

Environmental Remediation: Removal of polycyclic aromatic hydrocarbons



Dissertation submitted for the degree of philosophiae doctor (PhD)

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Preface

This thesis is a submission for the degree of philosophiae doctor (PhD) at the University of Bergen, Norway. The thesis has been structured to include an introduction, methodology, main results, conclusion, suggestions for further work, critique of methods and a collection of papers. The thesis consists of four (4) papers; two (2) published one (1) in press and one (1) manuscript. The papers are based on experimental work carried out in the Department of Chemistry of the University of Bergen (Papers I, II and IV) and the University of Agder, Kristiansand (Paper III).

The PhD program was sponsored by the Agder fund as part of an attempt to find remediation methods for environmental pollution since the West and East Agder districts are home to a number of industries including an aluminium processing plant which discharges hazardous compounds such as polycyclic aromatic hydrocarbons (PAHs) in its electrolytic hall process.

The thesis considers 3 methods of remediation of PAHs namely: pyrolysis, adsorption and photochemical degradation.

During the three year period of my doctoral studies, I have had the privilege of participating in 4 international conferences namely; NATO SFP 982590 Project Workshop in September, 2010 at Dubrovnik, the International Launching Ceremony of the International Year of Chemistry (IYC) in January 2011 at Paris, 15th Annual Green Chemistry and Engineering Conference & International Conference on Green and Sustainable Chemistry in June 2011 at Washington DC and a Statoil Travel Grant to attend ISPAC23 (23rd International Symposium on Polycyclic Aromatic Compounds) held in September 2011 at Munster. These exposures have broadened my horizon and offered the platform for constructive scientific discourse and exchange.

“This dissertation is dedicated to the Almighty God; creator of the universe and all that is in it, for your gifts of life, wisdom, knowledge, understanding, health, endurance and sustenance throughout this 3 year journey.

I certainly made it because you care”

Acknowledgement

I am grateful to my supervisors for their support throughout this journey; to Prof. Alfred Christy my supervisor and initiator of the doctoral project, Prof. George Francis my initial principal supervisor and personal academic coach and mentor, to Prof. Tanja Barth for accepting to be part of the supervisory team at a very crucial time and finally becoming my principal supervisor.

I say thanks to members of the Chemistry laboratory in Alcoa-Lista especially Karl, Dagfinn, Svein and Alfred who generously offered their time and resources in the initial stages of my research work.

I thank Prof. Leiv Sydnes of the Department of Chemistry (UiB) for his support in setting up the ultraviolet (UV) experimental work and Børge Hamre of the Department of Physics (UiB) for his help with lamp calibration.

I am also grateful to all members of the Tanja Barth Research Group for their friendship most especially Drs. Lucia and Bjarte for their useful suggestions on experimental design and instrumentation and to Solfrid and Haflide for sometimes standing in the gap.

For their continual friendship I wish to say thanks to Rianne Harmsen (UiB) and Dag Terje Abrahamsen (UiA). To Monika a colleague PhD student in UiA for her friendship and always lending her ears in times when I needed to vent, I say thank you.

I am thankful for the generous moral support and encouragement offered by Anne Bergit Jørgensen of UiA and Prof. Stein-Erik Lauritzen of UiB.

For their administrative and technical guidance and support, I am grateful to Guro, Hege and Nina of UiB and Ling, Hellen and Per of UiA.

I extend gratitude to my mentors and colleagues (past and present) of the Department of Chemistry, KNUST - Ghana.

I appreciate the Ghanaian communities in both Bergen and Kristiansand for their support shown in diverse ways.

I am grateful to Dr. William O. Oduro of the Industrial Research Institute of Ghana and Dr. Benjamin Bandowe of the University of Berne, Switzerland for proof-reading this work.

For their ever assured, immense, prayerful, and moral support as well as their belief in me, I am grateful to my parents; Joseph and Mary and my siblings; Joe, Fred, Pat, Micky and Joan.

Last but not least, I appreciate all friends and well-wishers who contributed in both small and great ways to make my dream of a finished PhD come true. God bless you all.

Abstract

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous persistent semi-volatile organic compounds. They are contaminants that are resistant to degradation and can remain in the environment for long periods due to their high degree of conjugation, and aromaticity.

PAHs are present in industrial effluents as products of incomplete combustion processes of organic compounds. Petroleum, coal and shale oil contain extremely complex mixtures of these PAHs, and their transport and refining process can also result in the release of PAHs.

It is therefore prudent that such effluents are treated before discharge into the environment.

In this project, different approaches to the treatment of PAHs have been investigated.

Hydrous pyrolysis has been explored as a potential technique for degrading PAHs in water using anthracene as a model compound. The experiments were performed under different conditions of temperature, substrate, redox systems and durations.

The conditions include oxidising systems comprising pure water, hydrogen peroxide and Nafion-SiO₂ solid catalyst in water; and reducing systems of formic acid and formic acid / Nafion-SiO₂ / Pd-C catalysts to assess a range of reactivities. Products observed in GC-MS analysis of the extract from the water phase include anthrone, anthraquinone, xanthone and multiple hydro-anthracene derivatives (Paper I).

In addition a modified version of the Nafion-SiO₂ solid catalyst in water oxidising system was tested; and reducing systems of formic acid and formic acid / Nafion-SiO₂ / Pd-C catalysts were adopted for the conversion of a mixture of anthracene, fluorene and fluoranthene. The rate of conversion in the mixture was high as compared to that of only anthracene (Paper II).

Also the use of LECA (Lightweight expanded clay aggregates) as an adsorbent (Paper III) for PAHs (phenanthrene, fluoranthene and pyrene) removal from water has been

successfully achieved as well as photodegradation (UV) studies of fluorene in different aqueous media (Paper IV).

List of Papers

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

Paper I

Nkansah, M. A., Christy, A. A. & Barth, T. (2011) The use of anthracene as a model compound in a comparative study of hydrous pyrolysis methods for industrial waste remediation. *Chemosphere*, Volume 84 (4): 403- 408

Paper II

Nkansah, M. A., Christy, A. A. & Barth, T. (2012) Catalytic oxidation and reduction of polycyclic aromatic hydrocarbons (PAHs) present as mixtures in hydrothermal media. *Polycyclic Aromatic Compounds* (In press)

Paper III

Nkansah, M. A., Christy, A. A., Barth, T. & Francis, G.W. (2012) The use of lightweight expanded clay aggregate (LECA) as sorbent for PAHs removal from water, *Journal of Hazardous Materials*, 217- 218: 360- 365

Paper IV

Nkansah, M. A., Christy, A. A., Barth, T. Francis, G.W. (2012). Preliminary photochemical studies of fluorene in various aqueous media (Manuscript)

Abbreviations

ATSDR	Agency for Toxic Substances and Disease Registry
BaA	Benzo[a]anthracene
BaP	Benzo[a]pyrene
DART	Direct Analysis in Real Time
DBahA	Dibenzo[a,h]anthracene
DCM	Dichloromethane
EtAc	Ethyl acetate
FLE	Fluorene
FLU	Fluoranthene
FWHM	Full Width at Half Maximum
GC-MS	Gas Chromatography-Mass Spectroscopy
HCl	Hydrochloric acid
KNUST	Kwame Nkrumah University of Science and Technology
MeOH	Methanol
NaOH	Sodium hydroxide
NAP	Naphthalene
PAHs	Polycyclic aromatic hydrocarbons

PHE	Phenanthrene
PYR	Pyrene
POPs	Persistent organic pollutants
UV	Ultraviolet
UiA	University of Agder
UiB	University of Bergen

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Papers

Paper I

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CHAPTER 1

1. Introduction

1.1 Polycyclic aromatic hydrocarbons: Physical and chemical properties

In the strictest definition, PAHs are composed of "two or more fused aromatic (benzene) rings. However, most people consider the most important criteria in classifying PAHs to be whether or not two benzene rings are present in the chemical structure. Biphenyl is considered by most environmental chemists to be a PAH even though the two rings are joined by only a single bond rather than fused (Irwin et al., 1997). However "fused aromatic rings" is probably the best definition. One can also use "carbocyclic systems" in describing some types of compounds (PAC, 1995).

PAHs are to a certain degree resistant to biodegradation (Maliszewska-Kordybach, 1999) and are sometimes included in a class of persistent organic pollutants (POPs) (Wild and Jones, 1995).

PAHs are hydrophobic compounds and their persistence in the environment is also linked to their low water solubility and electro-chemical stability (Cerniglia, 1992). Of the over 900 agents compiled by the International Agency for Research on Cancer (IARC), 400 have been classified as carcinogenic (this includes PAHs) (IARC, 2009).

The properties and environmental fate of PAHs are dependent on the number of rings and molecular weight. High molecular weight (HMW) PAHs are compounds with four or more fused benzene rings, whereas the low molecular weight (LMW) compounds consist of two to three fused benzene rings (Law et al., 2002). The low molecular weight PAHs are less persistent, highly volatile, slightly soluble in water and less carcinogenic but are

















toxic to fish and other marine organisms since they accumulate in their tissues (bioaccumulation) and are able to move up the food chain (biomagnification) and adversely affect humans upon consumption (Law et al., 2002).

High molecular weight PAHs persist (less volatile and more resistant to oxidation) and are more insoluble when alkyl substituent groups are attached to one or more rings. The substitution of an alkyl or chlorine group to PAHs changes the fate and characteristics making them more reactive and potentially more toxic than the parent PAHs (Irwin et al., 1997; Opperhuizen et al., 1993).

The observed effects caused by PAHs can be grouped according to their carcinogenicity, mutagenicity, teratogenicity, direct toxicity and/or combinations of all (Groenendijk, 1993). There are several hundred PAHs which often exist as mixtures rather than as single compounds (Chun et al., 2002).

The most common PAHs are anthracene, benzo(a)pyrene, chrysene, fluorene and pyrene (Environmental Programs Directorate, 2011) however benzo[a]pyrene (BaP) is commonly used as an indicator species for PAH contamination and most of the available data refer to this compound (Bull, 2008.) Details of the properties of the 16 PAHs of importance to the European Union (priority contaminants) are presented in Table 1.1.

Table 1.1: Physico - chemical properties of the 16 EU priority PAHs

#	Chemical name	MF	MW	Bp °C	CP	Vp, torr	S ₁₂₀ (mg/L)	Chemical structure
1	Acenaphthene	C ₁₂ H ₁₀	154.2078	95	-	10 ⁻³ -10 ⁻² at 20 °C	3.4 at 25 °C	
2	Acenaphthylene	C ₁₂ H ₈	152.1919	92-93	-	10 ⁻³ -10 ⁻² at 20 °C	3.93	
3	Fluorene	C ₁₃ H ₁₀	166.2185	116-117	-	10 ⁻³ -10 ⁻² at 20 °C	1.9	
4	Naphthalene	C ₁₀ H ₈	128.1705		-	0.0492	32	
5	anthracene	C ₁₄ H ₁₀	178.2292	218	3	2 x 10 ⁻⁴ at 20 °C	0.05-0.07 at 25 °C	
6	Fluoranthene	C ₁₆ H ₁₀	202.2506	111	3	10 ⁻⁶ -10 ⁻⁴ at 20 °C	0.26 at 25 °C	
7	Phenanthrene	C ₁₄ H ₁₀	178.2292	110	3	6.8 x 10 ⁻⁴ at 20 °C	1.0 - 1.3 at 25 °C	
8	Benzo[a]anthracene	C ₁₈ H ₁₂	228.2879	167	2B/B2	5 x 10 ⁻⁹ at 20 °C	0.01 at 25 °C	
9	Benzo[b]fluoranthene	C ₂₀ H ₁₂	252.3093	168.3	2B/B2	10 ⁻¹¹ -10 ⁻⁶ at 20 °C	-	
10	Benzo[k]fluoranthene	C ₂₀ H ₁₂	252.3093	215.7	2B	9.6 x 10 ⁻⁷ at 20 °C	-	
11	Chrysene	C ₁₈ H ₁₂	228.2879	255-256	3/B2	10 ⁻¹¹ -10 ⁻⁶ at 20 °C	0.002 at 25 °C	
12	Pyrene	C ₁₆ H ₁₀	202.2506	149-156	3	6.9 x 10 ⁻⁹ at 20 °C	0.14 at 25 °C	
13	Benzo[g,h,i]perylene	C ₂₂ H ₁₂	276.3307	278.3	3	~10 ⁻¹⁰	0.00026 at 25 °C	
14	Benzo[a]pyrene	C ₂₀ H ₁₂	252.3093	179	2B/B2	5 x 10 ⁻⁹	0.0038 at 25 °C	
15	Dibenzo[a,h]anthracene	C ₂₂ H ₁₄	278.34	262	2B/B2	~10 ⁻¹⁰	0.0005 at 25 °C	
16	Indeno[1,2,3-cd]pyrene	C ₂₂ H ₁₂	276.3307	163.3	2B/B2	~10 ⁻¹⁰	-	

MF: Molecular formula, MW: Molecular weight, Bp: Boiling point, Vp: Vapour pressure, CP: Cacinogenic potency, S: Solubility
 2A/B2: Probably carcinogenic to humans/Probable human carcinogen; 2B: Possibly carcinogenic to humans; 3: Not classifiable as to human carcinogenicity; Blank: Not tested for human carcinogenicity

Adopted from, IARC: International Agency for Research on Cancer; US EPA: US Environmental Protection Agency

1.2 Occurrence and environmental fate of PAHs

PAHs can be formed from both natural and anthropogenic sources, though the anthropogenic sources contribute most to the hazards associated with PAHs.

The natural sources of PAHs include biosynthesis by algae and bacteria as well as volcanoes and forest fires (Lee et al., 1981). Low to moderate temperature diagenesis of sedimentary organic material to form fossil fuel is also a natural source of PAHs (Neff, 1979).

The anthropogenic sources include products of incomplete combustion of organic material in the coal, petroleum and metal smelting industries (Keith, 1977; Bradley et al., 1994). They also include urban runoffs and deterioration of asphalt pavement surfaces and car tyres.

PAHs are ubiquitous and there exist several hundreds of them in the environment (Ramesh et al., 2004; Wild and Jones, 1995). They are usually found as a mixture containing two or more of these compounds and commercially available pure PAHs are usually colourless, white or pale yellow - green solids which are odourless or have a faintly pleasant odour (Buha, 2011).

Some PAHs are used in medicines, dyes, plastics and pesticides. Others are contained in asphalt used in road construction as well as found in substances such as crude oil, coal, coal tar pitch, creosote and roofing tar (ATSDR, 1995).

The natural and anthropogenic sources of PAHs and the ubiquitous global transport phenomenon result in the world-wide distribution of these compounds, which are subject to short and long-range transport, and are removed by wet and dry deposition onto soil, water and vegetation.

PAHs exist in air, water, soil and sediment at low concentrations with high thermal stability (Johnsen et al., 2004; ATSDR, 2006).

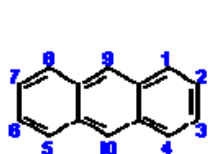
In air, PAHs are present in the gaseous phase or sorbed to particulates. PAHs having two to three rings are predominantly found in the vapour phase, those with four rings exist both in the vapour and particulate phase, and those with five or more rings exist predominantly in the particle phase (Jones et al. 1992). In surface water, PAHs can undergo volatilisation, photolysis, oxidation, biodegradation, bind to suspended particles or sediments (adsorption) or accumulate in aquatic organisms (with bioconcentration factors often in the 10-10,000 range). In sediments, PAHs can undergo biodegradation or accumulation in aquatic organisms. PAHs in soil can volatilise, undergo abiotic degradation (photolysis and oxidation), biodegrade, or accumulate in plants. PAHs in soil can also seep into groundwater and be transported within an aquifer (ATSDR, 1995).

Due to the widespread release of PAHs which consequently results in considerable health and environmental hazards (Ntainjua and Taylor, 2009), the European Union as well as the United States Environmental Protection Agency (USEPA) has specified permissible limits for the 16 priority PAHs (Campro Scientific, 2011; USEPA, 2008).

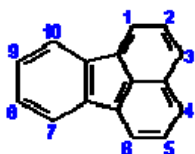
1.3 Reactivity of PAHs

Polycyclic aromatic hydrocarbons are classified as chemically inert and are mainly transformed into other polycyclic aromatic compounds (PACs) by electrophilic substitution reactions rather than addition (although addition reactions sometimes occur). Thus, large amounts of energy are required to transform an aromatic compound into a non-aromatic product. The electron distribution over the PAH molecule determines the positions of the molecule that are most reactive (Lee et al., 1981; Wheland, 1942 in Lundstedt, 2003).

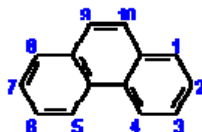
According to the work of Zander, naphthalene reactivity is higher for position 1 than 2 whilst anthracene and phenanthrene undergo redox reactions at positions 9 and 10, though the reactivity of anthracene is higher. Anthracene also forms an endoperoxide in the presence of light (Zander, 1979 in Lundstedt, 2003). Fluorene is most reactive at position- 9 while the other PAHs (like fluoranthene and pyrene) resemble anthracene and phenanthrene in terms of the types of reactions they undergo (Mojelsky and Strausz, 1986; Lloyd, 1989). The localisation energy concept seems to be the underlying principle that helps in explaining the mechanisms associated with PAH-degradation and PAH-derivative formation (Zander, 1979 in Lundstedt, 2003). The numbering system of the carbon atoms in all PAHs follows a systematic order with the exception of anthracene and phenanthrene (Lee et al., 1981). The numbered positions of the PAHs used in this study are shown in Figure 1.1.



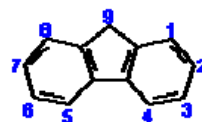
Anthracene



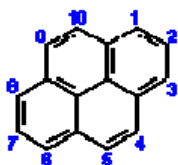
Fluoranthene



Phenanthrene



Fluorene



Pyrene

Figure 1.1: Chemical structures indicating numbered positions of selected PAHs

CHAPTER 2

2. Objectives of the study

2.1 General objective

PAHs are released as byproducts of industrial activities such as the electrolytic process in aluminium smelting plants. These PAHs end up in effluents like process water and sludge. It is therefore prudent that such effluents are cleaned before discharge into the environment. The primary objective of the study is therefore to determine clean-up procedures for aqueous polycyclic aromatic hydrocarbons.

2.2 Specific objectives

The specific objectives of the study are:

- To explore different hydrous pyrolysis approaches for the degradative remediation of anthracene (I).
- To explore catalytic hydrous pyrolysis for the degradative remediation of a mixture of PAHs (anthracene, fluorene and fluoranthene) (II).
- To explore lightweight expanded clay aggregates (LECA) as sorbent for the removal of aqueous PAHs (phenanthrene, fluoranthene and pyrene) (III), and
- To investigate the photochemical degradation of fluorene: A sparingly soluble PAH (IV).

CHAPTER 3

3. Overview of sources, cleanup methods and analytical measurement techniques for PAHs

3.1 Environmental polycyclic aromatic hydrocarbons, industrial perspectives and the need for remediation

Environmental monitoring of the levels of the 16 priority PAHs (Table 1.1) from anthropogenic sources is an issue of global concern (Wenzl et al., 2006). PAH emissions from industries are produced mainly by burning fuels such as gas, oil and coal (Chen et al., 2007) and in the industrial production of metals.

In the aluminium industry for instance, alumina is obtained from bauxite by the Bayer process. Aluminium is produced by reduction of alumina by the Hall-Heroult electrolytic process. Aluminium reduction cells are at present of two types: those with pre-baked anodes and those with baked-in-place anodes (Soderberg). PAHs are produced during the manufacture of the anode for modern "pre-bake" aluminium smelters as well as during the electrolytic process itself in the older (Soderberg) type facilities. Current air emission levels of PAHs from pre-bake plants are 0.05 kg per tonne and 0.25kg per tonne from Soderberg plants. In recent years levels have been reduced considerably. Modern plants based on pre-bake technology emit less than 0.01 kg per tonne (ECLAC, 2007; Electrochemistry Encyclopedia, 2008).

Other industrial activities like petroleum production and spillage, cement, bitumen and asphalt production, municipal and medical solid waste incineration, wood preservation products, commercial heating and power production stations (Pelletier et al., 1997; Eisler, 1987; Dyke, 1981) also release PAHs into the environment. These PAHs are released in gaseous emissions as well as in aqueous and solid effluents (Busetti et al., 2006; Slaski et

al., 2000). These contaminate air, soil and water bodies. Estimates of levels and probable types of PAHs released as a result of the various industrial activities from different countries is presented in Table 3.1.

Remediation of environmental organic pollutants such as PAHs include physical methods like soil washing, land filling, immobilisation; thermo-chemical methods like incineration, thermal desorption, radio frequency heating; chemical methods like oxidation, ion exchange, adsorption, absorption, electrolysis and chemical precipitation; bioremediation methods like natural attenuation, biostimulation and bioaugmentation and phytoremediation such as rhizofiltration, phytoextraction, phytostabilisation and phytodegradation (Rushton et al., 2007; Chun et al., 2002).

The following sub-sections will review literature on the cleanup methods used in this thesis, namely; thermal, sorption and photochemical procedures for the removal of PAHs.

Table 3.1: PAH emission from industrial processes for some countries

#	Source of emission	Likely emission /profile
1.	Coal Coking	PAHs: 15.2 mg/kg coal charged (general for most countries)
2.	Coal Conversion	PAHs: 1500 µg/g burnt coal (general for most countries)
3.	Petroleum Refining	PAHs:0.1 tpa (Canada), 11 tpa (Germany)
4.	Power plants using fossil fuel	PAHs: 0.15 tpa (Germany), PAHs: 0.1 tpa Norway , PAHs: 11 tpa Canada
5	Incinerators (refuse burning)	B(a)P: 0.001 tpa (Germany) , PAHs: 50 tpa (USA), PAHs: 2.4 tpa (Canada)
6	Aluminium Production (vertical process)	PAHs:1000 tpa (USA) , 930 tpa (Canada)
7	Iron & steel Production	PAHs: 34 tpa (Norway) , PAHs: 19 tpa (Canada)
8	Foundaries	PAHs: 1.3 tpa (Netherlands)
9	Sinter Process	PAHs:1.3 tpa (Netherlands)
10	Phosphorous Production	PAHs: 0.2 tpa (Netherlands)

* (tpa: tonnes per annum) **Source: IPCS, 1998**

3.2 Thermal approaches to the removal of polycyclic aromatic hydrocarbons

Thermal treatment of polycyclic aromatic hydrocarbons under controlled conditions is one of the more effective methods of degradation (Pakpahan et al., 2009). The method has applications at different reaction temperatures and under various conditions. Thermal degradation can occur at low, intermediate or high temperatures. It can also occur in the presence of additives with or without the presence of oxygen. Extraction with water or degradation in the presence of water is also a feasible method of PAH degradation (Lui et al., 2001).

3.2.1 Low temperature processes

Low-temperature thermal processes are generally classified as operating below 177 °C, though temperatures slightly above this are acceptable (Health care without harm, 2001). Uncontrolled low temperature thermal treatment of organic waste leads to the formation of PAHs with more than 4 rings while degradation occurs for only those with less than 4 rings (Pakpahan et al., 2009).

According to a study conducted on the thermal stability of benzo[a]pyrene (BaP), benzo[a]anthracene (BaA) and dibenzo[a,h]anthracene (DBahA) at temperatures 100-200 °C, the loss of each PAH, whether found as a solid or in solution depends on time. More of the original compounds were lost at 200 °C than at 100 °C (Chen and Chen, 2001). Low temperature thermal degradation of PAHs is sometimes enhanced in the presence of biochemical processes (Eriksson et al., 2003).

3.2.2 Intermediate temperature processes

Medium or intermediate temperature thermal processes usually take place between 177 - 370 °C (Health care without harm, 2001). Successful removal of PAHs from sediment by thermal desorption at 300 °C has been documented by Kopinke and Remmler (Kopinke and Remmler, 1995). Intermediate thermal treatments usually employ sub-critical water for the removal and H₂O₂ for the oxidation of PAHs (Pakpahan et al., 2009).

3.2.3 High temperature processes

High temperature thermal processes occur between 540 and 830 °C or higher and are typical for those utilised for medical waste treatment (Health care without harm, 2001). Treatment of medical waste by Wheatley and Sadhra at 800-1000 °C indicated that no PAHs were found in fly ash but high molecular PAHs (MW 228-252) were found in the bottom ash (Wheatley and Sadhra, 2004). Heating usually goes beyond 1000 °C in order to ensure the destruction of the higher molecular weight PAHs.

3.2.4 Hydrothermal processes (Hydrous pyrolysis)

Pyrolysis is a physico-chemical action belonging to the umbrella group of thermal processes. It is the thermal decomposition of organic material with no or very limited oxygen at temperatures ranging between 300 and 600 °C (Brown and Stevens, 2011).

Under hydrothermal conditions, toxic and refractory organic compounds undergo oxidation and reduction among other reactions, however oxidation is the most widely used method for waste remediation purposes (Rice and Steven, 1998).

Interest in the use of water as a 'green' solvent and reaction medium is increasing. This has resulted in a lot of research work on the reactions of organic molecules at hydrothermal sub-critical (100-350 °C, 5-20MPa) and supercritical water (≥ 374 °C, ≥ 22.1 MPa) conditions (Savage, 1999 in Kim et al., 2008).

The use of pressurised water (Pressurised Hot Water Extraction, PHWE) in removing PAHs from sludge and sediments has proved effective with maximum efficiency at 300 °C. When the temperature of water is increased above 380 °C, it is called Super-Critical Water (SCW) (Kronholm, et al., 2003) and the density of water decreases very rapidly up to 410 °C due to thermal expansion. The dielectric constant of water decreases with decreasing density. Supercritical water is a fluid with both liquid and gaseous properties and behaves as a non-aqueous fluid dissolving organic compounds like alkanes,

aromatics, etc. (Shaw et al., 1991). The use of SCW oxidation, PHWE and Wet Air Oxidation, WAO (hydrothermal oxidation with an external source of oxygen as oxidant) are very common methods of organic waste remediation (Onwudili and Williams, 2007; Kronholm, et al., 2003).

3.3 Adsorption processes for removal of polycyclic aromatic hydrocarbons from water

Adsorption or sorption of a substance involves separation by accumulation at the interface between two phases, such as a liquid and a solid or a gas and a solid. In principle adsorption can occur at any solid-fluid interface. The molecule that accumulates on the surface is called an adsorbate and the solid on which adsorption occurs is the adsorbent. Adsorption can be classified as chemisorption or physisorption. Chemical adsorption (chemisorption) involves an interaction caused by the formation of chemical bonds between the surface of solids (adsorbent) and adsorbate. The energy involved is similar to that of chemical reactions which can be exothermic or endothermic processes ranging from very small to very large energy magnitudes (Al-Anber, 2011).

Physisorption is a physical adsorption process which involves intermolecular forces like Van der Waals forces. The energies of interaction between the adsorbate and adsorbent have the same order of magnitude and there is no activation energy involved (Al-Anber, 2011).

Adsorbents of interest in water treatment include activated carbon; ion exchange resins; adsorbent resins; metal oxides, hydroxides, and carbonates; activated alumina; clays; and other solids that are suspended in or in contact with water (Summers and Snoeyink, 1999). Activated carbon remains the most widely used sorbent for water treatment to remove specific organic molecules responsible for taste, odour, mutagenicity and toxicity, as well as natural organic matter (NOM) responsible for colour (American Water Works Association, 1977).

Adsorption is central to a number of physical, biological and chemical processes and operations in environmental studies. Adsorption of dissolved impurities from solution has been widely employed for water purification and is currently viewed as a superior method for wastewater treatment and water reclamation. Sorption methods have been

proved to be effective for the removal of dissolved organic compounds including PAHs (Weber, 1972).

The factors that affect adsorption equilibrium are (i) surface area of adsorbent (larger surface area implies a greater adsorption capacity), (ii) Particle size (smaller particle sizes reduce internal diffusion and mass transfer limitation due to the penetration of the adsorbate inside the adsorbent. Thus, equilibrium is more easily achieved and nearly full adsorption capability can be attained), (iii) contact or residence time (the longer the time the more complete the adsorption will be) and (iv) solubility of solute (adsorbate) in liquid (Al-Anber, 2012).

3.3.1 Adsorption isotherms: Basic theories

Isotherms are generally used to predict and evaluate the sorption capacity of a sorbent (Chiang et al., 1993). Adsorption results in the removal of solutes from solution and their concentration at a surface, until the amount of solute remaining in solution is in equilibrium with that at the surface. This equilibrium is described by expressing the amount of solute adsorbed per unit weight of adsorbent q , as a function of C , the concentration of solute remaining in solution. An expression of this type is termed an adsorption isotherm. The most widely used isotherms for water and wastewater treatment applications are the Freundlich and the Langmuir equations (Weber, 1972).

The Langmuir isotherm is based on the assumptions that sorption is limited to one monolayer where all surface sites are equivalent (Langmuir, 1918 in Allen et al., 2004). The linearised Langmuir isotherm equation is mathematically expressed as in equation 3.1.

$$1/q_e = 1/Q_0 b + 1/C + 1/Q_0 \quad (3.1)$$

Where Q_0 is the Langmuir constant analogous to maximum amount of adsorption corresponding to complete monolayer coverage (mg/g) and b is the Langmuir constant which is related to the rate of adsorption intensity, q_e is mass of adsorbed pollutant per unit of sorbent (mg/g) at equilibrium, C (mg/l) is the concentration of dissolved adsorbate in solution.

The Freundlich isotherm is a non-linear model which is based on the assumption that the sorption system involves heterogeneous surfaces, limited sorption sites and potential energy interactions (Freundlich, 1906 in Allen et al., 2004). The Freundlich model is expressed mathematically as shown in equation 3.2.

$$q_e = K_F C^{1/n} \quad (3.2)$$

Where K_F and n are constants and $n > 1$

Data are usually fitted to the logarithmic form of the equation, which gives a straight line with a slope of $1/n$ and an intercept equal to the value of $\log K_F$ for $C = 1$ ($\log C = 0$) and C is the concentration of dissolved adsorbate in solution.

The intercept is roughly an indicator of sorption capacity and the slope, $1/n$, of adsorption intensity. The Freundlich equation generally agrees well with the Langmuir equation and experimental data cover moderate ranges of concentration (Weber, 1972).

3.4 Photochemistry

Photochemical processes are initiated by the absorption of a photon by a molecule. The functional groups that absorb photons are referred to as chromophores and include groups such as double bonds, carbonyls and aromatic systems (Jacobs, 2008).

When organic molecules absorb light they are converted to an electronically excited state (i.e the molecule attains a higher potential energy than the ground state energy) Absorption ranges of some chromophores are ; Simple alkene 190-200 nm ; Acyclic diene 220-250 nm , Cyclic diene 250-270 nm , Styrene 270-300 nm , Saturated ketones 270-280 nm , α , β -Unsaturated ketones 310-330 nm , Aromatic ketones/aldehydes 280-300 nm and aromatic compounds 250-280 nm (Konig, 2011). When a molecule absorbs radiation, one of the following can occur:

- i) Vibronic relaxation brings the molecule quickly into the new energy minimum structure for the excited state. Energy is released into the solvent.
- ii) Intersystem crossing leads to triplet states by spin inversion and the new energy minimum is reached by vibrational relaxation.
- iii) Emission of light and return to the ground state (eg. fluorescence, phosphorescence)
- iv) Quenching of the excited state: this involves energy transfer to another molecule.
- v) Radiationless deactivation: the molecule goes back to ground state by vibrational (thermal) deactivation (no light emission). The energy goes to the solvent/environment of molecule and
- vi) A photochemical reaction may occur (Konig, 2011).

3.4.1 Singlet oxygen and photochemical reactions

Singlet oxygen is the first excited state ($^1\Delta_g$) of molecular oxygen (O_2) which lies 22.4 Kcal/mol above the ground triplet state, $^3\Sigma_g^-$, (Frimer, 1985). Molecular oxygen has another singlet excited state ($^1\Sigma_g^+$) lying 31.5 kcal/mol above the triplet state.

The transition from the $^1\Delta_g$ state to the $^3\Sigma_g^-$ state is spin forbidden, thus the $^1\Delta_g$ O_2 is a relatively long-lived species. The $^1\Sigma_g^+$ state of oxygen however is short-lived due to a spin-allowed transition to the $^1\Delta_g$ state. Figure 3.1 represents the lowest singlet and triplet states of molecular oxygen (DeRosa and Crutchley, 2002).

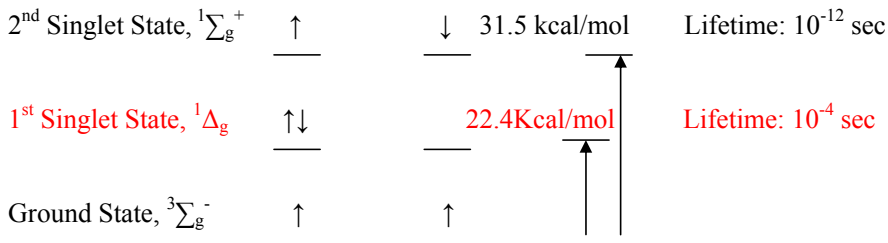


Figure 3.1: Lowest singlet and triplet states of molecular oxygen

Quenching: The deactivation of excited molecular oxygen by another species and the subsequent return of the molecular oxygen to the ground state is called quenching. The two types of quenching are:

- Physical quenching in which interaction leads to deactivation and no consumption of O_2 to form products is involved. The process can be expressed as shown in equation 3.3.



- Chemical quenching in which the quencher reacts with singlet oxygen to form products as shown in equation 3.4 (Wasserman and Murray, 1979).



3.4.2 Photochemistry of aqueous PAHs

The interaction of aqueous organic molecules (including PAHs) with light has received a lot of attention. This interaction occurs by two main routes, namely:

- (i) Direct photolysis: by directly absorbing light and being transformed afterwards and
- (ii) Indirect photolysis: involves the absorption of light by naturally present constituents defined as photosensitizers which produce reactive agents that subsequently react and transform or degrade other organic molecules (Jacobs, 2008).

Photolysis can come into play whenever an absorbing molecule can transfer energy, a proton or an electron to another species. Photosensitisation generally referred to as the transfer of energy from a photochemically excited molecule to an acceptor, most often oxygen to form a reactive transient form of oxygen, singlet oxygen ($^1\Delta_g$). Examples of photosensitizers of environmental importance are humic substances, flavins, PAHs, tetrapyrroles and mineral surfaces (Rodgers and Snowden, 1982).

Most PAHs can absorb surface solar radiation directly, allowing for the possibility of direct photodegradation. Indeed, several studies have shown that a number of PAHs are destroyed when irradiated with 313 and 366 nm light in pure water (Fasnacht and Blough, 2002). Reactions associated with the direct photolysis of organic compounds are usually kinetically simple and easily modelled in cases where the absorption spectrum of the compound and its quantum yield of disappearance are measurable.

Photochemical reactions of adsorbed PAH such as BaP have received a lot of attention and their modes of transformation and distribution are similar to that of PAHs in bulk-liquid phase (National Academy of Sciences, 1993). The photo-transformation of aqueous PAHs by singlet oxygen has been extensively studied and shown to give various oxygenated products including diones and endoperoxides. These partially oxidised intermediates are often more biodegradable than the parent compounds and they can

serve as primary substrates for reactions of the high-molecular-weight PAHs (Mueller et al., 1996).

In natural waters, the sun's radiant energy is associated with the degradation of organic compounds including PAHs and the rate of natural degradation reactions in most parts of the world surpasses the quantity (volume) of the waste released (Legrini et al., 1993).

The use of ultraviolet (UV) photo-degradation of PAHs as a treatment method has been studied extensively. UV photolysis has been used to eliminate chlorinated and nitrated aromatics, phenols and other hazardous wastes present in water. Low pressure Hg lamps emitting at 253.7 nm have been used in PAH degradation. Medium to high pressure Hg lamps (emitting mostly from 200 to 1000 nm with the most intense lines) have also been used for treatment of pure and substituted aliphatics as well as substituted aromatics. Most of these UV investigations were made in order to quantify the contribution of the electronic excitation of the organic pollutant in combined oxidation processes like $\text{H}_2\text{O}_2/\text{UV}$, O_3/UV and $\text{H}_2\text{O}_2/\text{O}_2/\text{UV}$ (Legrini et al., 1993; IUPAC, 2007).

3.5 Review of analytical procedures for the measurement of PAHs

Measurements of PAHs in environmental matrices mostly require difficult analytical chemical procedures as a result of the complexity encountered in environmental samples. This complexity is readily seen when one considers the general categories of phases into which environmental samples may be categorized, namely; aqueous, air (gaseous or condensates/particulate matter), oil or organic liquid, solids or sludge, biological samples and even multiphase samples (Poster et al., 2006).

Sampling, sample preparation, isolation and concentration from sample matrices are critical in the analytical determination of PAHs. Typical sample preparation procedures include extraction, concentration and clean-up (Speight, 2005). Extraction methods explored over the years include: Soxhlet, sonication, liquid-liquid extraction, purge and trap, headspace, shaking, vortex, solid-phase, supercritical fluid extraction, solid-phase micro extraction (SPME), stir-bar sorptive extraction (SBSE), miniaturized solid-phase extraction (SPE), liquid-phase micro extraction (LPME), membrane-assisted solvent extraction techniques (MASE) etc., (Tang and Isacsson, 2008). Sample concentration methods employed include; nitrogen blowing, vacuum evaporation, micro-Snyder column technique and adsorbent or cryogenic trapping (Tang and Isacsson, 2008; USEPA, 1996).

Some identification and quantification methods include the use of Gas Chromatography (GC), Gas Chromatography-Mass Spectrometry (GC-MS) and High Performance Liquid chromatography (HPLC).

In this thesis, liquid-liquid extraction was used in all cases where PAHs were extracted from aqueous media. Extracts were then dried with Na_2SO_4 , filtered with membrane filter (0.45 μm) and analysed by GC-MS.

However, the following sections review general sampling, extraction, clean-up and analysis protocols (including those employed in this research) for the analysis of environmental PAHs.

3.5.1 Sampling

Sampling procedures differ depending on the matrix in which PAHs are found.

3.5.1.1 Air sampling

As a result of the wide range of vapour pressures of PAHs, most atmospheric PAHs are adsorbed on particulate matter while some may exist in the gas phase (Noto et al., 1996). The sub-cooled liquid vapor pressures of 2- to 4-ring PAHs are greater than or equal to 10^{-6} torr at 298 K, and ambient air measurements have shown that while the 2- to 4-ring PAHs, as well as the 2-ring nitro-PAHs, are largely gas-phase species; the many ring species are mostly adsorbed on particulates. As of the early 1980s, sampling methods that were used were impingement, precipitation (thermal or electrostatic), cyclone, cascade impactor and high volume filtration through a porous filter which is the most common method for particulate PAHs determination (Lee et al., 1981).

Typical filters used are: glass-fiber, with a collection efficiency of 99% for $0.3\mu\text{m}$ particles, cellulose filters and others like the silver membranes. The National Institute of Occupational Safety and Health (NIOSH) and the Occupational Safety and Health Administration (OSHA) recommend filters with glass fiber as well as silver membranes for personal monitoring purposes (Lee et al., 1981).

Recently there have been additions to the sorbents used in filters for sampling namely sorbents and filters which contain PUF and XAD-2 (Li-bin et al., 2007).

3.5.1.2 Soil and sediment sampling

The purpose of soil sampling is to determine the presence of contaminants. There are two basic techniques for soil sampling. Samples can either be collected with (i) some form of core sampling through the drilling of boreholes, or (ii) by excavations or trenches in which the samples are cut from the soil mass with hand-held corers. Soil samples collected from a backhoe excavation, the ground surface, soil stockpiles or by means of a manual soil coring device are usually collected in a thin-walled stainless steel or brass cylinder at least 3 inches long. All samples should be packed in a cooler with dry or blue ice in a manner that should prevent damage during transport to the analytical laboratory. Temperature during transport should be maintained at 4°C or below. A thermometer should be placed in the cooler. Samples are kept at 4°C or below at the laboratory until they are analysed. Holding time should not exceed 14 days from the time of collection (Mason, 1992).

3.5.1.3 Water sampling

The collection, transport and storage of water samples if not properly done before analysis, could alter the final composition at the time of analysis. Inasmuch as plastics, polypropylene or polyethylene containers must be avoided in water sampling for PAHs (due to their predisposition to bacteria growth), the recommended containers are those made from PTFE (polytetrafluoroethylene), stainless steel and borosilicate glass (Petrick et al., 1996). It is recommended that water samples be stored at a temperature of +4°C for up to 24 hours or 96 hours at -20°C in stainless steel containers. However, extracts may be stored as long as one month in a freezer in glass vials closed with PTFE stoppers (Law and Biscaya, 1994).

Sample deterioration before analysis can occur as a result of (i) physical processes (e.g. analyte adsorption on the walls of samplers and vessels used and evaporation of volatile components), (ii) chemical reactions (e.g. oxidation, reduction and complexation) and (iii) biological reactions (e.g. photolysis and biodegradation) (Namie'snik, 2002).

3.5.2 Extraction

Soxhlet Extraction, Ultrasonic Agitation/Sonication and Mechanical Agitation which are conventional methods of extraction are still in use today. Modern extraction methods include Solid Phase Extraction-SPE (which is like a 'miniature chromatography') (Skoog et al., 2004), Supercritical Fluid Extraction (SCF) (mostly the use of CO₂ at critical temperature and pressure as a 'green' replacement to solvents) (Bell, 2009), Microwave-Assisted Extraction (MAE) (which utilises microwave energy to heat the solvent) (Lopez-Avila et al., 1994) and Membrane Extraction (ME) (Rawa-Adkonis et al., 2006). Improved forms of some of the conventional methods have also evolved.

3.5.2.1 Solvent Extraction

PAHs are known to be soluble in a wide range of organic solvents. Solvent extraction comes highly recommended for solid environmental samples particularly particulate matter from air and combustion effluent collected on filters (Lee et al., 1981). Solvents like acetone, benzene, cyclohexane, chloroform, methanol and other alcohols, acetic acid, benzene-methanol, petroleum ether, dichloromethane and tetrahydrofuran have been used. Acetone, benzene, cyclohexane have proved to be ~ 100 % efficient in Soxhlet Extraction of benzo[a]pyrene from filters among others (Lee et al., 1981). The use of ultrasonic vibration at room temperature has also been explored for extraction of atmospheric dust (Mitra, 2003).

Accelerated Solvent Extraction (ASE) or Pressurized Fluid Extraction (PFE) is a modern solvent extraction technique similar to Soxhlet extraction, except that the solvents are used near their supercritical region where they have high extraction properties and the solvent below its boiling point, enables a high penetration of the solvent in the sample. This method is unique because it allows high extraction efficiency with a low solvent volume (15-40 ml) and a short extraction time (15-20 min). The method is applicable to the extraction of water insoluble or slightly water soluble organic compounds (USEPA, 2007).

Liquid-Liquid Extraction (LLE) which involves the partitioning of an analyte between an organic solvent and aqueous solution has been widely used for the extraction of aqueous PAHs. Improved versions of LLE include Microscale Solvent Extraction-MSE, Single Drop Micro Extraction-SDE, Gulden Large Sample Extraction-GLSE and Continuous Liquid-Liquid Extraction-CLLE (Pino et al., 2002)

3.5.3 Concentration and clean-up

Clean-up methods for PAHs analysis include solvent partitioning and chromatographic procedures (column chromatography and thin layer chromatography). Adsorbents in use include silica, alumina (classical), florisil, BioBeads S-X3, polydimethylsiloxane, PDMS-divinylbenzene (PDMS-DVB), PDMS-Carbowax (Rawa-Adkonis et al., 2006)

The following are examples of some selected concentration and clean-up schemes that are adaptable to various matrices. Though these schemes were not directly employed in this research, they give a broad perspective on the pre-analysis treatment of PAH extracts.

3.5.3.1 Extraction and clean-up procedure of PAHs in soils and sediments used by Giger and Blumer

- i) Soxhlet extraction with methanol-benzene (75 ml each for 24 hr)
- ii) Partitioning into n-pentane (3x75 ml)
- iii) Concentration: S8 removal on Cu column (benzene-pentane eluent)
- iv) GPC on Sephalex LH-20 (20 g) (benzene-methanol eluent)
- v) Alumina (silica gel) chromatography, elution with n-pentane followed by CH_2Cl_2
- vi) Charge transfer complexation with trinitrofluorenone
- vii) PAHs concentrate ready for analysis (Lee et al., 1981).

3.5.3.2 Rosen procedure as used by Moore et al. for PAHs in air

- i) Cyclohexane extraction of 10-25 mg extractable material
- ii) Reduce in volume / TLC on silica gel
- iii) Isooctane extraction (separates aliphatics) / benzene extraction (separates aromatics) (Lee et al., 1981).

3.5.3.3 Summary of extraction and cleanup procedures for the determination of PAHs in Standard Reference Materials (SRMs) for Marine Sediments

The different approaches of the extraction of PAHs from an SRM have been presented in the Figure 3.2.

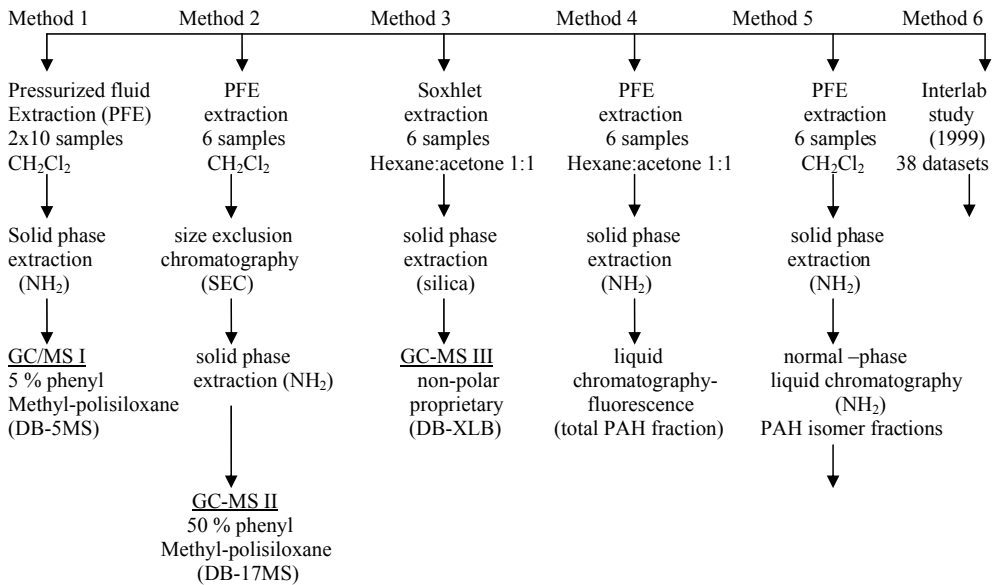


Figure 3.2: Methods for the determination of PAHs (Source Poster et al., 2006)

3.5.4 Identification and quantification

Column, paper, gel permeation and thin layer chromatography, High performance liquid chromatography (HPLC), LC-MS or HPLC-MS, Supercritical-Fluid Chromatography (SFC) LC-GC-MS, GCXGC-TOFMS, LC-ToFMS and GC-IRMS have successfully been used for identification and quantification of environmental PAHs. However, attention will be paid to the most widely used methods namely Gas Chromatography (GC) and Gas Chromatography-Mass Spectrometry (GC-MS), which was used in the instrumentation part of this dissertation). Detailed information on the techniques that were specifically used in this research is presented.

3.5.4.1 Gas Chromatography (GC)

Gas Chromatography (GC) is an analytical technique used to separate compounds based primarily on their volatilities and thermal stability. Gas chromatography provides both qualitative and quantitative information for individual Compounds present in a sample. If all or some of a compound or molecules are in the gas or vapour phase at 400-450°C or below, and they do not decompose at these temperatures, the compound can probably be analysed by GC.

Compounds move through a GC column as gases, either because the compounds are normally gases or they can be heated and vaporised into a gaseous state. The compounds partition between a stationary phase, which can be either a solid (Gas Solid Chromatography, GSC), or a liquid (Gas Liquid Chromatography, GLC), and a mobile phase (gas). The differential partitioning into the stationary phase allows the compounds to be separated in time and space (J&W Scientific, 1998).

In GLC usually referred to as GC, the stationary phase is almost always a relatively nonvolatile liquid. This liquid is coated on either solid particles or on the inside walls of a capillary tube.

The mobile phase in Gas Chromatography is an inert gas, usually helium but sometimes nitrogen or argon (Armarego and Chai, 2009). A schematic diagram of the GC set-up is shown in Figure 3.3.

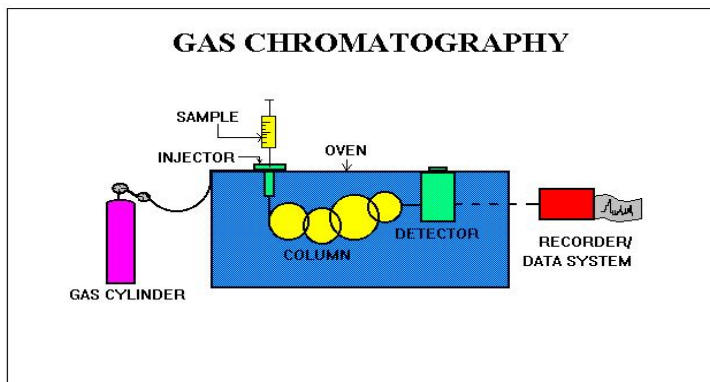


Figure 3.3: Schematic diagram of a Gas Chromatograph

In the 1950s and throughout the 1960s GC was used in the separation of smaller aromatic hydrocarbons like separation of xylene isomers and alkylated benzenes. Since PAHs cover a wide range of volatility, for example 218 °C and 525 °C are boiling points for naphthalene and coronene respectively, it is necessary to maintain high column temperatures in order to ensure elution of all the different sizes of molecules. In the 1960s, advances in columns for GC analysis of PAHs led to the introduction of thermostable silicone solid phases (Lee et. al., 1981).

With time conventional packed columns became undesirable due to their inability to separate complex isomeric mixtures of PAHs. Glass capillary columns were introduced which offered greater resolution and inertness. Thin- film coating of stationary phase also offered reduced temperatures required to elute high molecular weight molecules of PAHs. Typical stationary supports for columns for GC analysis have been silicone and carborane polymers (Lee et. al., 1981).

In the course of time eutectic mixtures were considered as solid support in an attempt to eliminate column bleeding. Graphitized carbon black solid support has been used with very little success as well as liquid crystalline phases such as N, N'-bis (p-methoxybenzylidene) - α , α' -di-p-toluidine (Lee et. al., 1981).

The traditional GC determination of PAHs has undergone a lot of innovations all aimed at better output. Modern approaches to GC analysis include Large-volume injection GC, fast GC, thermal desorption and others.

GC Detection systems

GC detection systems include Flame Ionisation Detector (FID), Thermal Conductivity Detector (TCD) and the Electron Capture Detector (ECD). FID is the most commonly used GC detector since it responds to any molecule with a carbon-hydrogen bond, is mass sensitive and destroys the sample afterwards (Lee et al, 1981; SRI Instruments, 2011). TCD is not as sensitive as other detectors but it is non-specific and non-destructive (Grob, 2004). ECD is selective to electronegative compounds; it is as sensitive as the FID but has a limited dynamic range and finds its greatest application in analysis of halogenated compounds (SRI Instruments, 2011).

3.5.4.2 Mass Spectrometry (MS)

Mass Spectrometry (MS) is an analytical technique used for mass identification and quantification and also acts as a detector for hyphenated methods. Mass spectrometry is essentially a "weighing" technique for molecules based on the motion of a charged particle, in an electric or magnetic field. The mass to charge ratio (m/z) of the ion affects this motion (Van Bramer, 1997).

MS has three essential components namely the ion source, the mass analyser and the detector (Figure 3.4). The sample under analysis is ionised and fragmentation of the charged particles may occur due to instability. The ions are then accelerated by the electric field and sent to the mass analyser where ions are separated according to their mass to charge ratios m/z . The separated ions are transferred to a detector and signals are

sent to a data system for the output mass spectrum. The ion source, the mass analyser and the detector are maintained under high vacuum to enhance ion mobility. Modern MS have all the components synchronised by a data control system (Ashcroft, 2011).

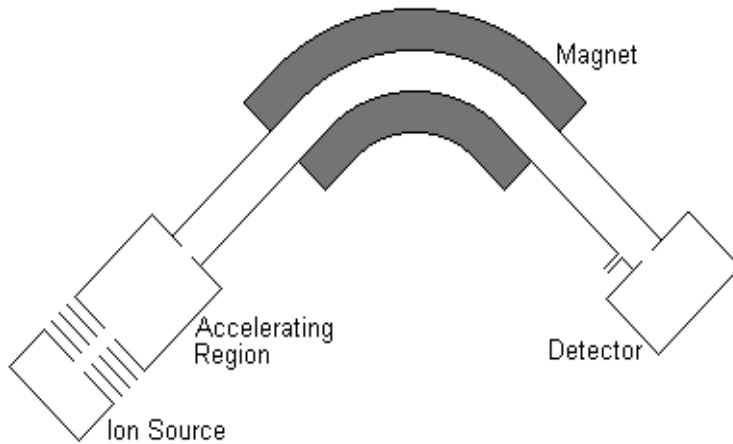


Figure 3.4: Schematic diagram of a simple Mass Spectrometer

I) Sample introduction

Before a sample goes through the process of ionisation, it has to be introduced into the MS. The choice of sample introduction method depends on the type of ion source in use as well as the sample complexity. Sample can be (i) introduced directly or (ii) treated by a prior separation method (mostly chromatography) which is normally coupled to the MS. This method normally involves the separation of the sample into components before they are consecutively sent into the MS individual analysis and identification (Ashcroft, 2011).

II) Sample ionisation

The sample ionisation methods available for MS are Matrix Assisted Laser Desorption Ionisation (MALDI) and Thermospray Ionisation (TSP) (typically not used for Mass Spectrometry analysis of PAHs) and Electrospray Ionisation (ESI), Atmospheric Pressure Chemical Ionisation (APCI), Chemical Ionisation (CI), Electron Impact (EI) Fast Atom Bombardment (FAB) and Liquid Secondary Ion MS (LSIMS) (used for samples such as PAHs) (Martin-Smith, 2004).

Electron Impact (EI)

Electron impact ionisation is the oldest and best-characterised of all the ionisation methods. In this method, gaseous analyte molecules interact with a beam of fast moving electrons. Electrons are usually accelerated through a potential difference 50-70 eV. The electron beam is produced from burning electrons off a tungsten-rhenium strip or coil of wire. When a high energy electron enters the electron density field of the gaseous sample molecule closely enough, energy is transferred to overcome the ionisation potential of the molecule which results in the ejection of an electron from the orbitals (bonding or non-bonding) of the molecule to form the molecular ion (M^+). Since the potential energy applied is sufficiently high, more electrons can be knocked off to produce +2 or +3 charges. Fragmentation of M^+ usually occurs because of the instability of the parent molecular ion. Compounds that are likely to produce multiple charge are those containing aromatic rings and hetero-atoms (hence PAHs). The analyte molecule can also absorb electrons at low energy ($\sim 0.1\text{eV}$) to form negative ions (Martin-Smith, 2004).

Direct Analysis in Real Time (DART)

DART is one of the recent modes of sample ionisation which when coupled with MS, gives high resolution mass measurements for gases, liquids and solids samples which may contain chemicals like pharmaceuticals, narcotics, metabolites, pesticides, PAHs and environmentally significant compounds (Cody et al., 2005).

DART involves atmospheric pressure interaction of sample and inert gas species, typically helium or nitrogen (containing atmospheric gases like water vapour and oxygen), that have been excited to a metastable state through an electrical discharge. Analytes present in the sample are ionised in the open air of the laboratory environment. This ionising medium is purged to retain only neutral species as the charged ones are removed prior to exiting the source. The DART is usually mounted close to the inlet of a mass spectrometer such as ToF-MS (Time-of-Flight-Mass Spectrometer). Thus, organic compounds in the sample can be determined directly, and in real time devoid of laborious analytical protocols (Cody et al., 2005).

III) Mass separation and analysis

The separation of ions in the mass spectrometer takes place within the mass analyser. There are different types of mass analysers which function on different physical principles but these devices separate ions with different m/z to allow for their separate detection. The different types of mass analysers available are magnetic sector analyser, electrostatic sector analyser, ion trap analyser, time-of-flight analyzer, ion cyclotron resonance (ICR) and Quadrupole analyser (De Hoffman and Stroobant, 2001).

Quadrupole analyser

The MS mass separation technique employed in this research was the quadrupole mass analyser which consists of four parallel rods. The opposing rods have the same polarity whilst adjacent rods have opposite polarity. Each rod is connected to a DC (direct current) and an RF (radio frequency) voltage. Ions produced in the source of the instrument are then focused and passed along the area enclosed by the quadrupoles. The motion of the ions will depend on the electric fields so that only those of a particular m/z will have a stable trajectory and thus pass through to the detector. The RF is varied to bring ions of different m/z into focus on the detector and thus build up a mass spectrum. The trajectory of the ions through the quadrupole is actually a very complex motion that is directly proportional to the mass of the ion, voltage on the quadrupole, and the radio

frequency. The ions would remain orbiting in the area between the poles with no translation along the length of the poles but for the fact that the ions have a constant velocity applied as they enter the quadrupole. Before entering the analyser, the ions travel through a potential of a certain voltage, usually created by ring electrode, in order to give the ions a constant velocity so they can transverse along the center of the quadrupole (Stafford et al., 1984).

Quadrupole mass spectrometers generally have two configurations in the modern laboratory. They are very commonly used in conjunction with either gas-chromatography or liquid-chromatography as a simple high throughput screening system. Quadrupoles can also be placed in tandem to enable them to perform fragmentation studies - the most common set-up is the triple quadrupole (Stafford et al., 1984).

Time-of-flight analyser

The Time-of-flight (ToF) mass spectrometer is based on a simple mass separation principle. ToF Analysers separate ions by time without the use of an electric or magnetic field. In a crude sense, ToF is similar to chromatography, except there is no stationary or mobile phase; instead the separation is based on the kinetic energy and velocity of the ions. When ionised species are accelerated by means of a constant homogeneous electrostatic field, their velocities are unambiguously related to their mass-to-charge ratio and times of arrival at a detector directly indicate their masses as shown in equation 3.5.

$$t = (2md/Ee)^{1/2} + L (m/2eV_0)^{1/2} \quad (3.5)$$

Where m = mass of particle, e = electronic charge, E = electrostatic field applied in source, d = length of accelerating region, L = length of field-free region, and V_0 = accelerating potential (Skoog et al., 1992).

Ions of the same charges have equal kinetic energies; kinetic energy of the ion in the flight tube is equal to the kinetic energy of the ion as it leaves the ion source shown in equation 3.6.

$$KE = mv^2/2 = zV \quad (3.6)$$

The time-of-flight instrument possesses a number of extraordinary advantages over most other types of mass analyser. Advantages of ToF include theoretically unlimited mass range, ideal where ionisation is pulsed or spatially confined, complete mass spectrum for each ionisation event, high transmission, no need for scanning the ion beam, spectra can be obtained for extremely small sample amounts (<10⁻¹⁸ mole in the most modern instruments), relatively low cost (Skoog et al., 1992).

IV) Detection and data analysis

A number of detector types are available. The selection of detector depends on the design of the instrument and the analytical applications that will be performed. A variety of approaches are used to detect ions usually based on their *m/z* ratio or their velocity. The Faraday cup detector, photographic plate, electro-optical ion detector and the electron multiplier are available but the later is the most popular detector currently in use (Hoffmann and Stroobant, 2007).

Electron multiplier

The detector within a mass spectrometer is typically an electron multiplier. The function of the electron multiplier is to detect every ion reaching it: i.e. ions of the mass specified at any particular instant by the mass filter. The mode of action of an electron multiplier is based on secondary electron emission. This occurs with the collision of ions or electrons with a charged anode called a dynode which leads to an avalanche of increasing number of electrons. A series of dynodes are so arranged that each succeeding beam of electrons

is directed to the next dynode. For example, if 4 electrons are released at the first dynode, then 16 will emerge from the second and so forth (Encyclopedia Britannica, 2011).

The millions of ions formed can be detected by an electrical circuit connected to a computer or data storage system. However other types of detectors exist which may be destructive or less frequently non-destructive.

The data obtained is used to generate a mass spectrum which shows intensity relative to mass/charge ratio, m/z . It should be noted that mass/charge ratio is calculated on the basis of elapsed time from scan start. The peak with the highest intensity is called the base peak (Hoffmann and Stroobant, 2007).

3.5.4.3 Gas Chromatography-Mass Spectrometry (GC-MS)

This is the method used for the determination of PAH levels in this dissertation.

A combination of GC and MS is a very effective approach to the identification and quantification of mixtures of PAHs which usually contain isomers. GC-MS combines the best features of both techniques and eliminates the disadvantages of each technique. The combined technique allows the GC to vaporise and separate the components of the sample and to sequentially introduce them into the MS source where distinct mass spectra of each component are obtained (Girard, 2005).

The mass spectra of many isomers are identical. It is therefore essential to be able to separate mixtures by high resolution capillary GC in order to eliminate any doubt in the identity of components.

Modern GC-MS systems have the quadrupole mass analyser which has a rapid scan speed and produces a number of mass spectra per peak. The number of spectra per peak can vary greatly, being determined either by time or by intensity changes etc. Since its introduction in 1972, the power of the combined GC-MS system for the analysis of PAHs

is evident in its wide application in the separation and identification of air particulates, combustion effluents, coal tar, aqueous industrial effluents, fossil fuels, tobacco and marijuana smoke condensates, carbon black, forest fire smoke and sediments.

In analyses where individual components have identical retention times, there could be interference which could result in too low or high concentration of the analyte of interest. Single ion monitoring (SIM) is one of the approaches at minimizing this interference. In this method, the mass spectrum is focused on a single mass to charge (m/z) value characteristic of the compound under consideration. This improves selectivity and sensitivity. Multiple ion detection (MID) can also be applied. It involves presetting a number of m/z values characteristic of the compound under consideration which thus improves selectivity since only compounds showing all of these ions will cause interference. Sensitivity is enhanced due to the longer time spent on each chosen mass. The MS acts as a detector in both cases (Lee et al., 1981).

CHAPTER 4

4. Materials and methods

The chemicals, equipment and analytical procedures used in the study are briefly described in this section. Detailed descriptions can be found in the Papers I-IV.

4.1 Materials

All reagents used were of analytical grade. Formic acid of 99 % purity was obtained from Riedel-de Haen®, Seelze-Germany. Anthracene, phenanthrene, fluorene, fluoranthene and pyrene of 98 % purity, acetone, ethanol, ethyl acetate, dichloromethane, sodium chloride, sodium hydroxide, concentrated hydrochloric acid, Nafion-SiO₂ and Pd-C were obtained from Sigma Aldrich, St. Louis, MO 63103-USA. LECA (Lightweight Expanded Clay Aggregate) was obtained from the Saint-Gobain Weber Company, Filtralite Department - Oslo, Norway.

4.2 Equipment

The major equipments used in the study are:

- Thermo Scientific Trace GC Ultra coupled with Thermo Scientific DSQ II quadrupole mass spectrometer
- Agilent Technologies 7820B GC / 5975 MSD system by Agilent Technologies from J&W Scientific- USA
- Zeiss Supra 55 VP FEG scanning electron microscope (SEM)
- Carbolite oven by, Hope Valley-UK

- Direct Analysis in Real Time, DART -100 ion source from IonSense Inc. (Saugus, MA, USA) interfaced to an AccuTOF[™] LC mass spectrometer from JEOL USA, Inc. (Peabody, MA, USA)
- Ramses-ACC-UV- Hyperspectral UVA/UVB Irradiance Sensor: 280 - 500 nm from Germany and
- Medium pressure mercury lamp with immersion well reactor system from the Photochemical Reactors Ltd. UK.

4.3 Hydrothermal reactions of anthracene

A 20 ml capacity cylindrical stainless steel (SS 316) reactor (Figure 4.1) was used in all reactions in this section with the exception of the peroxide reaction where a 5.0 ml narrow corrosion resistant stainless steel (SS 316) cylindrical tube reactor (Figure 4.2) was used (Paper 1).

4.3.1 Anthracene at 400 °C

Anthracene in the solid form was pyrolysed with water in a pre-heated oven set at 400 °C. The weight of the assembled reactor was determined before and after heating to ascertain any change in mass due to leakage. Time series were performed at durations of 24, 48, 72 and 96 hours. The product was extracted with GC-MS grade ethyl acetate by shaking for 15-20 minutes to ascertain complete extraction of products into the organic phase and analysed by GC-MS.



Figure 4.1: Disassembled reactor (20 ml) for pyrolysis oxidation reactions

4.3.2 Anthracene with formic acid at 400 °C

Anthracene was treated in a similar manner as described in section 4.3.1 above but with the addition of 0.1 ml of formic acid to the water phase before pyrolysis at 24, 48, 72 and 96 hours respectively.

4.3.3 Anthracene with H₂O₂ at 380 °C

Anthracene was hydrous pyrolysed in the presence of hydrogen peroxide (H₂O₂) in a pre-heated oven at 380 °C. The process was repeated for durations of 15 minutes to 1 hour. The product was extracted with GC-MS grade ethyl acetate and analysed by GC-MS.



Figure 4.2: Disassembled reactor (5 ml) for peroxide oxidation reactions

4.3.4 Anthracene with Nafion-SiO₂ at 300 °C

Anthracene was hydrous pyrolysed in the presence of Nafion-SiO₂ catalyst in a pre-heated oven at 300 °C for 1 hour. The process was repeated with an hourly increment of duration until all anthracene had degraded. The product was extracted with ethyl acetate and analysed by GC-MS.

4.3.5 Anthracene with formic acid / Nafion-SiO₂ / Pd-C catalysts at 300 °C

Anthracene was hydrous pyrolysed with HCOOH (formic acid) in the presence of Nafion-SiO₂ and Pd-C catalysts. Product was extracted with GC-MS grade ethyl acetate and analysed by GC-MS.

4.4 Hydrothermal reactions of mixture of PAHs (anthracene, fluorene and fluoranthene)

A 20 ml capacity cylindrical stainless steel (SS 316) reactor was used in all reactions in this section. Details of experiments can be found in Paper II.

4.4.1 Oxidation reaction system

A mixture of anthracene, fluorene and fluoranthene of equal mass ratios were hydrous pyrolysed in the presence of Nafion-SiO₂ catalyst in a pre-heated oven set at 300 °C. Ethyl acetate extract of the product was analysed by GC-MS.

4.4.2 Hydrogenation reaction system

A mixture of anthracene, fluorene and fluoranthene of equal mass ratios were hydrous pyrolysed with formic acid in the presence of Nafion-SiO₂ and Pd-C catalysts in a pre-heated oven set at 300 °C.

4.5 Sorption studies of phenanthrene, fluorene and pyrene with LECA

Sorption studies were performed with a special commercially available clay material called lightweight expanded clay aggregate (LECA) (Figure 4.3). The LECA used in the study was baked in a preheated oven at 320 °C for 3 hours.

Spike solution of concentration of 0.02 mg/l (phenanthrene, fluoranthene and pyrene) was prepared by adding 0.2 ml of ~ 0.1 mg/ml of standard solution to 1000 ml of doubly distilled water and shaking at 300 rpm for 2 hours to ensure a homogeneous distribution of the PAHs. A summary of the rest of the experiments have been presented in the sections below and details can be found in Paper III attached.



Figure 4.3: Leca particles of 1.5 - 2.5 mm size range

4.5.1 Batch experiments

Batch experiments were performed with a 100 ml aliquot of 0.02 mg/l. Aliquots were transferred into borosilicate glass bottles and 0.2 g of LECA was added. The bottles were covered with aluminium foil, screw capped and shaken for durations between 1 and 21 hours at 300 rpm. For each batch, a blank containing only distilled water and LECA was performed. PAH remaining in the solution before and after each LECA interaction was extracted with dichloromethane (DCM).

A second set of batch experiments were performed by increasing the mass of sorbent from 0.2 - 4.0 g for 21 h duration for each batch.

4.5.2 Extraction of PAHs

The amounts of PAHs in the solution before and after each LECA interaction were extracted by shaking with DCM (3, 4, 3ml) in a separating funnel. The combined dichloromethane extracts were dried with anhydrous Na_2SO_4 before GC-MS analysis.

4.5.3 Sorption isotherms

In order to obtain figures for the sorption isotherms, solutions of PAH (phenanthrene, fluoranthene and pyrene) of concentrations 0.0005, 0.0025, 0.005, 0.01 and 0.02 mg/l were shaken with 0.2 g each of LECA for 6 hours (the time period during which the most rapid sorption occurs). These concentrations are lower than the solubility of the individual PAHs in water and a realistic choice for this kind of study.

4.6 Photochemical studies of aqueous fluorene

A 0.1 ml aliquot of 20 mg/ml solution of fluorene was used to spike 1000 ml of distilled water to make 2×10^{-3} mg/ml of solution.

A summary of the rest of the experiments have been presented in the sections below and details can be found in Paper IV attached.

4.6.1 UV-Irradiation of aqueous fluorene

A 700 ml volume of the fluorene spiked water was transferred into a 1 liter immersion well reactor operated by 125 W power supplies with emission wavelength in the range of 250-500 nm. The aqueous solution was transferred into a 1 litre reactor and the lamp is immersed as shown in Figure 4.4. Batch irradiation experiments were performed for different 700 ml aliquots for durations of 1, 3, 6, 12, 18, 24 and 48 h durations.

4.6.2 Extraction of aqueous PAHs and analysis

A duplicate of 100 ml aliquots of spiked water solution were extracted with dichloromethane (3, 3, 4 ml, DCM) before and after each irradiation time by shaking in a separating funnel. The DCM extracts were combined, concentrated under nitrogen and GC-MS analysed for peak identification. Fluorene content was determined by peak comparison with a calibration curve. DART analysis was used for the confirmation of products identified by GC-MS.

4.6.3 Effect of pH on fluorene degradation

pH adjustments of distilled water were done with concentrated hydrochloric acid (HCl) and sodium hydroxide (NaOH) solutions to pH values of to ~ 3.0 and ~ 13 respectively. Solutions were then spiked, extracted and irradiated according to the procedures outlined in sections 4.6, 4.6.1 and 4.6.2.

4.6.4 Effect of salinity (NaCl) on degradation

A salt solution was prepared by dissolving 30 g of NaCl in distilled water and making it to the mark of a 1000 ml volumetric flask to make 30 % solution. The solution was spiked, extracted and irradiated according to the procedures outlined in sections 4.6, 4.6.1 and 4.6.2.



Figure 4.4: Photochemical reaction set-up

CHAPTER 5

5. Summary of major findings

This thesis follows the article- based approach and the following sections give a summary of the findings as presented in Papers I-IV attached.

5.1 Hydrous pyrolysis of anthracene under different conditions (Paper 1)

In the last several years, there has been the development of hydrothermal analytical techniques ideally suited to investigating the reaction of solid, liquid and gaseous hydrocarbons with water under conditions ranging from room temperature and pressure up to 450 °C and 2 Kb (Knauss et al, 1997).

Hydrous pyrolysis (mostly oxidative) is currently one of the principal thermal treatment methods for PAHs and chlorinated hydrocarbons (Knapp et al., 1998). Though hydrogenation by hydrous pyrolysis is not a typical treatment method for PAHs, several thermal methods have been successfully explored in the conversion of PAHs into hydrogenated forms of different degrees of hydrogen substitution (Jacinto et al., 2009; Yang and Stock, 1996).

In Paper I, the remediation of PAH contaminated industrial water using anthracene as a model compound is considered. The behavior of pure anthracene in a number of redox reaction conditions was considered. These include the use of Nafion-SiO₂, in a novel catalytic oxidation and hydrogenation of anthracene under different hydrous pyrolysis conditions at 300 °C. Distilled water and O₂ from air as oxidants for anthracene oxidation at 400 °C, a modified form of peroxide oxidation at 380 °C and formic acid

hydrogenation at 400 °C (Figure 5.1) were also considered. These methods proved effective with various degrees of anthracene reactivity. The extent of anthracene degradation was time dependent in all cases. The least effective method is the reduction with HCOOH (formic acid), which gave 47.2 % conversion of anthracene in 4 days. The most effective was the H₂O₂ (hydrogen peroxide) oxidation in which there was 100 % oxidation of anthracene to anthrone in 1 h reaction time. However, though H₂O₂ is considered quite environmentally safe due to its ability to break down into oxygen and water when dissolved in water, it is also very reactive (especially under pressure) and corrosive to reaction vessels (Yanong, 2012).

The Nafion-SiO₂ catalyst under hydrothermal conditions formed 9, 10-anthracene-dione while Nafion-SiO₂ catalyst combined with Pd-C and formic acid formed predominantly 9, 10 - dihydroanthracene and 1, 2, 3, 4 - tetrahydroanthracene.

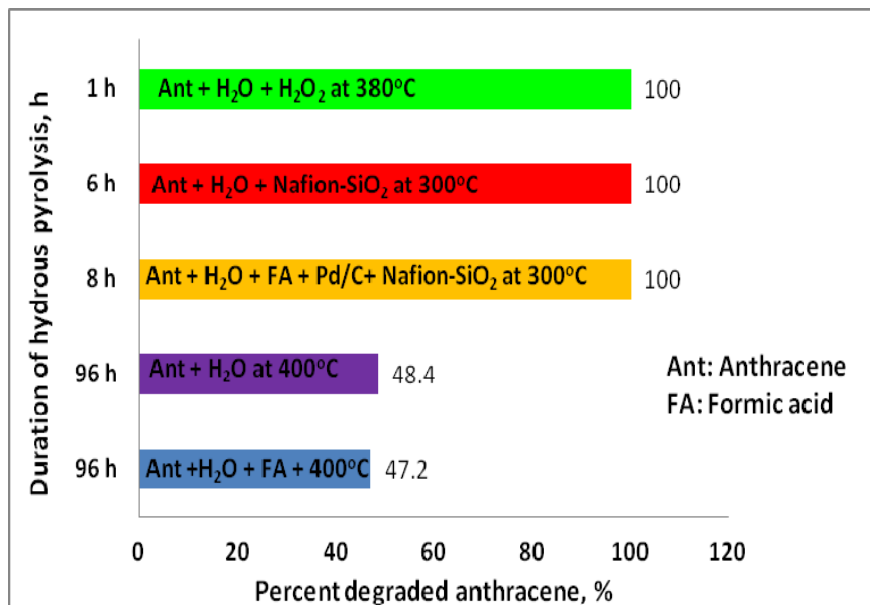


Figure 5.1: Duration of hydrous pyrolysis versus amount of degraded anthracene

5.2 Hydrothermal reactions of anthracene, fluorene and fluoranthene

(Paper II)

PAHs usually exist as mixtures in the environmental samples and though it is important to study their individual behaviours under reaction conditions, the reactivity in the presence of other compounds closely resembles what exists in nature.

Paper II looks at the behaviour of a mixture of fluorene, anthracene and fluoranthene under different catalytic hydrous pyrolysis conditions.

The PAHs in this paper were subjected to the catalytic oxidation and reduction systems described in Paper I with the aim of studying the reactivity of PAHs existing in a mixture.

Nafion-SiO₂, catalyst which was successfully used in the oxidation of anthracene in the presence of H₂O in Paper I, proved effective for the oxidation of anthracene when mixed with other PAHs as well as fluorene whilst fluoranthene remained stable under the reaction conditions. The resistance of fluoranthene to oxidation could be attributed to its high molecular weight due to the increased number of benzene rings. A strong oxidation system is more likely to achieve a reaction since it has been observed in the case of the use of ozone, peroxide and permanganate (Rivas, 2006).

This Nafion-SiO₂ catalyst system under hydrothermal conditions gave 100 % conversion of anthracene and fluorene to 9, 10- anthracene dione and 9H-fluorene-9-one respectively in 7 h (Figure 5.2). However it is worth noting that the oxidation reactions of anthracene both when studied alone and in the presence of other PAHs followed the first order kinetics with rate constants (k) of 0.3504 and 0.4514 respectively. The rate of oxidation of fluorene was however faster than that of anthracene with rate constant of 0.642. This could be attributed to the low molecular weight and the high reactivity of fluorene at position- 9 (Mojelsky and Strausz, 1996).

The C-9 position of fluorene ring is weakly acidic with estimated pKa of 22.6 in dimethyl sulphoxide (Bordwell, 1988). It undergoes deprotonation to give the stable fluorenyl carbanion ($C_{13}H_9^-$) which is nucleophilic in nature and allows electrophilic addition at the 9-position (Scherf and Brown, 1960).

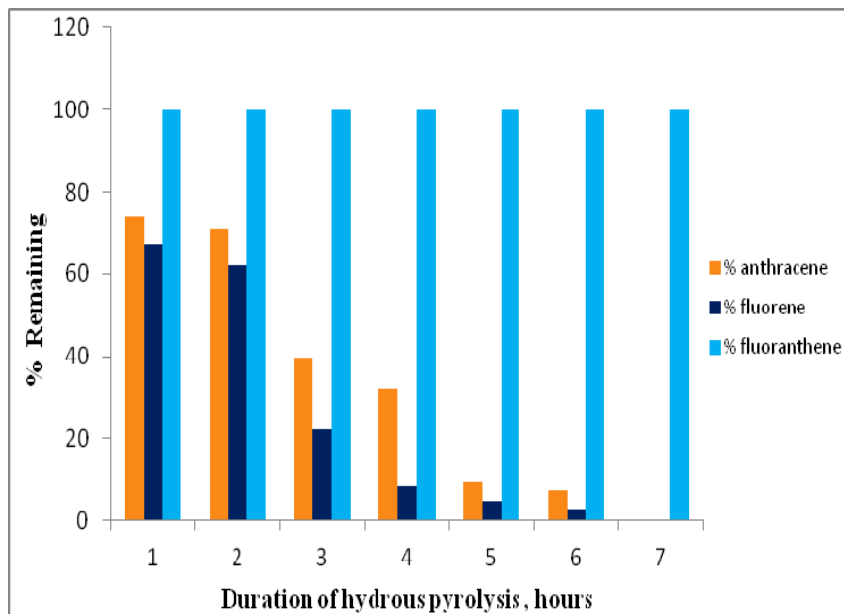


Figure 5.2: Percent PAHs remaining versus time of oxidative hydrous pyrolysis

In the second part of Paper II, a combination of Nafion-SiO₂ and Pd-C catalysts in the presence of H₂O and HCOOH was used for reductive hydrogenation purposes. The hydrogenation system also confirmed 100 % conversion for anthracene and 57.26 % conversion for fluoranthene while fluorene remained stable (Figure 5.3).

The reductive hydrogenation of anthracene and fluoranthene does not fit pseudo-first order kinetics. However it is worth noting that the rate of anthracene conversion in the mixture was faster as compared to when it was hydrous pyrolysed alone. The stability of fluorene can be explained by the fact that position-9 which is highly reactive is acidic (Mojelsky and Strausz, 1996) and not susceptible to the addition of hydrogen atoms (nucleophilic addition).

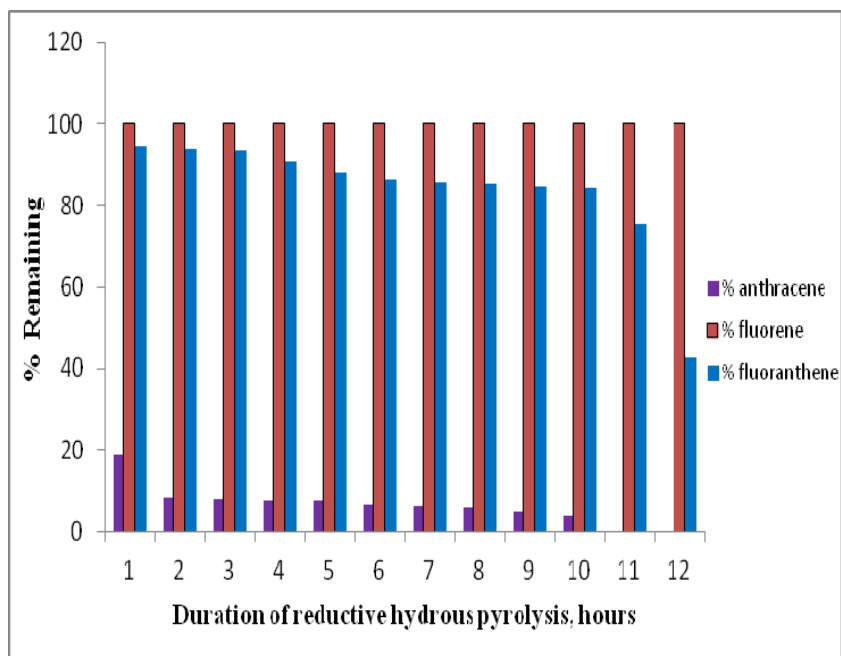


Figure 5.3 Percent of PAHs remaining versus time of reductive hydrous pyrolysis

5.3 The use of LECA in sorption studies of aqueous solution containing phenanthrene, fluoranthene and pyrene (Paper III)

The use of adsorption for the treatment of industrial waste water has been widely studied over the years due to the generally high removal capacity achieved and activated carbon is the most widely used material (Changchaivong and Khaodhiar, 2009).

Recently, a wide range of adsorbents of varied origins and capacities have been explored; and materials of both natural (organic and inorganic) as well as artificial sources have given different degrees of PAH removal (Crisafully et al., 2008 ; Hall et al., 2009 ; Jung et al., 2007; Khan et al., 2007; Yuan et al., 2010 ; Zeledon-Toruno et al., 2007).

In Paper III, the use of LECA as an adsorbent in the treatment of water contaminated by PAHs is considered. LECA finds wide application in the building and construction industry and has been used in treating heavy metal polluted water. The removal of PAHs with LECA as an adsorbent is novel since no such work has been reported.

A maximum of 92.61, 93.91 and 94.15 % removal of phenanthrene, fluoranthene and pyrene respectively was achieved when 4.0 g of LECA was shaken with 100 ml of aqueous solution containing ~ 0.02 mg/l of each PAH for 21 h. This is an improvement on the 70.7, 70.83 and 72.12 % of phenanthrene, fluoranthene and pyrene removal when 0.2 g of LECA was used.

Sorption was found to be independent of molecular weight but more on the hydrophobicity of the compounds involved, and the sorption process fitted quite well with the Freundlich isotherm.

The removal obtained for 4.0 g of LECA was 0.4631, 0.4696 and 0.4708 $\mu\text{g/g}$ for phenanthrene, fluoranthene and pyrene respectively. The usefulness of LECA as an

adsorbent compared favourably with other natural and synthetic kinds like leonardite (naturally occurring clay adsorbent) and p-phenylene-2,6-benzobisoxazole, PBO (a speciality product) in terms of removal capacity (Jung et al., 2007 ; Zeledon-Toruno et al., 2007). LECA was found to cost effective when compared to leonardite and PBO.

5.4 Photochemical Studies of aqueous fluorene (Paper IV)

Photolysis is one of the major degradation pathways for PAHs in the aquatic environment. Since PAHs are chromophore containing compounds, they readily absorb sunlight in the visible (400 -760 nm) and ultraviolet regions (280-400 nm) and are particularly sensitive to the photochemical effects of UV radiation (Arften et al., 1996).

As a result of the natural photochemical reactions associated with PAHs, artificial sources of UV have been used to study the possible reaction trends of aqueous PAHs in an attempt at achieving degradation and / or remediation (Shemer and Linden, 2007; Ledakowicz et al., 1999; Sanches et al., 2011).

Most of the work on photolysis of organic contaminants including PAHs in environmental samples involve a combination of UV irradiation and advanced oxidation processes like ozonation or the use of catalysts (like TiO₂), H₂O₂ or other oxidising agents (Beltran et al., 1995; Ledakowicz et al., 1999; Zhang, 2008); and sometimes a follow up with biodegradation (Guieysse et al., 2004; Cooper et al., 2010).

Paper IV reports the outcome of the use of an old fashioned medium-high pressure Hg lamp for UV-irradiation of aqueous fluorene solution; and the effect of irradiation time, pH and NaCl (salinity) on the extent of fluorene degradation.

Irradiation was done in a photochemical immersion well under closed static conditions for 1, 3, 6, 12, 18, 24 and 48 h durations.

The rate of degradation of fluorene in the various aqueous media followed pseudo-first order kinetics. The rate constant and R² of the rate curve as well as the amount of fluorene remaining after 48 h irradiation are presented in Table 5.1.

The outcome of the study indicated that the reaction medium had little significance on the extent of fluorene degradation though the reaction in the presence of NaCl gave the highest fluorene degradation rate.

Table 5.1: Kinetic parameters of fluorene degradation in different aqueous media

Reaction medium	R²	K/h⁻¹	% Fle removed after 48 h
Fle + neutral H₂O	0.910	0.039	95.95
Fle + HCl solution	0.986	0.018	92.35
Fle + NaOH solution	0.991	0.044	96.65
Fle + NaCl	0.716	0.049	97.15

*Fle: fluorene

5.5 Critique of cleanup techniques explored in this thesis

The methods considered in Papers I and II involve a combination of chemical and thermal treatment procedures. These techniques are among the most explored for industrial waste remediation. However, the most effective methods lead to the conversion of PAHs and other organic wastes to light hydrocarbons, CO₂ and H₂O which are environmentally benign (Kawahara et al., 1995; Ferrarese et al., 2008)

In the case where other polycyclic aromatic compounds (PACs) like oxygenated PAHs (O-PAHs) are formed, another challenge emerges, since O-PAHs have been documented to be more toxic than their parent PAHs (Huang et al., 1993; Shen et al., 2011). However, hydrogenated PAHs are less toxic (Jacinto et al., 2009).

The outcome of the thermal / chemical methods explored in this thesis either contained a percentage of the parent compounds, oxidised or hydrogenated derivatives. The products from the photochemical reaction with an artificial source of UV were also either O-PAHs or the parent compound.

Products of this nature require further treatment since they can generate problems if allowed to enter the environment. Some of the additional treatment methods available include biodegradation and advanced oxidation process (AOP) involving stringent oxidation conditions (Kawahara et al., 1995; Levitt et al., 2003; Ferrarese et al., 2008)

The removal of used of PAHs by adsorption with LECA proved effective with > 90% removal efficiency. The method is safe and requires no technical know-how to set up. LECA is an economical and available on the market and the PAHs adsorbed on LECA can be treated by either biodegradation or AOP as mentioned above.

The method based on the adsorption with LECA therefore turns out to be the most attractive of all the techniques explored in this study worth exploring on industrial scale.

CHAPTER 6

6. Concluding remarks and recommendations on future perspective

6.1 Concluding remarks

Three different clean-up approaches for aqueous polycyclic aromatic hydrocarbon removal have been presented.

The use of hydrothermal conditions for the conversion of anthracene alone as well as a mixture of PAHs (anthracene, fluorene and fluoranthene) to various oxidised and hydrogenated products has been successfully carried out.

Light weight clay aggregates (LECA) a commercially available and cost effective clay material has been used for the removal of aqueous phenanthrene, fluoranthene and pyrene.

Photochemical degradation of aqueous fluorene under acidic, basic and neutral conditions has been studied.

The outcomes of this research indicate that different methods, thermal, adsorptive and photolytic, alone or in combination with already established techniques should be considered for the removal of PAHs.

6.2 Recommendations on future perspective

- Polycyclic aromatic hydrocarbons with many rings (4 or more) could be explored to ascertain the effectiveness of the methods on them.
- Application of the pyrolysis, adsorption and photochemical methods explored in this thesis to real environmental samples to test their effectiveness.
- A look at biodegradation (which has proven to be one of the most environmentally benign and effective methods) and the possibility of removing the oxygenated PAHs (which are fit candidates for bacterial activity) generated in the pyrolysis and photochemical processes.
- Recovery of used LECA by thermal and biological methods.

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