 months. The use of high concentration of PAC could adsorb more PAH but there is negative effect of PAC in plant health after certain limit. Thus, optimization of PAC quantity is crucial part in designing CW bed media to obtain highest possible removal capacity of PAH in CW.

From analysing the environmental parameters for sample from all types of CWs, the DO measurement was observed less in the CW containing PAC when compare to CW containing only sand media, however, DO was independent of presence or absence of plant. The ORP data of CWs effluents revealed that the process in the CWs was under anoxic and anaerobic conditions in most of the cases, although detail biodegradation process has not been analysed in this study. The anaerobic condition was observed due to absence of opportunity to get in sufficient air into the system because CWs were covered with plastic and the extra air was not supplied. Thus to maintain aerobic process in CW system, supplying aeration system is required. However, there was not found any significant trend in pH values for effluent samples of different types of CWs, similar result was also found in past study. The temperature of CW system was independent of CW bed media or plant as the temperature measurements were same as that of room temperature.

Chapter 9

Conclusions and recommendations

9.1 Conclusions

In this study, effect of urbanisation on stormwater quality, different types of storm water pollutants and potential concern about PAHs among other pollutants are identified. The background on PAHs, their sources, types, physicochemical properties, process of entering in stormwater runoff and effects on human health and environment are learnt through available literatures. Moreover, different types of treatment methods in removing stormwater PAHs are identified through previous studies as well as by performing laboratory experiments.

PAHs are organic micro-pollutants ubiquitous in the environment. The main source of PAHs in urban environment is the anthropogenic activities such as vehicular exhaust, spill and leakage of petroleum products, industrial manufacturing process and waste incineration. Due to high coverage of urban area with artificial infrastructures, PAHs are accumulated on the surfaces such as highways, roads, parking lots and these PAHs are transferred to nearest water body by snow melt and storm runoff by degrading the urban water quality.

Due to eco-toxicological effect of PAHs into the environment, evaluation of a cost effective and environmental friendly technique of PAHs remediation has become of particular concern. A number of methods have been investigated to treat PAHs from storm water as well as contaminated soils and sediments to mitigate the possible risk of PAHs on the environment and human health. Physical, chemical, thermal, biological and phytoremediation processes which comprise sorption, incineration, thermal desorption, radio frequency heating, oxidation, ion exchange, photolysis, adsorption, electrolysis, chemical precipitation, natural attenuation, biostimulation, bioaugmentation, surfactant enhanced, rhizofiltration, phytoextraction, phytostabilisation and phytodegradation techniques are the major treatment methods of PAHs from stormwater and contaminated soil and sediments. Among them use of CW system is of particular importance in removing storm water PAHs because CW system has possessed less operation and maintenance cost as well as comprises multi treatment options (physical, chemical, biological and phytoremediation) to remove PAHs. Furthermore, due to detoxification of PAHs (adsorbed into bed media of CW) by phytoremediation and

biodegradation process, there is not produce by-product to further contaminate the environment and therefore, CW system has become one of the best management practices.

Sorption is the main technique in PAH remediation from aqueous media because of less aqueous solubility nature of PAHs and their high affinity to be adsorbed into solid phase. In CW system, the aqueous PAHs would adsorbed by CW bed media. Different types of materials could be used as bed media such as sand, sediments, activated carbon, biochar, organic mineral amended clay, cellulose, and membranes. The effectiveness of sorption of PAHs depends on the properties of the adsorbent, operating variables such as pH, ionic strength, temperature, existence of competing organic or inorganic compounds and contact time including the adsorbent production processes. Moreover, studies demonstrated that selecting a right adsorbent media and operating parameters, removal efficiency could be achieved up to 100%.

Laboratory experiment on PAHs sorption was carried out with phenanthrene as a model PAH and PAC, GAC, zeolite and bentonite as PAH adsorbents. PAC, GAC and bentonite are very effective in phenanthrene adsorption with 100, 92.79 and 80.25% efficiency respectively. However, zeolite is less effective in comparison to other 3 types of adsorbents with only 25.04% phenanthrene removal efficiency. Based on analysis of results from phenanthrene adsorption test, PAC was selected as phenanthrene adsorbent to mix with sand as CW bed media.

PAC and GAC were further considered for kinetic and isotherm analysis as PAC and GAC possess greater phenanthrene adsorption capacity when compared to bentonite and zeolite. The equilibrium condition was reached within 5 h for PAC and within 48 h for GAC. The correlation coefficient obtained from second order kinetic model was 1 for both adsorbents (PAC and GAC), however, 0.94 for PAC and 0.98 for GAC from first-order kinetic model. Furthermore, the q_e values obtained from second-order kinetic model is more closed to q_{exp} when compare to q_e obtained from first-order kinetic model indicating second-order kinetic model better fits than first order moel in PAH adsorption with activated carbon. Moreover, isotherm study was also carried out for PAH adsorption with PAC and GAC. The adsorption data were not in fitted Langumuir isotherm model, however, adsorption data were fitted in Freundlich isotherm models with correlation coefficient of PAC as 0.91 and that of GAC was 0.95.

The PAHs could be removed from aqueous media by using CW mainly through adsorption method and effluent could be discharge into relevant water bodies. However, it is very crucial to detoxify adsorbed PAHs into bed media of CW. There are many techniques such as extraction with solvent, surfactant enhanced bioremediation and phytoremediation to treat PAH from CW bed media, from bank sediments as well as from contaminated soils.

PAHs solubilisation is the main factor in removing PAHs with organic solvents. To evaluate PAH solubility with organic solvents, laboratory experiments were conducted on phenanthrene solubilisation with acetone, hexane and methanol in their single and mixed forms for varying amounts of initial phenanthrene. Furthermore, effect of mixing time during batch solubility test was also considered. From the analysis of experimental results, organic solvents were found to be effective in phenanthrene solubility. Furthermore, phenanthrene solubility was found proportional to the amount of phenanthrene used initially. Moreover, there is positive effect of duration of mixing in phenanthrene solubility with result up to 84.16% solubility with methanol at 120 h.

The SER is one of the promising techniques in removing PAHs from soil and aqueous media with the selection of a proper surfactants and environments for the targeted PAHs. The micellar solubilisation of PAHs found to be more effective in the mixed system when compared to the single micellar system due to the reduction of the surfactant quantity and level of surfactant pollution to the environment. Biosurfactants have many potential advantages such as biodegradability, lower toxicity and a wide range of environmental resilience. Moreover, selection of proper type and quantity of synthetic surfactants could also improve PAHs solubilisation and biodegradation up to > 99.99% without adverse impact to the environment. Furthermore, SER of PAHs depends on many parameters such as surfactant concentration, PAHs hydrophobicity, temperature, pH, salinity and dissolved organic matter.

Solubilisation of PAH in the surfactant micelle is the main mechanism of SER of PAHs. To explore the solubilisation capacity of anionic and nonionic surfactants in their single and mixed micellar systems, laboratory experiments were considered. Based on analysis and discussion of laboratory experimental results, SDBS was found effective in phenanthrene solubilisation when compared to SDS. Anionic-nonionic mixed surfactants systems were very effective in phenanthrene solubilisation when compared to single surfactant systems. The

highest phenanthrene solubility was obtained at anionic-nonionic surfactants ratio 1:9 among the various proportions considered in the experiments. Furthermore, phenanthrene solubility increased with increase of surfactant concentration from 1 to 5 mM for all systems. Moreover, Tween20 was found more effective when compared to Tween80 in phenanthrene solubilisation for all tested proportion of anionic-nonionic systems for all concentrations of surfactants.

The experimental results of CW explored that the plant based experiment is possible inside the laboratory by keeping the blinds of window opened to get sunlight and by providing proper amount of water and nutrients. Furthermore, *Dianella revoluta* can remove phenanthrene which was revealed by higher removal efficiency of CW3 (84.38%) than CW2 (78.6%). Positive effect of PAC in CW was found as phenanthrene removal of CW2 (78.6%) was greater than CW1 (53.6%). The adsorption of phenanthrene was increased with increased amount of PAC which could be observed from phenanthrene removal efficiency of CW2 (78.6%) and CW4 (92.2%), however, there might be negative effect of 0.05% PAC on plant survivability. For example, plant was totally dried after 14 weeks in CW4. In presence of 0.002% PAC by weight of sand there was not any negative effect of PAC on *Dianella revolute* plant as plant was healthy until 5 months.

From analysis the environmental parameters of effluents from all types of CWs, the DO measurement was observed less in the CW containing PAC when compare to CW containing only sand media, however, DO was independent of presence or absence of plant. The ORP data of CWs effluents revealed that the process in the CWs was under anoxic and anaerobic conditions in most of the cases, although detail biodegradation process has not been analysed in this study. The anaerobic condition was observed due to absence of opportunity to get in sufficient air into the system because CWs were covered with plastic and the extra air was not supplied. There was not found any significant trend in pH values for effluent samples of different types of CWs. The temperature of CWs was independent of CW bed media or plant as the temperature measurements were same as that of room temperature.

The PAH removal technique developed in this study is environmental friendly and consists of low cost. The developed technique in this study is CW system which is the green technology

due to consisting of natural process such as phytoremediation to decontaminate aqueous as well as adsorbed PAHs. Moreover, CW media used in this study are sand, plants and only 0.002 to 0.05% PAC which are low in cost when compare to PAHs treatment techniques involving machinery system such as thermal process and chemical process. The proposed technique is cost effective compared to available technique where PAC has been used in PAH remediation. In past studies, minimum of 2% PAC by weight of soil has been considered to adsorb PAH. This is the first study where only 0.002 to 0.05% of PAC by weight of sand has been used in CW and observed effective PAHs remediation (up to 95.37%).

9.2 Recommendations

As the main aim of the study is to develop recommendations for environmental friendly and low cost technique to remove urban stormwater PAHs, the study developed very important and valuable recommendations to improve the PAH removal efficiency of constructed wetlands. These recommendations will be very useful for authorities, managers and engineers in decision-making and developing sustainable solutions for PAH removal from stormwater.

The major recommendations developed from this study are:

- Optimization of PAC proportion in sand media (as CW bed) can be evaluated from laboratory experiments for PAH removal in CW.
- Biodegradation is very important process to detoxify the PAHs adsorbed into CW bed media. Therefore, biological degradation of PAHs in CW can be extended.
- Storm water PAHs remediation by using CW can be extended for other common stormwater PAHs such as anthracene, fluoranthene and chrysene which are also under USEPA priority list.
- PAHs removal from stormwater can be investigated by using CW with GAC and sand as PAH adsorbing media because GAC is better in bio-accessibility when compared to PAC.
- *Dianella revoluta* can be compared with *Lolium Perenne* (ryegrass) which is common PAHs removal plant in remediation of common stormwater PAHs.
- Rhamnolipids can be compared with Tween20 for phenanthrene solubilisation by performing batch solubility test as biosurfactants are less toxic when compared to synthetic surfactants.

- Furthermore, Rhamnolipids can be compared with Tween20 in regards to biodegradation of phenanthrene by *Pseudomonas aruginosa* through batch tests as *Pseudomonas aruginosa* is common microorganism in phenanthrene degradation.

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APPENDIX

Appendix A: Tables and Figures for PAH adsorption by PAC and GAC

Table A1: Intensity of Spectrofluorometer for known concentration of standard phenanthrene solutions

SN	Phenanthrene concentration ($\mu\text{g/L}$)	Intensity	Emission wave length for peak
1	0.006	3.841	326.33
2	0.012	3.668	333.93
3	0.024	3.883	351.00
4	0.049	4.53	350.93
5	0.098	5.213	348.33
6	0.195	6.77	350.60
7	0.195	6.737	365.27
8	0.391	9.975	365.47
9	0.781	17.198	365.33
10	1.563	31.332	365.53
11	3.125	59.288	365.47
12	6.25	116.635	365.40
13	12.5	234.73	365.67
14	25	468.745	365.67
15	50	930.431	365.67

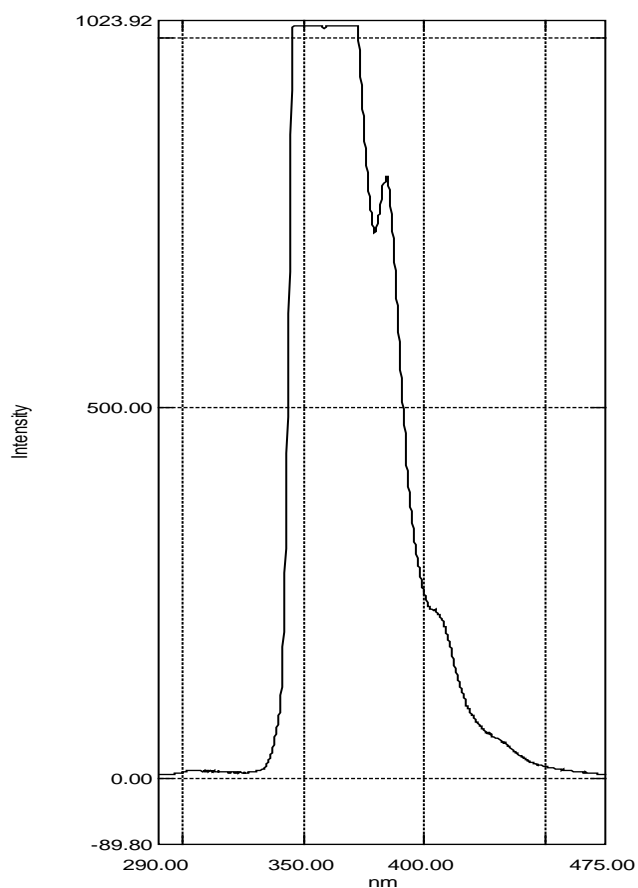


Figure A1: Spectrum for 54 µg/L at (EX250.0_EM290.0_475.0= 365.6)

Table A2: Phenanthrene removal efficiency with PAC at different interval of time

t (h)	Residual phenanthrene (µg/L)			Phenanthrene removal efficiency (%)
	Sample I	Sample II	AVG	
0.25	0.479	0.523	0.501	98.75
0.5	0.427	0.504	0.466	98.84
1	0.366	0.372	0.369	99.08
2	0.334	0.289	0.312	99.22
3	0.280	0.279	0.280	99.30
4	0.264	0.215	0.240	99.40
5	0.227	0.231	0.229	99.43
6	0.206	0.248	0.227	99.43
24	0.227	0.227	0.227	99.43

Table A3: Phenanthrene removal efficiency with GAC at different interval of time

t (h)	Residual phenanthrene ($\mu\text{g/L}$)			Phenanthrene removal efficiency (%)
	Sample I	Sample II	AVG	
0.25	36.009	34.695	35.352	11.62
0.5	30.274	24.815	27.545	31.14
1	27.718	21.266	24.492	38.77
2	22.122	18.347	20.235	49.41
3	19.949	19.984	19.967	50.08
4	15.916	16.055	15.986	60.04
5	13.475	13.472	13.474	66.32
6	11.116	11.061	11.089	72.28
7	9.907	9.972	9.94	75.15
24	2.73	2.69	2.71	93.23
27	2.029	2.035	2.032	94.92
48	1	0.995	0.998	97.51
72	0.997	0.998	0.998	97.51

Table A4: Parameter of kinetic model for phenanthrene adsorption by PAC

t (h)	q_e ($\mu\text{g/mg}$)	q_t ($\mu\text{g/mg}$)	$q_e - q_t$	t/q_t	$\text{Log}(q_e - q_t)$
0.25	1.99	1.97	0.01	0.13	-1.86
0.5	1.99	1.98	0.01	0.25	-1.92
1	1.99	1.98	0.01	0.50	-2.15
2	1.99	1.98	0.00	1.01	-2.37
3	1.99	1.99	0.00	1.51	-2.58
4	1.99	1.99	0.00	2.01	-3.20
5	1.99	1.99	0.00	2.51	-4.00

Table A5: Parameter of kinetic model for phenanthrene adsorption by GAC

t (h)	qe (µg/mg)	qt (µg/mg)	qe-qt	t/qt	Log (qe-qt)
0.25	0.39	0.04648	0.343545	5.378657	-0.4640164
0.5	0.39	0.124555	0.26547	4.014291	-0.5759846
1	0.39	0.15508	0.234945	6.448285	-0.6290338
2	0.39	0.197655	0.19237	10.11864	-0.7158627
3	0.39	0.200335	0.18969	14.97492	-0.7219556
4	0.39	0.240145	0.14988	16.6566	-0.8242563
5	0.39	0.265265	0.12476	18.84908	-0.9039246
6	0.39	0.289115	0.10091	20.75299	-0.9960658
7	0.39	0.300605	0.08942	23.28637	-1.0485653

Table A6: Effect of mass of PAC on phenanthrene adsorption kinetic

t (h)	20 mg PAC			Phenanthrene removal (%)	200 mg PAC			Phenanthrene removal (%)
	Phenanthrene residual (µg/L)				Phenanthrene residual (µg/L)			
	Sample I	Sample II	AVG		Sample I	Sample II	AVG	
2	0.373	0.322	0.348	99.1	0.175	0.148	0.162	99.6
4	0.103	0.023	0.063	99.8	0.115	0.008	0.062	99.8
24	-0.048	-0.044	-0.046	100	-0.055	-0.102	-0.079	100

Table A7.1: Residual phenanthrene after adsorption with varying mass of GAC

t (h)	Phenanthrene residual (µg/L)					
	20 mg PAC		100 mg PAC		200 mg PAC	
	Sample I	Sample II	Sample I	Sample II	Sample I	Sample II
2	12.386	11.976	4.038	4.053	0.247	0.252
4	4.301	3.999	0.972	0.965	0.181	0.177
24	4.269	3.997	-0.121	-0.141	-0.333	-0.326
48	1.532	1.385				
72	1.104	0.958				
120	-0.104	-0.16				

Table A7.2: Effect of mass of GAC on phenanthrene adsorption kinetic

t (h)	AVG Phenanthrene residual ($\mu\text{g/L}$)			Phenanthrene removal (%)		
	20 mg GAC	100 mg GAC	200 mg GAC	20 mg GAC	100 mg GAC	200 mg GAC
2h	12.181	4.046	0.25	69.5	89.89	99.38
4h	4.15	0.969	0.179	89.6	97.58	99.55
24h	4.157	-0.131	-0.33	89.6	100.00	100.00
48	1.459			96.35		
72	1.031			97.42		
120	-0.132			100		

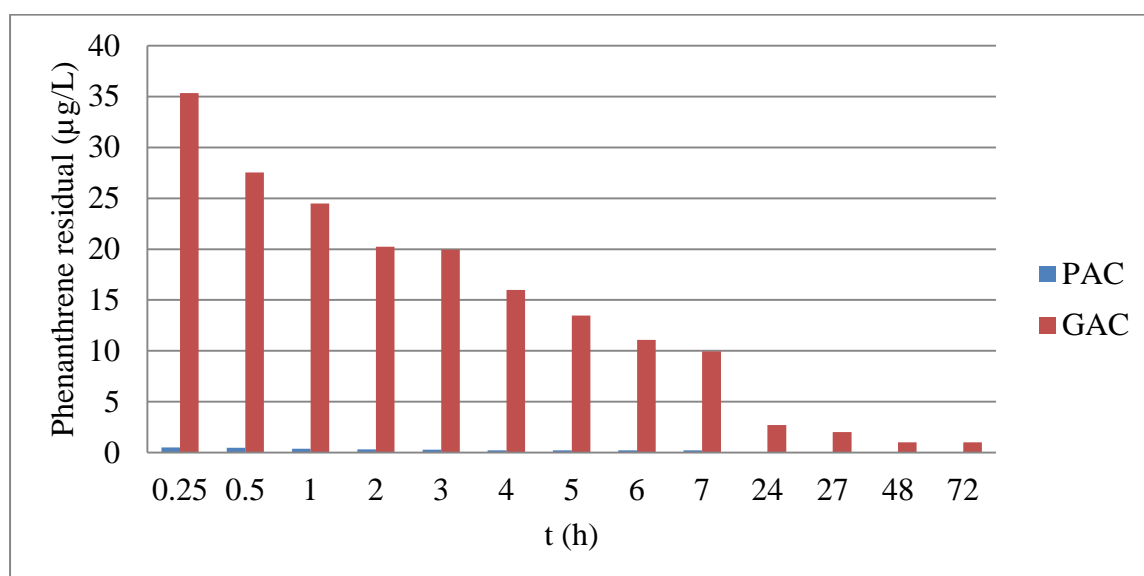


Figure A2: Residual phenanthrene in supernatant after adsorption with PAC and GAC

Table A8: Isotherm parameters for adsorption of varying initial concentrations of phenanthrene with PAC

Initial phenanthrene concentration ($\mu\text{g/L}$)	Equilibrium phenanthrene concentration (Ce) ($\mu\text{g/L}$)			Phenanthrene absorption by PAC (q_e) ($\mu\text{g/mg}$)	Ce/q_e (mg/L)	Log (Ce)	Log (q_e)
	sample I	sample II	AVG				
5	0.004	0.002	0.003	0.250	0.01	-2.52	-0.60
10	0.043	0.039	0.041	0.498	0.08	-1.39	-0.30
20	0.131	0.128	0.130	0.994	0.13	-0.89	0.00
30	0.189	0.191	0.190	1.491	0.13	-0.72	0.17
40	0.227	0.227	0.227	1.989	0.11	-0.64	0.30

Table A9: Isotherm parameters for adsorption of varying initial concentrations of phenanthrene with GAC

Initial phenanthrene ($\mu\text{g/L}$)	Equilibrium phenanthrene concentration (Ce) ($\mu\text{g/L}$)			Phenanthrene absorption by GAC (q_e) ($\mu\text{g/mg}$)	Ce/q_e (mg/L)	Log (Ce)	Log (q_e)
	sample I	sample II	AVG				
5	0.148	0.153	0.151	0.045	3.10	-0.82	-1.31
10	0.196	0.203	0.200	0.098	2.04	-0.70	-1.01
20	0.372	0.383	0.378	0.196	1.92	-0.42	-0.71
30	0.744	0.73	0.737	0.292	2.52	-0.13	-0.53
40	1	0.995	0.998	0.390	2.56	0.00	-0.41

Appendix B: Tables for solubility of PAH with organic solvents

Table B1: Standard and detected phenanthrene concentrations, area of peaks and retention times observed in GC-FID.

Phenanthrene standard concentrations ($\mu\text{g/L}$)	Phenanthrene detection with GC-FID ($\mu\text{g/L}$)	Area of peak	Retention time (minute)
1000	1014.49	0.248	8.14
500	466.02	0.1101	8.15
250	255.38	0.0571	8.15
125	121.58	0.0235	8.16
62.5	79.25	0.0128	8.16

Table B2: Results from GC-FID for phenanthrene solubilisation with single solvent system for varying initial phenanthrene amounts

Initial phenanthrene (mg/L)	Phenanthrene solubility ($\mu\text{g/L}$)								
	With acetone			With hexane			With methanol		
	Sample I	Sample II	AVG	Sample I	Sample II	AVG	Sample I	Sample II	AVG
25	179.10	177.38	178.24	182.41	212.74	197.57	560.53	441.50	501.01
37.5	289.77	254.23	272.00	207.79	245.65	226.72	699.07	698.99	699.03
50	277.06	187.02	232.04	n.a.	330.33	330.33	964.85	837.71	901.28

n.a. = not applicable

Table B3: Phenanthrene solubilisation results for different proportions of organic solvents

Initial phenanthrene (mg/L)	Phenanthrene solubility (µg/L)								
	Acetone-Hexane (1:1)			Acetone-Hexane (1:3)			Acetone-Hexane (3:1)		
	Sample I	Sample II	AVG	Sample I	Sample II	AVG	Sample I	Sample II	AVG
25	258.81	172.42	215.61	170.57	184.14	177.36	151.92	205.35	178.64
37.5	232.71	263.66	248.19	n.a.	265.68	265.68	255.63	237.57	246.60
50	262.60	295.89	279.25	343.78	374.60	359.19	305.52	334.19	319.86

Table B4: Phenanthrene solubilisation with methanol at various intervals of time

Initial phenanthrene (mg/L)	Phenanthrene solubility (µg/L)					
	72 h			120 h		
	Sample I	Sample II	AVG	Sample I	Sample II	AVG
25	20858.80	16383.46	18621.13	22249.64	18307.05	20278.34
37.5	29467.96	21973.41	25720.69	25789.82	30388.47	28089.14
50	35690.90	33224.86	34457.88	40814.23	43346.89	42080.56

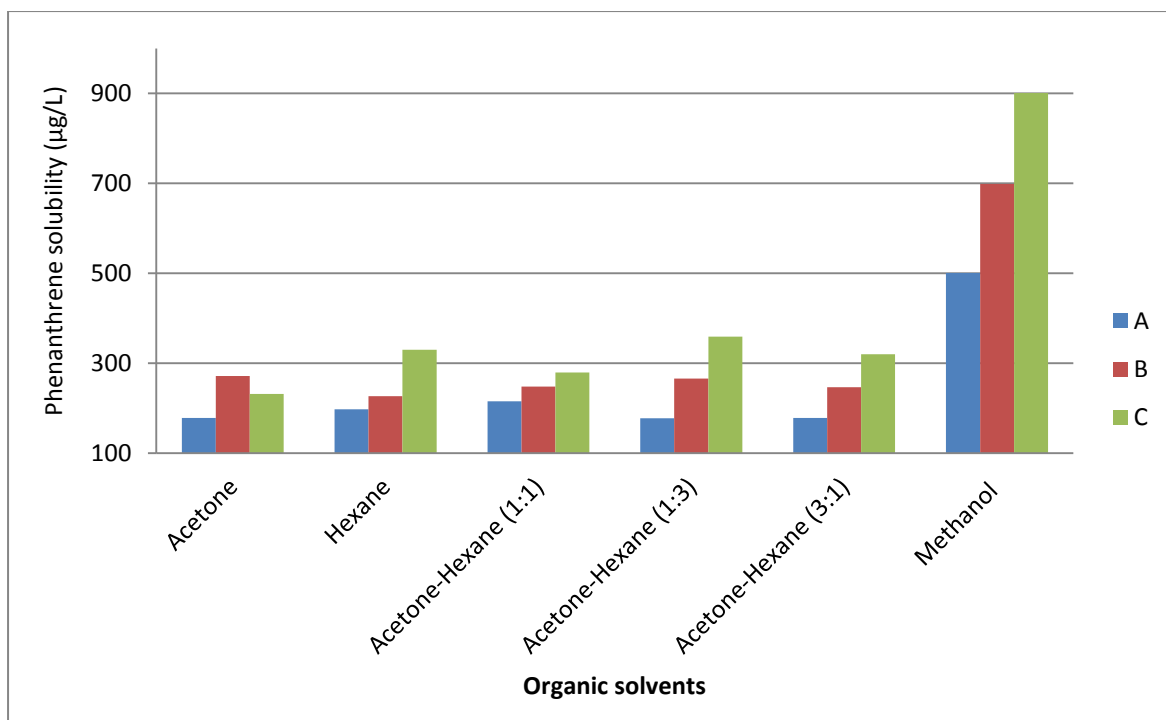


Figure B1: Phenanthrene solubility with organic solvents in single and mixed systems

Note: A= initial phenanthrene 25 mg/L, B= 37.5 mg/L and C= 50 mg/L

Appendix C: Tables for solubility of PAH with anionic and nonionic surfactants

Table C1: Phenanthrene concentrations, peaks and retention times observed in GC-FID for standard calibration curve

Phenanthrene standards (µg/L)	Phenanthrene detection with GC-FID (µg/L)	Area of peak	Retention time (minute)
1000	999.89	0.219	7.805
500	491.8451	0.1142	7.797
250	265.1335	0.0674	7.785
125	134.206	0.0404	7.783
62.5	54.6829	0.024	7.783
31.25	22.9926	0.0174	7.782

Table C2: Phenanthrene concentrations, intensity and wavelength for peaks in Spectrofluorophotometer for standard calibration curve

SN	Phenanthrene concentrations (mM)	Intensity	Emission wave length for peak
1	0.004	24.415	EX250.0_EM290.0_325.0=305.8
2	0.008	29.229	EX250.0_EM290.0_325.0=305.0
3	0.016	36.186	EX250.0_EM290.0_325.0=305.4
4	0.031	38.715	EX250.0_EM290.0_325.0=303.8
5	0.063	57.653	EX250.0_EM290.0_325.0=304.4
6	0.125	91.117	EX250.0_EM290.0_325.0=305.8
7	0.25	141.986	EX250.0_EM290.0_325.0=305.0
8	0.5	228.949	EX250.0_EM290.0_325.0=305.0
9	1	451.919	EX250.0_EM290.0_325.0=305.2

Table C3: phenanthrene solubilisation with single and mixed for initial phenanthrene concentration 2 g/L

Surfactants	Phenanthrene ($\mu\text{g/L}$)			
	Sample I	Sample II	Sample III	AVG
SDS	413.62	375.32	199.22	329.39
SDBS	448.65	459.84	567.71	492.07
SDS- Tween80 (1:9)	2810.73	3810.83	1419.99	2680.52
SDBS- Tween80 (1:9)	1660.18	3444.77	4087.16	3064.03

Table C4: phenanthrene solubility and intensity results for varying proportions of SDBS-Tween80 at total concentration 0.5 mM

Anioni- nonionic	Phenanthrene (mM)			Intensity		
	Sample I	Sample II	AVG	Sample I	Sample II	AVG
1:9	-0.007	-0.008	-0.008	25.917	25.680	25.799
2:8	-0.021	-0.023	-0.022	20.180	18.979	19.580
4:6	-0.057	-0.058	-0.058	4.674	4.553	4.614
6:4	-0.060	-0.060	-0.060	3.592	3.592	3.592
8:2	-0.061	-0.061	-0.061	3.204	-0.061	1.572
9:1	-0.061	-0.061	-0.061	3.179	3.108	3.144

Table C5: phenanthrene solubility and intensity results for varying proportions of SDBS-Tween20 at total concentration 0.5 mM

Anioni- onionic	Phenanthrene (mM)			Intensity		
	Sample I	Sample II	AVG	Sample I	Sample II	AVG
1:9	0.156	0.159	0.158	94.632	95.984	95.308
2:8	0.112	0.091	0.102	76.023	67.034	71.529
4:6	-0.015	-0.018	-0.017	22.638	21.397	22.018
6:4	-0.044	-0.045	-0.045	10.407	9.770	10.089
8:2	-0.053	-0.053	-0.053	6.605	6.719	6.662
9:1	-0.056	-0.056	-0.056	5.263	5.198	5.231

Table C6: phenanthrene solubility and intensity results for varying concentrations of surfactants for SDBS-Tween80 ratio 1:9

Surfactants (mM)	Phenanthrene (mM)			Intensity		
	Sample I	Sample II	AVG	Sample I	Sample II	AVG
1	0.068	0.094	0.081	57.310	68.563	62.937
2	0.199	0.219	0.209	112.760	121.247	117.004
3	0.322	0.302	0.312	164.256	155.803	160.030
4	0.366	0.360	0.363	182.777	180.308	181.543
5	0.467	0.482	0.475	225.654	231.885	228.770

Table C7: phenanthrene solubility and intensity results for varying concentrations of surfactants for SDBS-Tween20 ratio 1:9

Surfactants (mM)	Phenanthrene (mM)			Intensity		
	Sample I	Sample II	AVG	Sample I	Sample II	AVG
1	0.216	0.271	0.244	119.911	142.842	131.377
2	0.354	0.327	0.341	177.795	166.351	172.073
3	0.468	0.486	0.477	226.065	233.385	229.725
4	0.540	0.692	0.616	256.209	320.238	288.224
5	0.774	0.777	0.776	354.761	356.110	355.436

Table C8: Phenanthrene solubilisation with anionic-nonionic mixed micelles (1:9) for various concentrations.

Surfactants (mM)	SDBS-Tween80		SDBS-Tween20	
	Phenanthrene (mM)	Intensity	Phenanthrene (mM)	Intensity
1	0.081	62.937	0.244	131.377
2	0.209	117.004	0.341	172.073
3	0.312	160.03	0.477	229.725
4	0.363	181.543	0.616	288.224
5	0.475	228.77	0.776	355.436

Appendix D: Tables and figures for PAHs removal by using CW

Table D1: Residual phenanthrene and phenanthrene removal efficiency for adsorption test

Adsorbents	Residual phenanthrene ($\mu\text{g/L}$)					Phenanthrene removal efficiency (%)
	Sample I	Sample II	AVG	Standard Daviation (SD)	SD error	
PAC	-0.326	-0.309	-0.3175	0.012	0.009	100
GAC	2.793	2.974	2.88	0.128	0.091	92.79
Bentonite	7.543	8.246	7.90	0.497	0.352	80.25
Zeolite	27.81	32.117	29.96	2.154	2.154	25.04

Table D2: Residual phenanthrene ($\mu\text{g/L}$) in effluents of CW1, CW2 and CW3 for different intervals of time

CW	Weeks													
	W1	W2	W3	W4	W5	W6	W7	W8	W9	W10	W12	W15	W17	W20
CW1	38.66	36.29	34.73	29.70	28.40	25.06	19.69	19.88	18.56	18.65	19.35	19.32	19.34	19.66
CW2	23.29	19.61	14.97	13.50	12.95	12.26	10.82	9.33	8.69	8.37	7.56	9.21	8.56	8.66
CW3	9.37	8.38	7.70	7.50	7.21	6.87	6.68	6.79	6.86	6.25	6.34	6.81	6.66	6.74

Table D3: Phenanthrene removal efficiency (%) of CW1, CW2 and CW3 for different interval of time

CWs	Weeks													
	W1	W2	W3	W4	W5	W6	W7	W8	W9	W10	W12	W15	W17	W20
CW1	3.35	9.28	13.17	25.74	29.00	37.36	50.78	50.31	53.60	53.38	51.62	51.70	51.66	50.84
CW2	41.79	50.99	62.58	66.25	67.64	69.36	72.95	76.67	78.29	79.09	81.11	76.97	78.60	78.34
CW3	76.58	79.06	80.76	81.24	81.98	82.82	83.30	83.02	82.86	84.38	84.15	82.97	83.34	83.14

Table D4: Residual phenanthrene ($\mu\text{g/L}$) in effluents of CW4 and CW5 for different intervals of time

CWs	Weeks										
	W1	W2	W3	W4	W5	W6	W7	W8	W10	W12	W15
CW4	7.65	6.30	5.96	5.25	4.86	3.58	3.14	3.12	3.74	4.03	4.16
CW5	3.19	2.63	1.95	1.85	2.46	2.09	2.32	2.65	6.99	7.00	

Table D5: Phenanthrene removal efficiency (%) of CW4 and CW5 for different interval of time

CWs	Weeks										
	W1	W2	W3	W4	W5	W6	W7	W8	W10	W12	W15
CW4	80.89	84.26	85.11	86.88	87.85	91.05	92.15	92.20	90.65	89.92	89.61
CW5	92.02	93.42	95.13	95.37	93.84	94.78	94.19	93.37	82.51	82.51	

Table D6: Effluent phenanthrene concentration at various depths of CW

Depth from top of CW media (mm)	Residual phenanthrene ($\mu\text{g/L}$)			Phenanthrene removal (%)
	Side I	Side II	AVG	
50	10.214	10.73	10.47	73.82
250	6.525	7.435	6.98	82.55
450	3.541	3.529	3.54	91.16

Table D7: DO (mg/L) for effluents from five CWs

CWs	Weeks						
	1	2	5	7	10	12	15
CW1	5.73	2.31	2.07	2.04	1.99	1.94	3.4
CW2	2.45	2.1	1.37	1.33	1.29	1.07	2.35
CW3	4.88	4.71	1.7	1.67	1.1	1.03	2.39
CW4	-	2.38	1.91	1.25	1.17	-	-
CW5	-	1.34	0.92	0.85	0.74	-	-

Table D8: ORP (mv) for effluents from five CWs

CWs	Weeks						
	1	2	5	7	10	12	15
CW1	150	119	-114	-126	-130	-175	-73
CW2	125	80	-113	-123	-147	-159	-83
CW3	130	141	-28	-48	-79	-85	-97
CW4	-	-28	-40	-81	-94	-	-
CW5	-	-18	-38	-50	-79	-	-

Table D9: pH measurement for CWs

CWs	Weeks						
	1	2	5	7	10	12	15
CW1	6.29	7.05	7.15	7.04	6.94	6.41	5.74
CW2	6.31	6.91	7.34	6.94	6.83	6.36	6.1
CW3	6.35	6.62	7.64	6.73	5.42	5.23	6.23
CW4		6.23	6.12	5.25	5.66	-	-
CW5		5.65	5.42	5.19	5.19	-	-

Table D10: Temperature measurement for CWs

CWs	Weeks						
	1	2	5	7	10	12	15
CW1	20	20	20	21	23	23	23
CW2	20	20	20	21	23	23	23
CW3	20	20	20	21	23	23	23
CW4	0	21	23	23	23	-	-
CW5	0	21	23	23	23	-	-

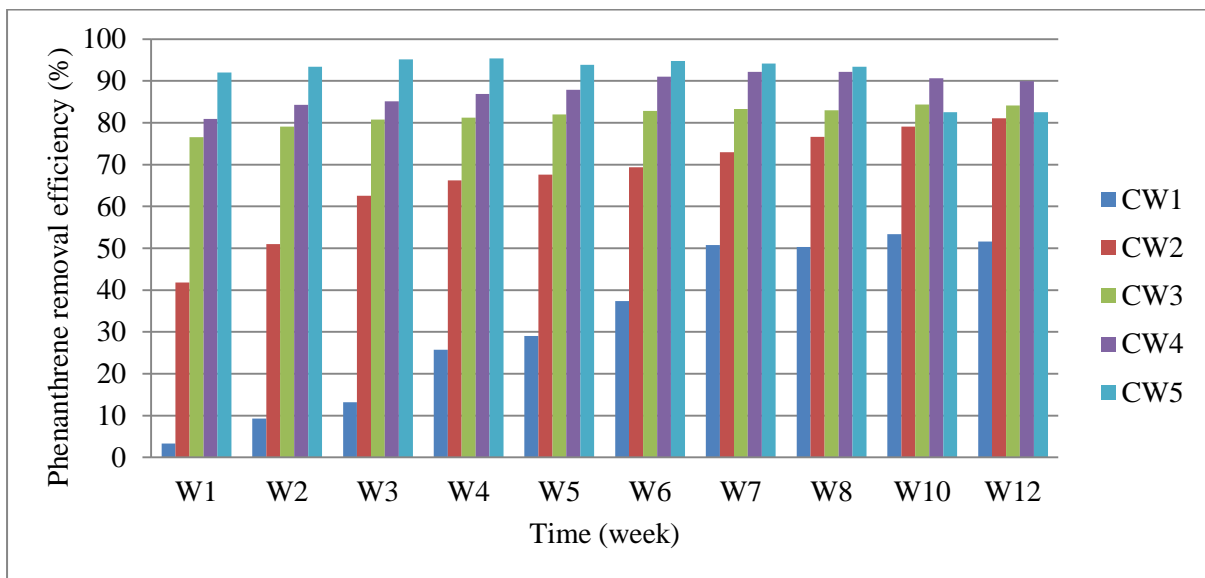


Figure D3: Comparative presentation for phenanthrene removal efficiency in five types of CWs for 1to 12 weeks

Appendix E: Photographs of laboratory instruments used in experiments

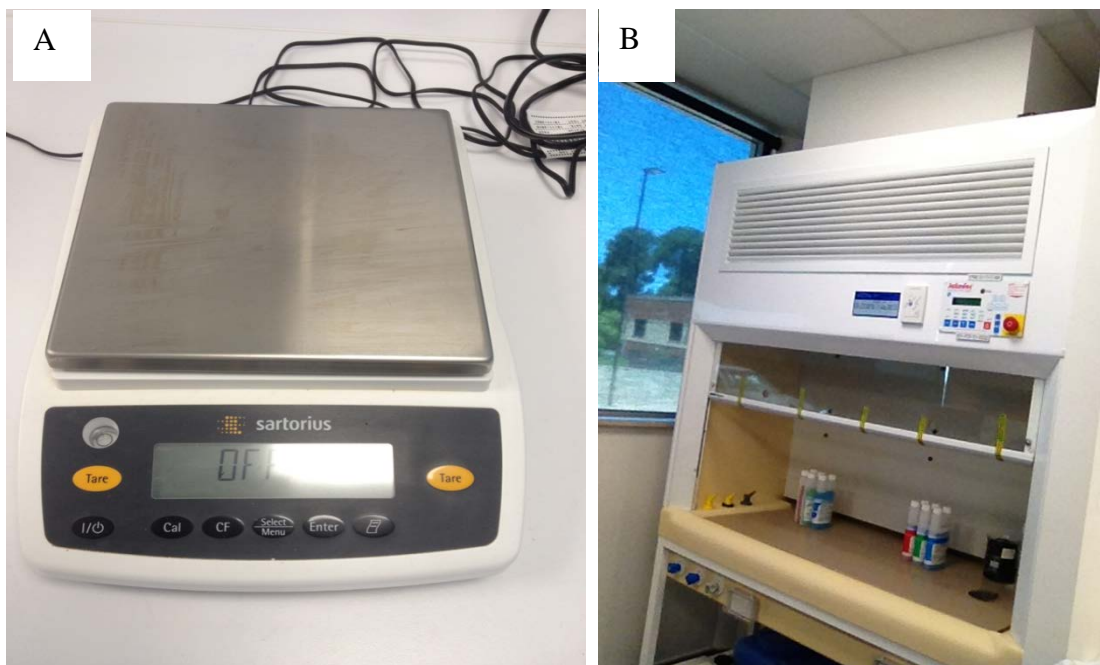


Figure E1: Weighing machine (A), Fume hood (B)

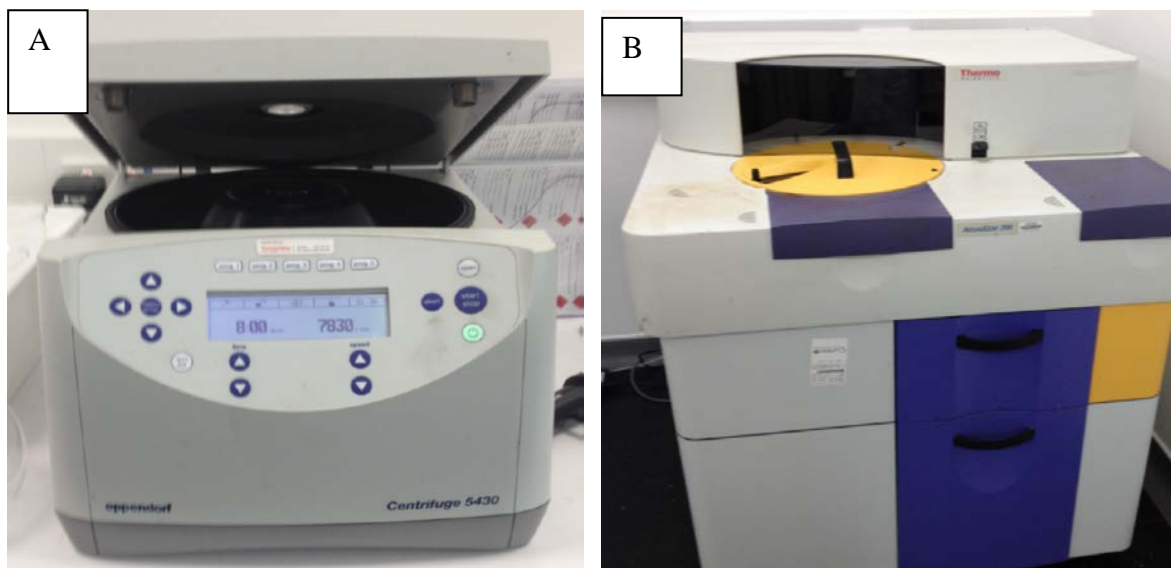


Figure E2: Centrifuge (A) and Aquakem (B)



Figure E3: Spectrofluorophotometer used to analyse PAH



Figure E4: Gas-Chromatography (GC)



Figure E5: pH meter (A), DO meter (B), ORP meter (C), Thermometer (D)