DETERMINATION, DEGRADATION AND REMOVAL OF POLYCYCLIC AROMATIC HYDROCARBONS

Ph.D. THESIS

by

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INDIAN INSTITUTE OF TECHNOLOGY ROORKEE
ROORKEE-247 667 (INDIA)
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A THESIS

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ROORKEE

CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled **"DETERMINATION, DEGRADATION AND REMOVAL OF POLYCYCLIC AROMATIC HYDROCARBONS"** in partial fulfilment of the requirements for the award of the Degree of Doctor of Philosophy and submitted in the Department of Chemistry of the Indian Institute of Technology Roorkee, Roorkee is an authentic record of my own work carried out during a period from July, 2010 to September, 2015 under the supervision of Dr. Bina Gupta, Professor; Department of Chemistry, Indian Institute of Technology Roorkee, Roorkee.

The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other Institute.

(HIMANSHU GUPTA)

This is to certify that the above statement made by the candidate is correct to the best of my knowledge.

Date:

(Bina Gupta)
Supervisor

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ABSTRACT

Polycyclic aromatic hydrocarbons (PAHs) are among the few toxic materials present ubiquitously in the environment. Pollution is growing explosively as a result of rapid industrialization in the developed and developing countries. The degradation of the environment, mainly in urban areas, is a global issue. The problem is acute in the developing countries where the implementation of the legislation is poor. A variety of inorganic and organic pollutants get access to the terrestrial and aquatic bodies from various sources. Out of these the organic pollutants are larger in number as compared to inorganic pollutants. The organic pollutants are of particular concern because of their toxicity and bioaccumulative nature mainly due to their tendency to bind with protein molecules. A majority of the organic pollutants easily degrade in the environment but some of them persist for a longer time and are known as persistent organic pollutants (POPs). POPs include insecticides, pesticides, dioxins, polychlorinated biphenyls (PCBs) and PAHs etc. Among the POPs, polyaromatic hydrocarbon (PAHs) is a major category of pollutants. PAHs are of prime concern because of their ubiquity, undesirable concentrations encountered in the industrial, domestic and agricultural wastes, potential for magnification in the food chain and harmful biological effects. Large volumes of PAHs are released into the environment from various sources such as bitumen and asphalt industries, petrochemical industries, rubber tire manufacturing, waste incineration and thermal power plants. After emission from various sources and due to persistent characteristics, PAHs can disperse into the environment through atmospheric transport and deposit on the soil surface. The wastewater containing PAHs is released directly to the fresh water systems by the various industries resulting into the contamination of fresh water. The relentless release of PAHs results in irrevocable hazard to the human health and environment. Agency for Toxic Substance and Disease Registry (ATSDR, Georgia) governed by U.S. Department of Health and Human Services has reported a large number of ecotoxicolgical effects of PAH exposure such as leukaemia, leukoplakia, hematuria, buccal-pharyngeal cancer, bladder cancer and respiratory disorders.

The PAHs released into the environment, are partitioned into the air, water and soil on the basis of their properties. An understanding of PAH distribution is essential to design remedial measures for PAH contamination. Determination of PAHs in various segments of ecosystem is important as all of us are affected in some way or the other by their presence in the environment. Soil ecosystem is the ultimate repository for most of the hydrophobic organic

contaminants such as PAHs. The top layer of the soil is relatively more polluted as a result of atmospheric deposition. The contaminated soil is not only harmful for humans, but also for biota - plants and microorganisms. In the last two decades, a number of studies have been carried out globally to monitor PAH contamination and designate major emission sources of PAHs at various sites. Different research groups have monitored the levels of PAHs in ambient air and soils of various cities of India. Delhi, the capital of India is one of the top ten polluted cities of the world. A few research groups have monitored PAH contamination in different compartments of the ecosystem such as air, water and soil of Delhi. In the present study a large area of Delhi covering interstate bus terminals, busy traffic sites, thermal power plants and crematorium has been monitored. A total of seven PAHs including both low molecular weight PAH namely naphthalene, fluorene, phenanthrene, anthracene and high molecular weight PAH namely fluoranthene, pyrene and benzo[a]pyrene were selected for the study. The low molecular weight congeners show long range atmospheric transport and disperse to a wider extent and are abundant as compared to high molecular weight PAHs. Benzo[a]pyrene is generally considered as an environmental indicator to assess the toxicity due to high molecular weight PAHs.

Once PAHs are released in the environment, they impair the quality of air, water and soil depending on their persistence. Due to high prevalence, persistence and harmful effects on human health the studies on polycyclic aromatic hydrocarbons have been lately focused on developing efficient remediation methods for PAH contamination. In the last two decades, thermal desorption and biodegradation methods have been studied for the treatment of polluted soils. These methods have some limitations such as high cost and slow biodegradation of high molecular weight PAHs. Photocatalytic degradation of PAHs is an efficient and cheap process for the remediation of contaminated soil. The degradation of PAHs and the type of metabolites formed depend upon the chemical nature of PAH, type of medium and environmental conditions. Sometimes the metabolites are more toxic than the parent compound. In order to keep a proper track of the cycle of these materials a careful study on their persistence in soil under different environmental conditions is required. In view of the above premise photocatalytic degradation of pyrene and benzo[a]pyrene has been studied in soils of different pH in the presence of iron oxides. The metabolites have been identified and probable pathways proposed.

Widespread concern over toxicity and environmental impact of pollutants have led the scientists and environmentalists to develop effective and cost effective technologies for the removal of toxic pollutants from water and wastewater systems. Adsorption is a simple, versatile and powerful technique for the removal of pollutants from water and wastewater systems. An adsorbent is considered as low cost if it is abundant, requires a little processing, by product or waste product of any industry. Therefore, agricultural, municipal and industrial wastes have been used as low cost adsorbents in their natural form or after physical or chemical modifications. In the case of aquatic ecosystem, generally, the high molecular weight PAHs settle down on the sediments, whereas, low molecular weight PAHs are highly available in the overflowing water systems based on their solubility. In view of this, studies on the adsorption of low molecular weight PAHs from water were planned. Activated carbon is the most widely used adsorbent for the removal of pollutants. Several raw materials such as rice husk, coconut husk, plant bark, vegetable waste and chicken waste have been used for the synthesis of activated carbon. In the present study, two different waste materials viz banana peels and waste vehicular tires have been used to develop activated carbons. Banana peels are easily available and cheap raw materials for the development of efficient adsorbents. India is the largest producer of banana and hence the largest producer of banana peels waste. On the other hand, automobiles have become an essential means of transportation in our daily life and a huge number of vehicular tires are discarded every year. Vehicular tires do not decompose easily due to their cross-linked structure, presence of stabilizers and additives. Therefore, these are disposed by incineration and landfilling, which pose serious environmental pollution. In the present study, banana peels and waste vehicular tires have been converted to activated carbons which have been utilized for the removal of polycyclic aromatic hydrocarbons from aqueous systems. The adsorption studies were focused on the removal of three low molecular weight PAHs namely, naphthalene (Naph), fluorene (Flu) and phenanthrene (Phen) from aqueous systems.

For convenience and clarity of presentation, the subject matter of the thesis has been divided into following six chapters:

I. General Introduction

II. Materials, Methods and Techniques

III. Distribution, sources and toxic potential of PAHs in urban soils of Delhi, India

IV. Photocatalytic degradation of benzo[a]pyrene and pyrene and identification of

degradation products

V. Adsorption of polycyclic aromatic hydrocarbon on banana peel activated carbon

VI. Adsorption of polycyclic aromatic hydrocarbon on vehicular tire activated carbon

Chapter I gives a brief idea about the terrestrial and aquatic pollution by PAHs. The sources of polycyclic aromatic hydrocarbons are highlighted. The objective of the present study and need to carry out determination and removal of PAHs is discussed. The relevant literature on different aspects has been included in the respective chapters.

Chapter II deals with the details of sampling and preservation of the samples. The methodology used for the extraction, filtration and clean up of the samples is also discussed. Soil samples were analysed using RP-HPLC procedure and the water samples were analysed using UV spectrophotometer. The results obtained for the determination of PAHs in urban soils of Delhi were subjected to statistical analysis such as principle component analysis, hierarchical cluster analysis. The degradation products formed after photocatalytic degradation of PAHs were analysed using LC-MS. The synthesis of five iron oxide photocatalysts and activated carbons from waste materials is also described. Various instrumental techniques employed for the characterization of photocatalysts and adsorbents have been discussed in brief.

Chapter III embodies a systematic study on PAHs distribution in soils of Delhi, in pre-winter and post-winter seasons. Investigations were focused on seven PAHs namely Naphthalene, Fluorene, Phenanthrene, Anthracene, Fluoranthene, Pyrene and Benzo[a]pyrene. In order to draw some latent and relevant information the data were subjected to multivariate statistical analysis. The isomer pair ratios, principle component analysis were employed to ascertain the major sources of PAHs in soils of Delhi. Hierarchical cluster analysis was performed for the assessment of risk associated with the studied sites. The work will provide an overview of PAH levels in the soils of Delhi region due to different sources. Moreover the data will act as a benchmark for further studies.

Chapter IV describes the decay profiles and metabolic pathways of benzo[a]pyrene and pyrene on laboratory synthesized pure iron oxides as well as in soils of varying pH in presence of goethite under UV irradiation. Among the investigated iron oxides, goethite has fastest photocatalytic activity. The effect of various parameters such as photocatalyst dose, soil pH, wavelength of irradiation, presence of oxalic acid on the degradation of B[a]P and pyrene is discussed. The results suggest fast and efficient degradation of B[a]P and pyrene in the presence of goethite and oxalic acid. The photodegradation of B[a]P and pyrene occurs through the oxidative metabolism. The degradation pathways of the said PAHs in three different types of soil are illustrated. Identification of metabolites suggest that in acidic soil in presence of goethite, B[a]P is converted to smaller PAH, pyrene in 120 h. The metabolite study of pyrene suggests that, pyrene is degraded to smaller hydrocarbons, naphthalene, phenanthrene and their derivatives. Some of the metabolites such as diones, diols and epoxides, reported to be toxic, disappear after 120 h in all the three soils. The results of the study thus provide an efficient method for the remediation of PAHs and also provide a data bank for toxicological analysis.

Chapter V includes studies on the adsorption of polycyclic aromatic hydrocarbons on activated carbon developed using banana peel waste. Three PAHs with less than four rings, namely, naphthalene, fluorene, phenanthrene were chosen for the study due to their high availability in different water and wastewater systems. The adsorption data was subjected to Freundlich and Langmuir isotherms. The effect of various parameters such as contact time, adsorbent dose, pH and temperature on the adsorption was evaluated. Different thermodynamic parameters were calculated to ascertain the nature and spontaneity of the adsorption. The negative values of Gibb’s free energy change, $\Delta G°$, and the positive value of enthalpy change, $\Delta H°$, reveal the spontaneity and endothermic nature of the adsorption process, respectively. The desorption studies suggest that the adsorbent can be readily regenerated using NaOH solution in 50 % ethanol which is cheap and easily available.

Chapter VI discusses adsorptive removal of PAHs from aqueous system using activated carbon developed from waste vehicular tires. The adsorption of PAHs was achieved with varying contact time, adsorbent dose, solution pH, adsorbate concentration and temperature. Langmuir and Freundlich isotherm models were applied and thermodynamic parameters were evaluated. The regeneration of activated carbon is achieved using 1 M NaOH in 50 % ethanol. The work not only provides a solution for the tire disposal problem but also provides a cheap and highly efficient adsorbent for the treatment of wastewater generated by various industries.

The thesis concludes with a brief discussion on the findings of the present investigations. Based on the results an attempt has been made to offer remedial measures to conserve and avoid further deterioration of the environment. The results suggest that photodegradation of PAHs can be used for the treatment of soils of polluted sites. A major fraction of the domestic and industrial waste getting access to surface water bodies is untreated. More treatment plants have to be installed and the plants operating under efficiency are to be upgraded. The small scale industries located in various areas should be connected to the common treatment plants to ensure that no effluent enters freshwater systems. The levels of pollutants in soil and water should be regularly monitored.

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LIST OF PAPERS PUBLISHED/ACCEPTED/COMMUNICATED

1. Photocatalytic degradation of polycyclic aromatic hydrocarbon benzo[a]pyrene by iron oxides and identification of degradation product by **Himanshu Gupta** and Bina Gupta, Chemosphere, 138, 924-931, 2015.

2. Adsorption of polycyclic aromatic hydrocarbons on banana peel activated carbon by **Himanshu Gupta** and Bina Gupta, Desalination and Water Treatment, 2015 (In Press).

3. Iron oxide mediated degradation of mutagen pyrene and determination of degradation products by Bina Gupta and **Himanshu Gupta,** International Journal of Environment Science and Development, 6(12), 908-912, 2015.

4. Distribution, sources and toxic potential of PAHs in urban soils of Delhi, India by **Himanshu Gupta** and Bina Gupta, Journal of Environmental Chemical Engineering (Under Revision).

5. Trace metal fractionationation in water and sediments of urban river system by Rahul Kumar, Manviri Rani, **Himanshu Gupta**, Bina Gupta, Chemical Speciation and Bioavailability, 26(4), 200-209, 2014.

6. Distribution of persistent organic pollutants in urban aquatic systems by Rahul Kumar, Bina Gupta, **Himanshu Gupta**, Manviri Rani, International Journal of Scientific Research in Environmental Sciences, 2(7), 233-243, (2014).

7. Vehicular tire as potential adsorbent for the removal of polycyclic aromatic hydrocarbons by **Himanshu Gupta** and Bina Gupta, (Under Communication).

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2. Synthesis and characterisation of different iron oxide nanoparticles and their utilization for the disintegration of priority pollutant pyrene, Bina Gupta and **Himanshu Gupta**, Proceedings of Advances in Materials and Processing Challenges and Opportunities (AMPCO 2012) – An International Conference at Indian Institute of Technology Roorkee (IIT Roorkee), Uttarakhand, INDIA, Nov., 2nd -4th, (2012).

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5. Adsorption of PAHs on activated carbons derived from waste materials, **Himanshu Gupta**, Cognizance-a technical event, IITR, Roorkee, INDIA, March 27th -29th, (2015).

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LIST OF ATTENDED WORKSHOPS

1. Fifth BRNS-AEACI "**Winter School on Analytical Chemistry-2012**" organised by Association of Environmental Analytical Chemistry of India, C/o Bhabha Atomic Research Centre, Trombay Mumbai, INDIA in Department of Chemistry, IIT Roorkee, INDIA during Dec. 3rd – 10th, (2012).

2. Workshop on **"Using Web of Science for Research"** organized by Mahatma Gandhi Central Library IIT Roorkee, on Feb. 27th, (2015).

3. Workshop on **"Checking of Plagiarism in Scientific Writing using Turnitin Software"** organized by Mahatma Gandhi Central Library IIT Roorkee, on April 17th, (2015).

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Exploding urbanization and industrialization often combined with improved standards of living have resulted in deleterious effects on the quality of the environment. Due to rapid growth of industrialization in the past few decades, large amounts of undesirable wastes are being discharged in the environment threatening the survival of living beings on the earth. In the recent years, the problems regarding pollution are becoming more global and awareness about the environmental problems is increasing continuously. Environmental awakening has led many scientists to focus on the assessment of environmental impact of various industrial pollutants. The first victims of the environmental pollution are the terrestrial plants and aquatic bodies in the vicinity of urban areas that experience heavy pollution due to industrial effluents, toxic chemicals, industrial fumes and vehicular traffic. The increasing industrialisation and use of hazardous chemicals is responsible for the lack of access to clean air, water and soil in many parts of the world [1-11].

Air, water and soil are the basic necessities of human life as they are necessary for the physiological existence of human beings. Air is necessary for the existence of life, as every living being requires air for respiration. Besides respiration, air supports water cycle, pollination of crops, maintains humidity and temperature on earth surface, generates electricity and conducts sound. Water is another basic necessity of human life. Besides drinking, water is necessary for domestic purposes, irrigation, industries, power generation and aquatic organisms. Soil acts as natural habitat for bacteria, fungi insects and worms etc. which in turn increase nutrient value of soil. Soil plays an important role for the growing of plants, water filtration, production of food, clothes and wood etc. Most of the industries release toxic fumes to the atmosphere, dispose off their effluents to the nearest water body whereas, soil receives pollution through landfilling by soild waste, deposition of atmospheric fallouts and industrial discharge. There is a need for the availability of hygienically safe air, water and soil which are low in toxic organic chemicals.

In the forgoing discussion attention has been drawn towards the increasing pollution of the environment and the probable sources of pollution. Due to a large scale increase in pollution, present day society is facing a number of environmental issues which are growing in size and complexity day by day, threatening the survival of mankind on earth. In developing countries the increasing growth of human population, exploitation of resources and rapid industrialization are responsible for degradation of existing environmental components. India is a very typical example of developing nations receiving significant pollution from various sources due to rapid industrialisation and urbanisation. Constant efforts are being made by the Indian government as well as other agencies to decrease air, water and soil pollution but these are not enough until every human being participates actively and cooperates to build a pollution free environment.

With large scale industrialization, atmospheric air, water reservoirs and soil ecosystems are getting polluted with undesirable organics and inorganics. Out of these, the organic pollutants are larger in number than the inorganic ones and their number is continuously increasing. A large number of these pollutants persist for a longer time in the environment and are known as persistent organic pollutants, (POPs). POPs are organic compounds such as pesticides, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCB's), polybrominated diphenyl ethers (PBDEs) which are resistant to degradation and have adverse effect on human health as well as environment. POPs are transported across international boundries far from their sources, even at places where they have never been used. The fate and behavior of organic pollutants in aquatic and terrestrial environment is of paramount importance due to their key role in the biological cycles. Pollutants, particularly persistent organic pollutants, once released into the environment may accumulate in the food products [12-17] and ultimately find way into the human body [18, 19]. Among the POPs polycyclic aromatic hydrocarbons (PAHs) is a major category. These are of major concern because of their ubiquity, mutagenicity/carcinogenicity, bioaccumulative nature and ability of transportation to longer distances as well as in food chain. These pollutants are getting deposited on surface aquatic and terrestrial bodies in large quantities through various anthropogenic activities resulting in ecological imbalance.

Polycyclic aromatic hydrocarbons (PAHs) are recognized as potent carcinogens or mutagens and are listed as priority pollutants by the United States Environmental Protection Agency (USEPA) and European commission (EC). PAHs are introduced into the aquatic and terrestrial systems as a result of both, natural activities, namely forest fire, volcanic eruption and anthropogenic activities like incomplete combustion of fuels, cigarette smoke, vehicular traffic, fumes and wastewater releases from various industries. PAHs may also be contributed by oil spillage and tire abrasion [20, 21]. PAHs contributed by industrial and domestic waste play a significant role in deterioration of the urban aquatic and terrestrial bodies. After emission from various sources and due to persistent characteristics, PAHs can disperse into the environment through atmospheric transport and deposit on the soil surface. These pollutants are thus capable of long range atmospheric transport affecting pristine regions far from their source of origin. Humans are exposed to PAHs due to direct contact with contaminated air, water or soil. PAHs exposure to human beings is more through soil as compared to water or air [22]. Urban areas are more contaminated as compared to the rural areas due to high vehicular traffic and increased industrialization. Industrial sources include burning of fuels such as coal, wood, oil, gas and processing of raw materials. Different group of researchers have monitored the levels of PAHs in soil [23-26], sediment [27-29] and air [30-32] in various parts of the world. Reports are also available on the presence of PAHs in various water and wastewater systems [33-35].

The release of PAHs is an unavoidable output of the various industries but this results into a long term hazard for the environment. The agony of the industrial plants is that on one side there are pressures to expand and modernize the plant, on the other hand, the units are being closed down due to poor environmental management. PAHs enter into the environment through various anthropogenic activities and cause air, water and soil pollution depending on their persistence in different matrices. PAHs present in all the segments of environment are inherently toxic and accumulate in the food products by atmospheric deposition from air, translocation in plants through contaminated soil and in seafood through polluted water. Moreover, the food products also get contaminated during the cooking processes such as grilling and roasting [36]. PAHs settle down on soil and water surface through atmospheric fallout from air. On the other hand, PAHs being volatile reach air through evaporation from soil or water. Human beings are exposed to PAHs through inhalation of polluted air, consumption of contaminated food or water and dermal contact with impaired soil. The fate of PAHs and their interrelated network in the environment is illustrated in Fig. 1.1.

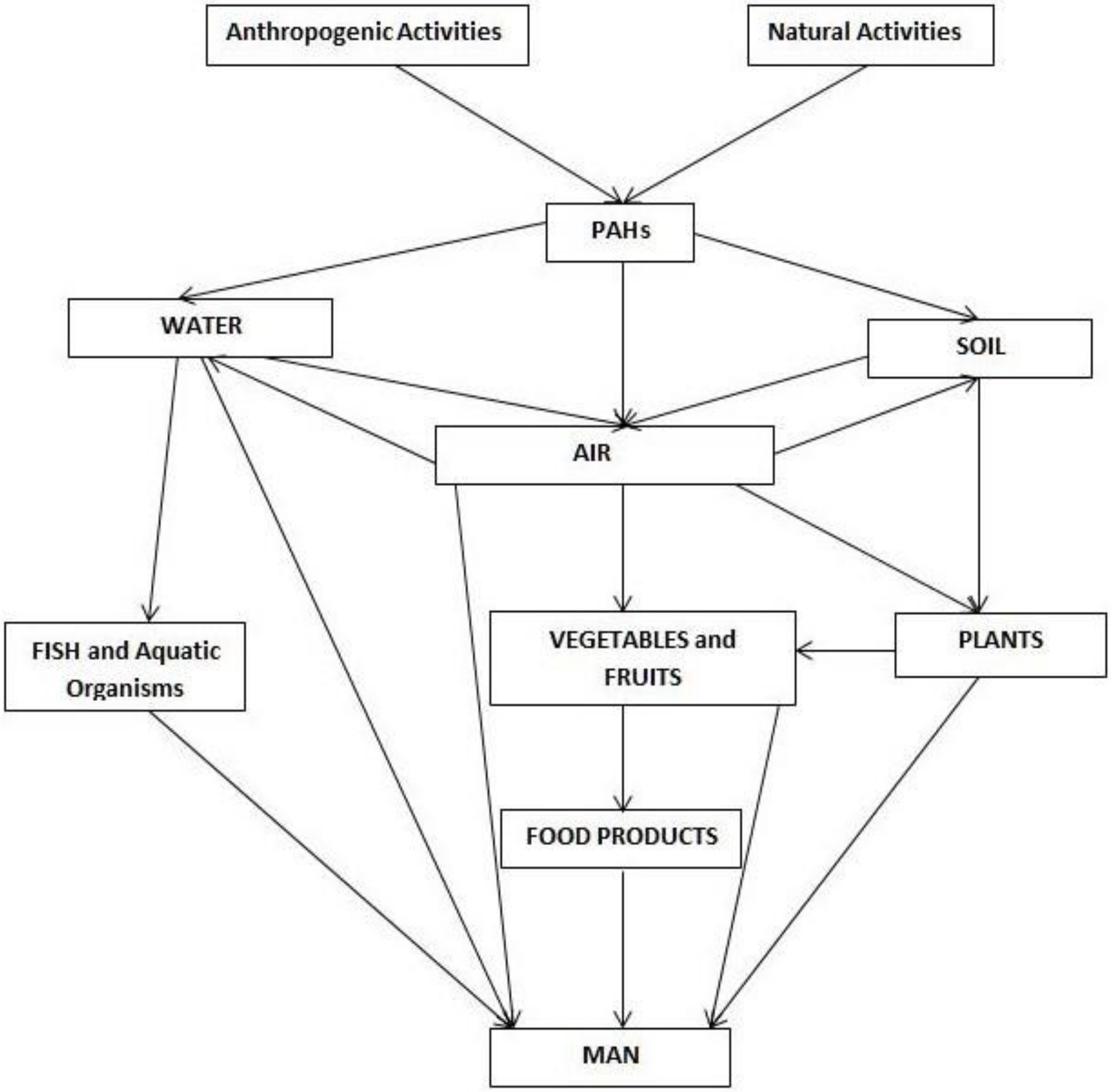

Fig. 1.1: Interrelated network of PAHs in the environment

The occurrence of PAHs in the environment is of concern due to their carcinogenic and mutagenic properties and their ability to exert toxic effects [37-41]. Because of their hydrophobic nature and low vapor pressure PAHs tend to accumulate in the soil. The PAHs pollution has been widely used to assess the potential impact of anthropogenic activities on soil surfaces because their occurrence in the soil is closely linked to the urban activities. PAH degradation on soil surface and their toxic potential has therefore been the focus of numerous studies [42-50]. Table 1.1 gives an idea about PAH contamination in soils in various parts of the globe in last one and half decade.

Table 1.1: Overview of PAHs concentrations in soils worldover

Location	No. of PAHs	B[a]P [a] (µg kg^{-1})	Σ_7 PAH [b] (µg kg^{-1})	Reference
IGI Airport Delhi	12	182-260	1931-2848	[51]
Traffic sites Delhi	16	153-461	450-1970	[22]
Agricultural Soils Delhi	16	18-71	381-1985	[52]
Urban soil, China	16	23-402	226-3335	[26]
Burnt woodland soil, Spain	8	2-48	15-303	[53]
Urban Soils, New Orleans	17	132 -410	1210-3531	[54]
Urban Soils, Detroit	17	188-1040	1184-9964	
Tokushima, Japan	13	N.D.-3.56	66-1571	[55]
Novi sad, Serbia	16	20-127	86-790	[24]
Warsaw, Poland	14	50-187	520-1233	[23]
Motorway, France	17	86.07	515	[56]
Airport, France	17	18.42	142	
River Basin, France	14	0.44-284	365-3190	[57]
Surface soils, Switzerland	16	2-69	31.5-271	[58]
Bonn, Germany	15	N.D.-20	9-123	[59]
Kola Peninsula, Russia	1	30-200	NA	[60]
Moscow, Russia	21	0.06-31	63-1190	[61]
Agricultural Soils, South Korea	16	0.42-294	10.95-1345	[62]
Background Soils, UK	15	35-60	289-358	[63]
Background soils, Norway	15	3-9.3	76-123	
El Paso, Taxas	15	N.D.-364	1.4-1399	[64]
Natural Reserve, Italy	16	1.9-39	20-262	[65]
Shanghai, China	18	N.D.-3130	9.5-16070	[66]
Agricultural Soils, Ghana	16	N.D.-50	300-1200	[67]
Pearl River Delta, China	15	0.07-29.67	16.65-297	[68]
Tianjin, China	16	41-331	766.7-3551	[69]
Tenerife Island, Atlantic Ocean	26	0.09-700	1.5-718	[70]
Urban Areas, Hong Kong	14	10.7	97.25	[71]
Polluted areas, Delhi	7	74-383	956-2714	Present study

a – Benzo[a]pyrene is an environmental indicator for PAH contamination

b – Total concentrations of seven PAHs included in the present study

In view of the widespread occurrence, persistence and harmful effects of PAHs on human population present studies were undertaken. There are 16 PAHs declared as priority pollutants by USEPA. Based on their abundance in the environment four low molecular weight PAHs (less than four ring) Naphthalene, Fluorene, Phenanthrene, Anthracene and three high molecular weight PAHs (more than four ring) Fluoranthene, Pyrene and benzo[a]pyrene were selected for the present study.

Soil ecosystem is the ultimate repository for most of the hydrophobic organic contaminants such as PAHs. The top layer of the soil is relatively more polluted as a result of atmospheric deposition. The contaminated soil is not only toxic to humans, but also for plants and microorganisms [22]. Therefore, studies were planned to monitor the levels of PAHs in an urban soil witnessing unprecedented growth in industrialisation and urbanisation. Periodical monitoring of environmental pollutants is very important as it reveals the state of environment, whether getting worse or better. It helps in assessing the progress and impact of remediation programmes being run. The data obtained is also helpful in designing and implementing new policies for environmental management. With this approach, Delhi, the Indian capital, listed as one of the top ten polluted cities of the world [22, 72] has been selected for the present study. Public transport, private vehicles, small scale industries, crematoria and thermal power plants are the major contributors of PAHs in Delhi region. Different researchers have monitored the levels of PAH in ambient air of various parts of India [73-75], but only a few studies are available on PAH concentrations in soils of Delhi region [22, 52]. Locations in the vicinity of power plants, busy traffic lights and bus stops have been the center of some studies, but no study reporting the contribution of crematorium as a source of PAHs has appeared. In the present study, sites near crematorium were also selected for monitoring of PAHs.

In order to draw some latent and relevant information the data were subjected to multivariate statistical analysis. Isomer pair ratio and principal component analysis were employed to ascertain the major sources of PAHs in soils of Delhi. PCA-MLR (principal component analysis with multiple linear regression) was performed to identify the profiles of PAH sources. Hierarchical cluster analysis was performed for grouping of sites with high potential risk. Toxic equivalency factors (TEFs) were employed to evaluate the toxic potential of various sites. The work will provide an overview of PAH levels in the soils of Delhi region due to various sources. Moreover the data will act as a benchmark for further studies.

Polycyclic aromatic hydrocarbons due to ubiquitous distribution, persistence and toxic effects have necessitated the development of efficient methods for remediation of PAH contaminated soil. Reports appearing from time to time reveal that the number and concentration of organic pollutants in the environment is continuously increasing. Thus, development of new and eco-friendly methods for the removal of these pollutants has become a challenging task. Methods like containment and thermal desorption have been used for the removal of environmental pollutants. These methods have limitations such as containment is not a permanent solution and thermal desorption leads to high costs [76]. Researchers are also focussing on the application of oxidation processes for the faster decay of organic pollutants present in the environment [77-79]. Both microbial and photocatalytic degradation processes have been used for various organic pollutants [80-83]. Among these photocatalytic degradation has proved to be of real interest for degrading organic contaminants. Photocatalysis is an efficient and economical method for remediation of contaminated soils in a relatively short time. Photocatalytic degradation of various pollutants in different environmental matrices has been the subject of many research reports [84-91]. Literature survey reveals that most of the work reported on PAH degradation in the literature is on microbial degradation of these compounds. Scattered references are documented on photocatalytic degradation of some PAHs under laboratory conditions. So it was planned to study the decay profile of some selected PAHs in the presence of iron oxides as photocatalysts.

Out of the sixteen PAHs included in priority pollutants, benzo[a]pyrene and pyrene are very important due to their carcinogenic and mutagenic character, respectively. Once released, they remain in the environment for longer duration and find their way into air, water, soil and food chain. Benzo[a]pyrene and pyrene were selected as representative PAH for photocatalytic degradation studies. Benzo[a]pyrene is a five ringed PAH and one of the most hazardous member of the priority pollutants list. Pyrene is a four ringed PAH and comparatively less hazardous than benzo[a]pyrene.

PAHs settle down in soil from atmosphere and undergo degradation forming various degradation products depending on their persistence and environmental conditions. Soil acts as a reservoir for the PAHs and their residues in the environment. There is a need to monitor the PAH levels as well as nature and fate of PAH residues in soil. Therefore, it will be interesting to study the fate of PAHs when they undergo photocatalytic disintegration under different conditions. Degradation of PAHs and the types of metabolites formed depend upon the chemical nature of the PAH, type of medium and the environmental conditions. A meaningful evaluation of the toxic effects of a PAH can be had from the knowledge of its persistence and the metabolites formed in addition to its toxicity. Sometimes the metabolites formed may be more toxic than the parent compounds. In such cases the nature and persistence of metabolite is also significant for the assessment of toxicity. The data on the photocatalytic degradation of PAHs and identification of degradation products under different soil conditions are scarce. Therefore, studies were also focused on the identification of metabolites of B[a]P and pyrene during their photocatalytic degradation in soil.

Water is one of the most important necessities of human life. Inspite of the fact that three-fourth of the earth is covered with water, fresh water resources constitute only a few percent of total water on earth. Due to continuous depletion of freshwater reservoirs, the world is facing fresh water crisis. Urbanisation, industrialisation and domestic activities further contaminate the fresh water resources. Discharge of various industrial effluents in water streams and fields is another serious problem, leading to the deterioration of quality of surface water and ground water. In the present scenario, the treatment of wastewater is one of the biggest challenges for the global environmentalists. Several international agencies such as WHO and EPA are putting efforts to combat the problem of water pollution. During the last decade adsorption has been used as an efficient and universal method for the water treatment as it is economical, eco-friendly and applicable to a wide range of pollutants. The technique is helpful for the conversion of low cost waste materials to the value added products. At present, the researchers are focusing on the development of new, more efficient and cost effective adsorbents from various waste materials.

In this context, two different waste products, namely, banana peel and waste rubber tires have been used as raw materials for the development of cheap, efficient and easily acquirable adsorbents for the removal of pollutants from aqueous systems. In the present study, the synthesized activated carbons were used for the removal of three PAHs namely, naphthalene (Naph), fluorene (Flu) and phenanthrene (Phen) from aqueous system. Naphthalene, fluorene and phenanthrene are low molecular weight PAH, present naturally in coal tar and are used as moth repellent, wood preservative and are starting material for the synthesis of several compounds such as resins [92]. The three PAHs with less than four rings were chosen for the study due to their high availability in different water and wastewater systems. The adsorption data was subjected to freundlich and Langmuir isotherms. The effect of various parameters such as contact time, adsorbent dose, pH and temperature on the adsorption was evaluated. Different thermodynamic parameters were calculated to ascertain the nature and spontaneity of the adsorption. The study not only provides an efficient method for the removal of naphthalene, fluorene and phenanthrene, but also serves as a base for the removal of other PAHs.

For the sake of clarity and convenience in presentation the work embodied in the thesis has been divided into following six chapters

I. General introduction
II. Materials, Methods and Techniques
III. Distribution, sources and toxic potential of PAHs in urban soils of Delhi, India
IV. Photocatalytic degradation of benzo[a]pyrene and pyrene and identification of degradation products
V. Adsorption of polycyclic aromatic hydrocarbons on banana peel activated carbon
VI. Adsorption of polycyclic aromatic hydrocarbons on vehicular tire activated carbon

Finally the thesis ends with a brief discussion on the findings of the present investigations in the form of **conclusions**.

The study has been helpful in determining the levels of PAHs in soils of various sites of urban city Delhi receiving pollution from various sources. The data can be useful for different government and non-government agencies engaged in restoration programs. Furthermore, the study also suggests remediation methods for the contamination of PAHs using cheap, efficient and easily acquirable photocatalysts or adsorbents. The remediation methods studied can be easily incorporated in various industrial treatment plants and can be used by various agencies involved in remediation of environmental matrices.

The relevant literature has been cited with utmost care. However, if any important contributions are omitted, they are unwittingly or due to unavailability of the information and/or judgemental error. Hence, the author would like to apologize for any such omission, if any. In order to avoid repetition the detailed literature on the determination, degradation and removal of PAHs from various environmental matrices has been provided in the respective chapters. Despite of necessary attention to restrict repetition, at times it has become unavoidable.

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INTRODUCTION

PAH analysis in soil samples is a complicated exercise involving several steps like sample collection, preservation, processing and analysis and data interpretation. Every step has its own importance and demands a special skill for its execution. The sample collection is a crucial step because the collected sample should represent the true scenario of the environment from which it is withdrawn. There are several sampling methodologies as per the demand of the study. After collection of the sample its preservation should be performed with utmost care. Analysis requires the sample in its natural/undisturbed state. Degradation of analyte or contamination of the sample during its collection and preservation will lead to misleading results. The analysis requires suitable extraction methods because if the extraction methods are not able to leach the analyte completely from the matrix, it may lead to suppressed results. On the other hand the enhanced results may be obtained due to contamination and other reasons. In view of this extraction methods must be selected carefully. Subsequently, the sample is cleaned from the remaining interfering impurities before subjecting it to assay. Adsorption column chromatography finds an extensive use for the clean up of the sample and nowadays standard cartridges are available for the said purpose. Sometimes the impurities of the reagents contribute significantly to the results. Hence, the reagent blanks should be run.

Selection of the technique for the analysis should be based on the criteria like accuracy, precision, sensitivity and selectivity. For monitoring of PAHs in different environmental segments and industrial wastes, various analytical techniques namely, spectrophotometry [1,2], voltammetry [3], liquid-liquid microextraction [4], polarography [5], capillary electrophoresis [6], ultrafiltration [7] are in vogue. Chromatography in its different forms such as column [8], thin layer [9], gas [10] and high performance liquid chromatography [11-13] have also been employed for PAH determination. Amongst these, chromatographic techniques are preferred for the qualitative and quantitative evaluation as well as separation of the PAHs and their metabolites. GC and HPLC are more popular chromatographic technique for the said purpose.

HPLC is quite advantageous as it easily provides the option of collecting the fraction for subsequent analysis. Furthermore, HPLC, quickly and accurately determines the PAHs which are not easily amenable to analysis by GC at room temperature. Several types of detectors namely, ultra violet (UV), diode array, fluorescence, refractive index and amperometric are generally equipped with HPLC. However, UV detector is most widely used, as a large number of organic compounds can be analysed with this detector. HPLC is very effective as far as the separation is concerned but is not equally good for the identification or confirmation. Therefore, hyphenated systems where liquid chromatograph is coupled with mass spectrometer are in vogue. This requirement is particularly important when the metabolites are also to be identified along with the parent compound. Thus liquid chromatograph-mass spectrometer (LC-MS) instrument provides an efficient way for analyzing the PAHs with better sensitivity and greater scope [14-17].

Reported literature reveals that reversed phase columns are better for the separation of PAHs than normal phase columns [18]. Reversed phase columns with C-8 or C-18 stationary phase and monomeric or polymeric packing have been widely used [19-21]. With regards to mobile phases, methanol, acetonitrile or their mixtures with water/buffers are generally used in isocratic or gradient mode [22-26]. After completion of the analysis data should be processed in such a way that the desired and the latent information may be available. Multivariate statistical techniques are very useful for the said purpose.

Present chapter provides detailed information about the chemicals and materials used, sample collection and preservation, instrumentation, sample analysis and data interpretation.

2.1 Reagents and Materials

All the chemicals and reagents used were of analytical grade. Naphthalene (Naph), fluorene (Flu), phenanthrene (Phen), anthracene (Anth), fluoranthene (Fln), pyrene (Pyr) and benzo[a]pyrene (B[a]P) were supplied by Sigma-Aldrich and their purity was checked by HPLC. Acetonitrile, methanol and dichloromethane used were of chromatographic grade (Rankem, India). Ultrapure water obtained from (arium pro, Sartorius, Germany) was used throughout the studies. Anhydrous sodium sulphate (E. Merck, India) and florisil (Himedia) (mesh size 60-100) used for column chromatography were of analytical grade. All the chemicals were used without further purification.

Stock solutions of individual PAH (100 mg L^{-1}) were prepared in methanol. Combined standard solutions of PAHs were prepared by mixing appropriate volumes of individual PAH solution followed by dilution with methanol. All the stock solutions were stored in dark under refrigeration. It was checked that the stock solution when stored at 4 ^{0}C is stable for four months.

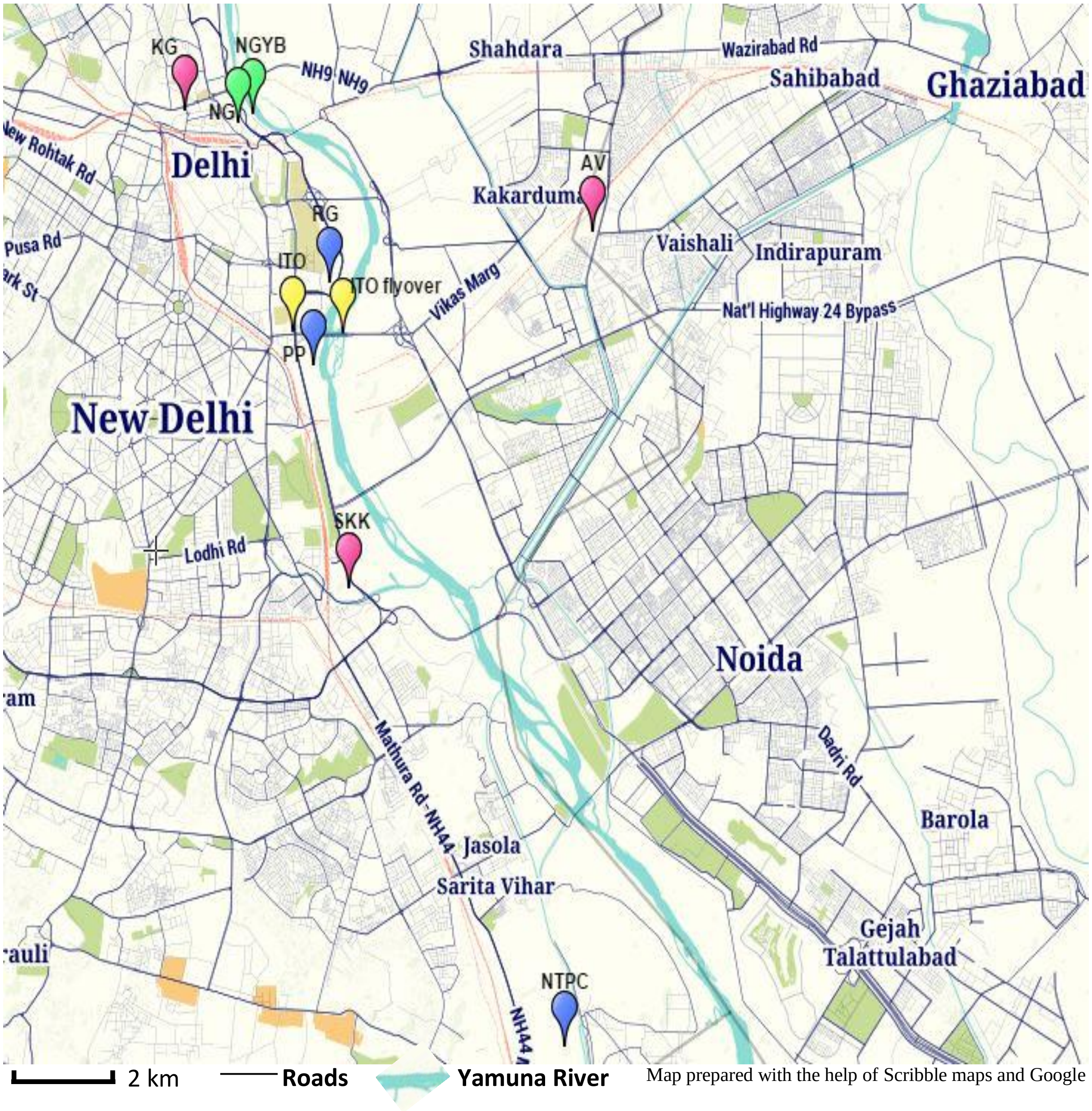
2.2 Collection and Preservation of Soil Samples

2.2.1 Monitoring Studies

Prior to use the labwares and polyethylene bags were kept in 10% (v/v) nitric acid solution for 24 h, washed with double distilled water followed by rinsing with ultrapure water and dried in a dust free environment. Soil samples from ten polluted sites of Delhi were collected in pre-winter (October, 2012) and post-winter (March, 2013) seasons. The samples were collected with stainless steel auger from a depth of 5 cm and placed in previously treated polythene bags. Composite samples were prepared by mixing five replicate samples from the same site. Samples were placed immediately in ice-box containing polar bricks and taken to the laboratory on the same day and preserved in deep freezer at 4ºC. The samples were homogenized and passed through 2 mm sieve to prepare the representative sample in the laboratory.

Sampling sites:

Delhi, the national capital of India, covers an area of 1483 kms. Delhi is surrounded by Indo-Gangetic plains (North and East), Aravalli hills (South), Thar desert (West). The river Yamuna marks the north-eastern to the south eastern boundary of the territory and is the major drinking water source for the people of Delhi. Population of the territory is about 16 million with a population density of about 11000 per sq. km. (2011 census). The urban population of Delhi is 97.5 % and only 2.5% is the rural population (2011 census). Both summer and winter seasons prevail in Delhi. In summer (March to June), the temperature rises upto 40-45 °C, whereas, in winters (November to February) falls upto 4-5 °C. The rainfall (June to August) in Delhi is 714 mm. Due to rapid industrialization and urbanization, total cropped area of Delhi is reducing every year (2.57 per cent per year). In 2000-01, 52816 hectares of the land was cropped, whereas, only 35178 hectares in 2012-13.



Map prepared with the help of Scribble maps and Google

Thermal Power Plants

RG – Rajghat Themal Power Plant
PP – Pragati Power Plant
NTPC – National Thermal Power Plant, Badarpur

Bus Terminals

KG – Kashmere Gate
AV – Anand Vihar
SKK – Sarai Kale Khan

Heavy Traffic Sites

ITO – Income Tax Office
ITO flyover–Income Tax Office flyover

Crematorium Sites

NG – Nigambodh Ghat
NGYB –behind Nigambodh Ghat at Yamuna Bank

Fig. 2.1: Map showing sampling sites and its surroundings

Industries, vehicular traffic, crematorium, power plants and domestic burning are the major contributors of PAHs in the city. A total of ten sites were selected in the city on the basis of above anthropogenic activities (Fig. 2.1). Three of these sampling sites are near the thermal power plants i.e. badarpur (NTPC), Rajghat (RG) and Pragati power plant (PP). Badarpur and rajghat thermal power plants are coal based and governed by National Thermal Power Corporation Limited and Indraprasth Power Generation Company Limited, respectively. Pragati power plant is gas based and governed by Pragati Power Corporation Limited. These three sites receive pollution from thermal power plants as well as nearby vehicular traffic. Two out of the ten sampling sites (ITO, ITO flyover) are near income tax office and have maximum traffic density in Delhi [27]. Three sites are near Inter State Bus Terminals, namely, Anand Vihar (AV), Kashmiri Gate (KG) and Sarai Kale Khan (SKK), where pollution is mainly due to the interstate and intercity buses and other diesel, petrol or CNG operated vehicles. One of the sampling sites (NG) is near the crematorium, Nigambodh ghat, where more than 50 pyres are burned every day and the last site (NGYB) is on the banks of Yamuna behind the Nigambodh ghat, which mainly receives pollution from wood burning at Nigambodh ghat (NG).

Sites near the power plants receive PAHs through fumes generated by burning of coal. At ITO and ITO flyover sites, the vehicular traffic as well as the gaseous PAHs translated through air from the power plant are responsible for pollution. At bus terminals, the PAHs accumulate due to burning of fuels in the buses, three wheelers and other private vehicles as well as through the abrasion of vehicular tires. The sites near crematorium get contaminated due to regular burning of wood with pyres. The site specific activities are briefed in Table 2.1.

2.2.2 Decay Studies

Soil samples for decay studies were collected from three different places, Uttarkashi and Roorkee (Uttarakhand) and Sriganganagar (Rajasthan), India, sieved to less than 75 mm and conditioned in an autoclave at 121^0C twice for 30 min. for complete sterilisation. Sand, silt and clay contents of different soils were determined by method described elsewhere [28]. Organic carbon content was determined by loss on ignition method [29]. The pH of different soils was determined using Indian standard method [30]. Characteristics of the three soils are given in Table 2.2.

Table 2.1: Description of sampling sites and major activities at the sites

S.N.	Station code	Name of sampling station	Activities*
1	ITO	Income Tax Office	V, TPP
2	ITO flyover	Flyover near ITO	V
3	NTPC	National Thermal Power Corporation	TPP, V
4	IP	Indraprasth Power Plant	TPP, V
5	PP	Pragati Power Plant	TPP, V
6	AV	Anand Vihar	V
7	KG	Kashmiri Gate	V
8	SKK	Sarai Kale Khan	V
9	NG	Nigambodh Ghat	W, V
10	NGYB	Yamuna bank behind NG	W, V

* V (Vehicular traffic), TPP (Thermal Power Plant), W (Wood burning)

Table 2.2: Physio-chemical characteristics of the soils

Characteristics	**Uttarkashi**	**Roorkee**	**Sriganganagar**
pH	5.4	6.8	8.1
Clay (%)	1.49	5.36	2.23
Sand (%)	87.73	70.71	83.08
Silt (%)	10.78	23.93	14.69
Organic carbon (%)	0.65	0.55	0.51

2.3 Extraction of PAHs

Prior to determination, extraction and clean up of PAH is required to remove undesirable constituents. Several extraction procedures ranging from simple to soxhlet extraction have been used to extract PAHs from soil for the analysis. Some of the commonly employed methods are liquid liquid extraction [31], solid phase extraction [32], solid phase microextraction [33], matrix solid-phase dispersion [34], microwave assisted extraction [35-37] and ultrasonic or sonication assisted extraction [38-41]. In spite of a vast literature on the extraction procedures for PAH analysis, none of the methods can be rated as the standard or universal method. The adopted method will depend upon the nature of the PAH and the medium from which it is to be extracted. On the other hand it is true that the existing information on the extraction of PAHs can provide a handy guide for developing a quantization procedure. An idea about the various extraction techniques being used for PAHs can be had from the review by Lau et al. [42]. The review proved useful in selecting suitable extraction methods for the analysis of PAHs in the present study.

Several procedures for the extraction of PAHs from soil were tried and judged on the basis of recovery and interferences encountered. Based on the results, extraction methods involving use of DCM and acetonitrile were selected. Percentage recoveries of PAHs with the two solvents are given in Table 2.3.

Table 2.3: Percentage recovery of PAHs from the soil samples

PAH	% Recovery with DCM	% Recovery with ACN
Naphthalene	83.19 %	--
Fluorene	88.84 %	87.44 %
Phenanthrene	91.04 %	89.32 %
Anthracene	88.11 %	87.39 %
Fluoranthene	93.96 %	91.39 %
Pyrene	95.79 %	98.26 %
Benzo[a]pyrene	93.62 %	97.84 %

It is evident from the results that all the seven PAHs are recovered with DCM in the range 83-95% ± 3%. However, with ACN as solvent, naphthalene is not extracted but pyrene and benzo[a]pyrene show better recovery than DCM. So for monitoring studies where all the seven PAHs are to be recovered from the soil DCM was used as solvent. The extraction of pyrene/benzo[a]pyrene from soil for decay studies was carried out with ACN.

2.3.1 Extraction and clean up of PAHs for monitoring studies

Soil (10 g) samples collected from different sites were ultrasonicated twice with 20 mL of DCM (20 x 2) at 40-45 °C for 1 h [43]. The two extracts were combined and centrifuged at 3000 rpm for 15 min. The resulting solution was reduced to an appropriate volume using rotary evaporator and kept for *in situ* clean up (Fig. 2.2). A thin layer of anhydrous sodium sulphate followed by 1 g of florisil was packed in a glass column to perform *in situ* clean up. Before introducing PAH sample, 5 mL of acetonitrile was passed through the column and discarded. After elution of the sample the column was rinsed with 8 mL of acetonitrile. The solvent was evaporated using rotary evaporator and the residue was dissolved in 5 mL acetonitrile. The solvent dichloromethane was exchanged to acetonitrile.

2.3.2 Extraction and clean up of PAHs for decay studies

Iron oxide (0.1 g)/soil sample (1 g) spiked with pyrene/B[a]P was first extracted with 5 mL ACN for 40-45 min in an ultrasonic bath at 20-25°C [44] and centrifuged at 3000 rpm for 10 min and kept for *in situ* clean up (Fig. 2.3). The clean up of the sample was performed by anhydrous sodium sulphate and fluorisil column. The column was rinsed with 5 mL of ACN, which was discarded. The sample was passed through the column and the column was rinsed with 8 mL of acetonitrile. The sample was concentrated to appropriate volume using rotary evaporator and analysed by HPLC. It was also checked that the recovery of pyrene/B[a]P with 5 mL ACN is same as that achieved with 10 mL ACN.

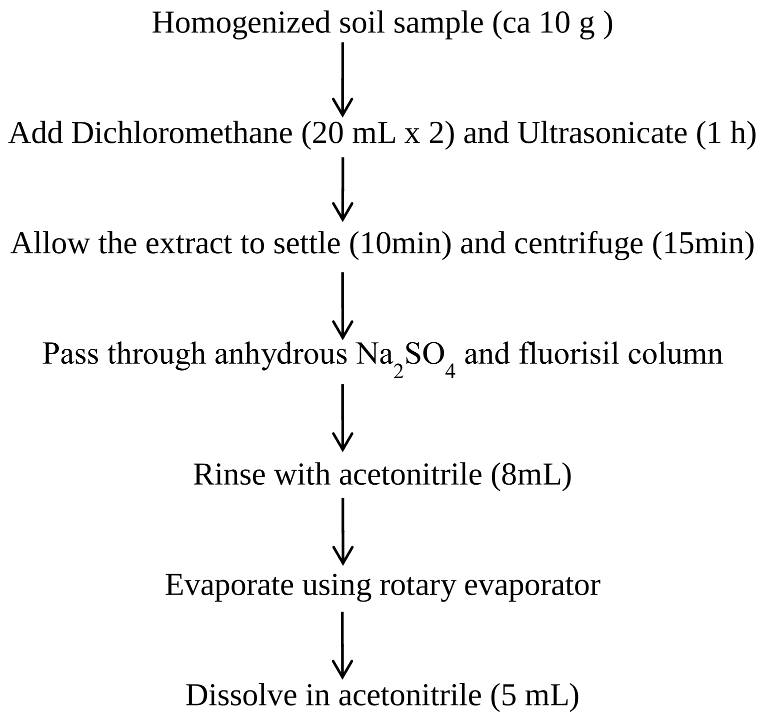


Fig. 2.2: Flowsheet for the extraction of PAHs from soil samples

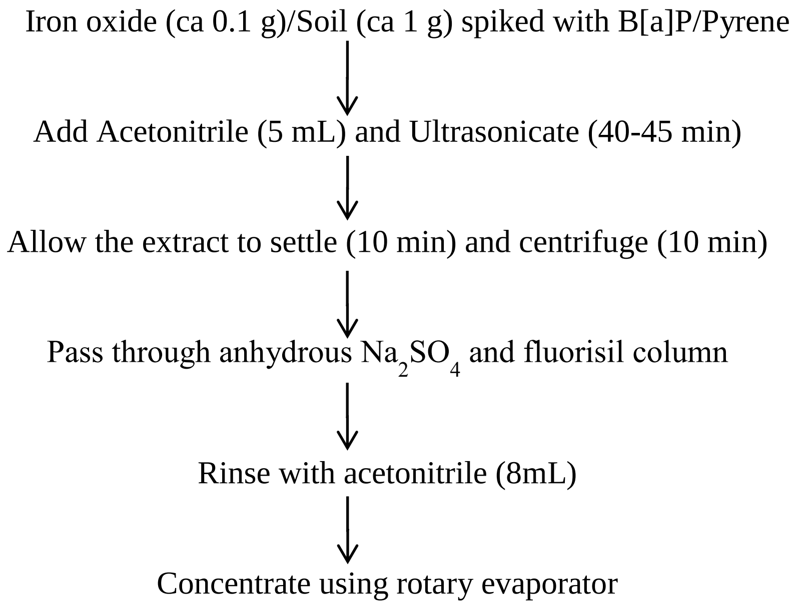


Fig. 2.3: Flowsheet for the extraction of B[a]P/Pyrene from soil samples

2.4 Synthesis of different iron oxides

Iron oxides are efficient, cheap and easily acquirable photocatalysts. There are sixteen types of iron oxides, hydroxides and oxide-hydroxides [45]. Out of these two oxide-hydroxides, namely, goethite (α-FeOOH), akaganeite (β-FeOOH) and three oxides, namely, magnetite (Fe_3O_4), maghemite (γ-Fe_2O_3) and haematite (α-Fe_2O_3) were selected for the photodegradation studies on B[a]P and pyrene. The said iron oxides were synthesized in the laboratory using reported methods. (i) Goethite was synthesized using precipitation method [45] involving addition of 4M solution of potassium hydroxide to 50 mL of 1 M solution of ferric nitrate dropwise with constant and rapid stirring until pH of the solution reaches 13-14. After 10 min stirring, same volume of potassium hydroxide was further added to make the solution highly alkaline. A red brown precipitate obtained was diluted 10 times employing ultrapure water. It was kept in an oven for 72 h at 70-75 °C. Goethite was obtained as light yellow coloured precipitate which was washed 5-6 times with double distilled water and dried in an oven at 50-55 °C. (ii) Akaganeite was prepared by withstanding 2 L of 1 M ferric chloride at 70°C for 48 h. The obtained precipitate was dried in an oven at 50 °C [45]. (iii) Magnetite was prepared by stirring equal volumes of 1 M ferric nitrate and 0.5 M ferrous sulphate solutions for 5 min and adding liquid ammonia to adjust the pH between 9.7 and 10.6 [46]. (iv) Haematite was obtained by heating goethite at 245°C in muffle furnace as indicated by TGA/DTA. (v) Maghemite was obtained by heating magnetite at 224°C as suggested by TGA/DTA pattern.

2.5 Preparation of activated carbon from banana peel

Banana peel was used as a precursor for preparing activated carbon using the method described by Srinivasakannan and Bakar [47]. Banana peels were dried overnight in an oven at 70°C. The dried banana peels were allowed to soak with 60% phosphoric acid for overnight. The soaked samples were kept in a muffle furnace at 200 °C for semi-carbonization for 4 h. The semicarbonised material was cooled to room temperature. The dried material was again heated in furnace at 500 °C for 2 h for activation. The activated material (BPAC) thus obtained was repeatedly washed with ultrapure water to remove all the acid from the material and washing was continued till the wash liquor was neutral. The obtained carbonaceous material was finally washed with 0.1 M sodium hydroxide solution, followed by ultrapure water. The products were dried in hot air oven for 5 h at 105 °C and subjected to size reduction so that the material passes through 75 μm mesh.

2.6 Preparation of activated carbon from vehicular tire

The method described by Gupta et al. [48] was followed to prepare activated carbon from waste vehicular tire. Waste vehicular tire collected from an automobile repairing workshop was cut into small pieces, washed thoroughly with ultrapure water and dried at 100 °C for 2 h in an oven. The obtained material was carbonized at 500 °C for 5 h in a muffle furnace. This carbonised material was treated with H_2O_2 (30%) solution and kept at 60 °C for 24 h to oxidise adhered impurities. The material was cleaned with ultrapure water to remove H_2O_2 and placed in an oven at 110°C for 2 h. Two grams of the obtained material was mixed with 8 gm of KOH and kept at 900 °C in a silica crucible for 2h in muffle furnace. The ash content was removed using 1 M HCl solution followed by ultrapure water and dried at 100 °C. The dried product obtained is referred as vehicular tire activated carbon (VTAC).

2.7 X-Ray Diffraction (XRD) and Field Emission Scanning Electron Microscopy (FE-SEM)

Synthesized iron oxides and activated carbons were characterized by X-ray diffraction studies. Powder X-ray diffraction patterns were obtained using Bruker AXS D8 powder diffractometer with Cu K_α radiation (40 kV, 45 mA, λ= 1.5418 Å) and 2°/min goniometer speed was employed for the analysis. ZEISS Ultra plus microscope at 15 kV was employed for Field Emission Scanning Electron Microscope (FE-SEM) images. The XRD patterns and FE-SEM images of iron oxides and activated carbons are given in the respective chapters.

2.8 UV-VIS Spectrophotometry

The concentrations of PAHs in water before and after adsorption were measured using UV-Vis spectrophotometer (UV-2450, Shimadzu Corporation, Kyoto, Japan). Naphthalene, fluorene and phenanthrene were analysed at 275, 262 and 250 nm, respectively.

2.9 BET surface area

BET surface area of the prepared activated carbons was assessed using Micrometics Instrument (Norcros, USA).

2.10 Fourier transform infrared spectroscopy (FTIR)

Functional groups present on the activated carbons before and after the adsorption of PAHs were analysed by Fourier transform infrared spectroscopy (FTIR) (Nicolet 6700, ThermoScientific, USA).

2.11 High performance liquid chromatography (HPLC)

For monitoring and photodegradation studies, the extracted PAH samples were analysed by HPLC using Agilent 1100 series, (Agilent Technologies, USA) chromatograph equipped with UV detector. The analysis was carried out on an Octadecyl end capped RP-C_{18} column (250 x 4.6mm, 5µm). Twenty microliters (20 µL) of the sample were injected each time and the flow rate of 1 mL min^{-1} was maintained. The system was operated at ambient temperature. The limit of detection for HPLC was 1 µg mL^{-1}.

2.12 Optimization of parameters for the analysis by HPLC

The conditions for HPLC analysis were optimized by varying different parameters such as mobile phase composition, UV detector wavelength, flow rate of the mobile phase and injection volume. With a view to get the best recovery and resolution, several mobile phases were examined. A binary solvent system comprising of acetonitrile and water in gradient mode was optimised as an eluent with a flow rate of 1 mL min^{-1} for the analysis of mixture of seven PAHs. The gradient elution method is as follows: 60% acetonitrile for 23 min, linear ramp to 90 % ACN within 2 min and holding at 90 % ACN for 5 min. The chromatogram showing separation of the seven polycyclic aromatic hydrocarbons is given in the Fig. 2.4.

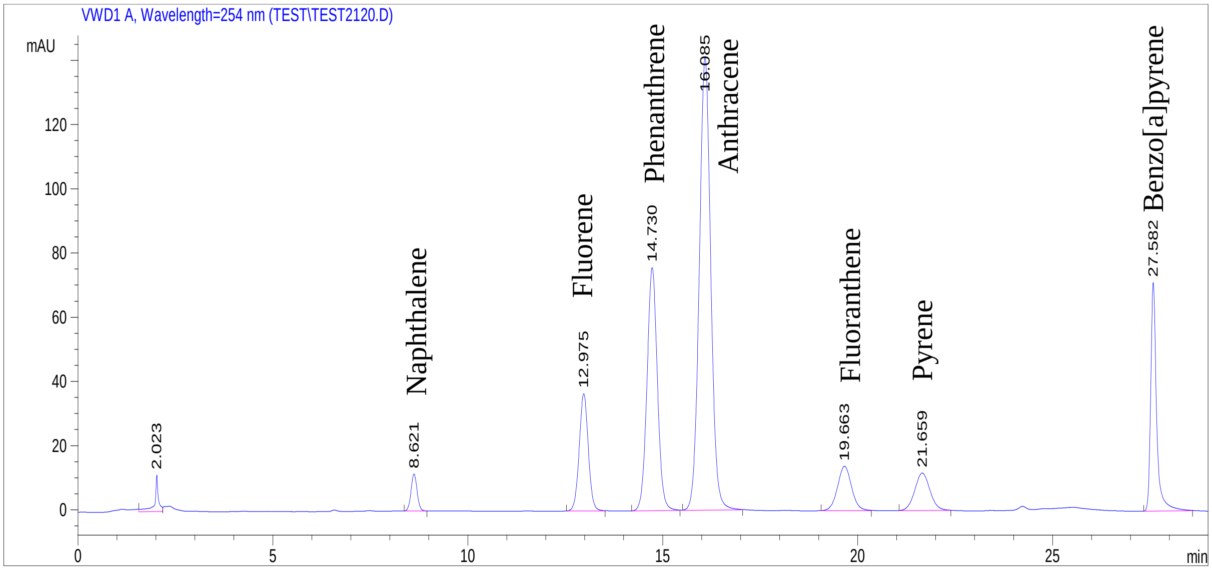
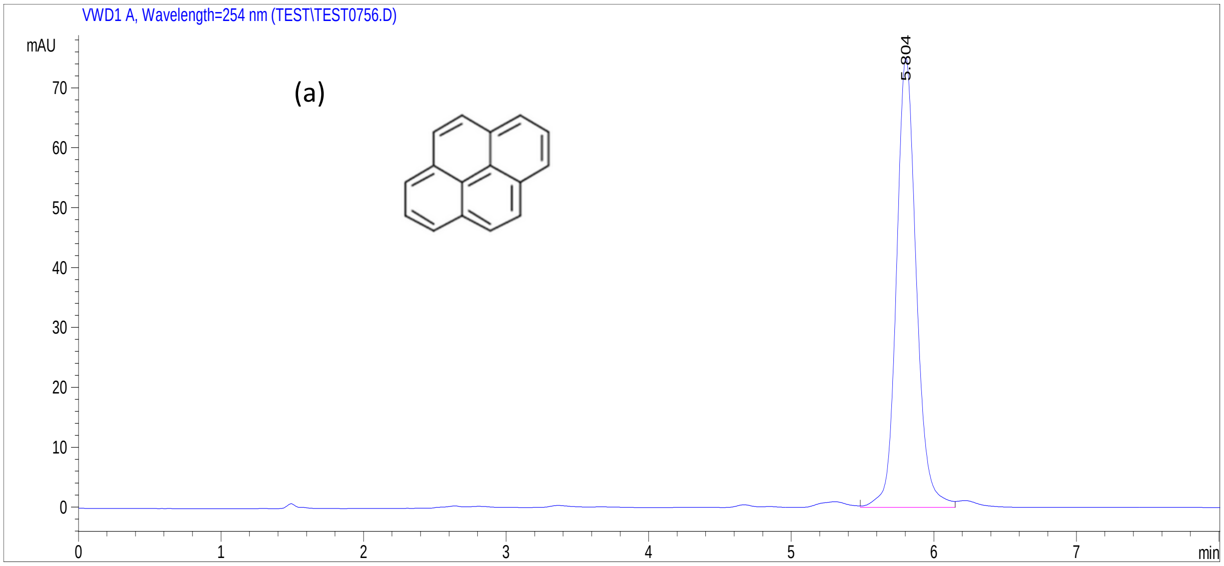


Fig. 2.4: HPLC Chromatogram of polycyclic aromatic hydrocarbons for gradient mode

For decay studies, binary solvent system comprising of acetonitrile : water (90:10) in an isocratic mode was optimised as an eluent and a flow rate of 1 mL min^{-1} was found suitable for the determination of benzo[a]pyrene or pyrene. Twenty microliters (20 µL) of the sample were injected each time and chromatographic signals were observed at 254 nm wavelength at ambient temperature. Calibration plot for individual PAH in combined standard solutions or individual standard solutions was accomplished by plotting standard peak area verses concentration. The plots obtained were linear and used to calculate response factors for determination of concentration of individual PAH. Linear plots (r^2=0.99) were obtained in the concentration range 1- 100 µg mL^{-1}. The retention time for the elution of pyrene and benzo[a]pyrene were found to be 5.8 and 7.0 min, respectively. The chromatogram for the pyrene and benzo[a]pyrene are shown in Fig. 2.5 (a&b).



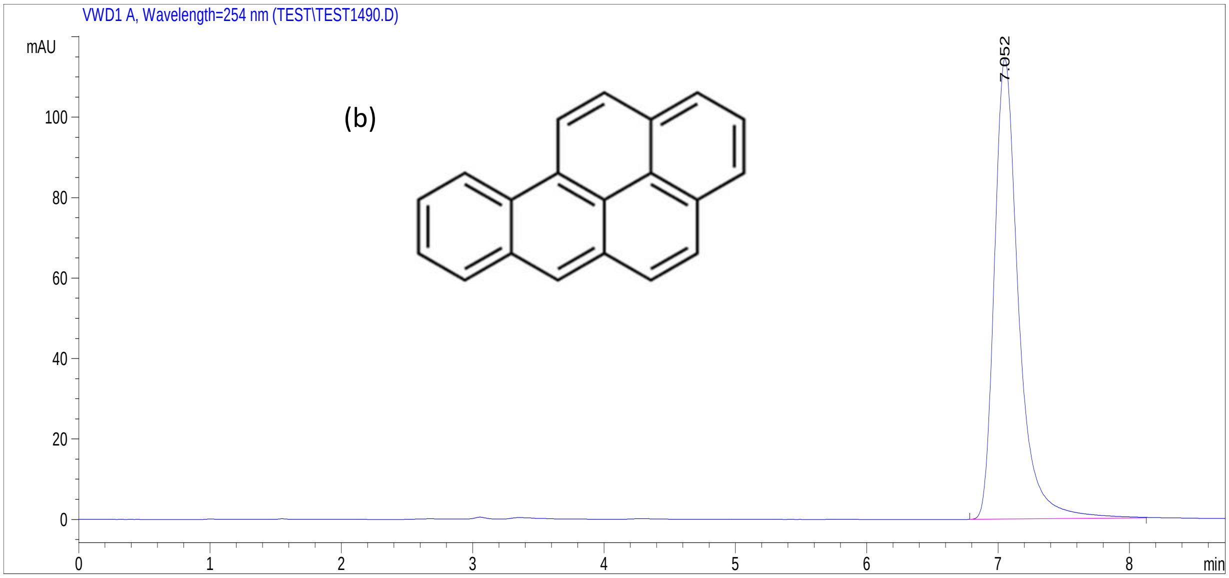


Fig. 2.5: HPLC Chromatograms of (a) pyrene and (b) benzo[a]pyrene for isocratic mode

2.13 Liquid chromatography with mass spectrometry (LC-MS)

LC-MS was used for the separation and identification of metabolites of benzo[a]pyrene and pyrene. A Shimadzu LC-MS-8030 (Shimadzu Corporation, Kyoto, Japan) instrument with Labsolutions software version consisting of automatic injection, a binary pump and UV-Vis detector coupled in series with a mass selective detector equipped with an electron spray ionization source, was employed for identification of metabolites. An

Octadecyl end capped RP-C_{18} column (100 x 1.6 mm) and acetonitrile : water (70:30) mobile phase with a flow rate of 0.2 mL/min was used for LC-MS study. Ionization of analytes was carried out using ESI mode. The optimum chromatographic and mass spectrometric conditions are listed in Table 2.4.

Table 2.4: Parameters for LC–MS analysis

LC separation	
Solvent A	Acetonitrile (70%)
Solvent B	Water (30%)
Flow rate (mL min^{-1})	0.2
Time (min)	30
MS detection	ESI
Drying gas flow (L min^{-1})	10.0
Drying gas temperature(^{0}C)	250
Nebulizer pressure (psi)	10
Capillary voltage (V)	4000
m/z range	50–400

2.14 Adsorption studies

Working solutions of PAHs (20 mg L^{-1}) were prepared from stock solutions (100 mg L^{-1}) using 20% methanol for dilution. The solutions were stored in airtight glass bottles in deep freeze at 4°C. Ultrapure water was used throughout the analysis. The solution pH was adjusted using HCl and NaOH solutions and determined using digital pH meter (Toshniwal industries, India). Julabo GmbH, Germany thermostat was used to study the effect of temperature on adsorption.

Adsorption studies were carried out in batch mode at 25±2°C. Thirty millilitres of a PAH solution of a known concentration were taken in a conical flask and optimum amount of the adsorbent was added. The mixture was shaken on a mechanical shaker for appropriate time at pH 7 (unless otherwise mentioned) and left for 5 minutes to attain equilibrium. The samples were filtered through Whatmann filter no. 42 and analysed using UV spectrophotometer at 275, 262 and 250 nm for naphthalene, fluorene and phenanthrene, respectively. The analysis was carried out in triplicate. The amount of PAH adsorbed per gram of adsorbent q_e, was evaluated from the mass-balance equation:

$$q_e = V(C_0 - C_e)/W \qquad (1)$$

where V is the volume of the solution (L), C_0 is the initial concentration of the adsorbate solution (mg L^{-1}), C_e is the concentration of the adsorbate in liquid phase at equilibrium (mg L^{-1}) and W is the mass of the adsorbent (g).

The adsorption data obtained at different temperatures was used to draw Langmuir and Freundlich isotherms. The Langmuir isotherm predicts the existence of monolayer coverage of the adsorbate at the outer surface of the adsorbent [49]. The linear form of Langmuir adsorption model is given below:

$$1/q_e = (1/Q°b)(1/ C_e) + (1/ Q°) \qquad (2)$$

where Q° is the measure of adsorption capacity of monolayer (mg/g) and b is the Langmuir constant. The plot between $1/q_e$ and $1/ C_e$ is a straight line with a slope corresponding to 1/Q°b and intercept to 1/ Q°. Based on the Langmuir constant b and initial concentration C_o, the values of separation factor, R_L, were calculated using equation -

$$R_L = 1/(1 + bC_o) \qquad (3)$$

Freundlich isotherm [48] demonstrates the multilayer adsorption involving heterogeneous surfaces. The isotherm is expressed by the following equation:

$$q_e = K_f C_e^{1/n} \qquad (4)$$

where K_f and n are Freundlich constants. The linear form of the equation obtained by taking logarithm on both the sides is given below:

$$\log q_e = \log K_f + 1/n \log C_e \qquad (5)$$

A plot of $\log q_e$ versus $\log C_e$ gives a straight line with a slope of 1/n and intercept of $\log K_f$.

2.15 Statistical Analysis

Three statistical techniques namely Pearson’s Correlation analysis, Principal Component Analysis with multiple linear regression (PCA-MLR) and Hierarchical Cluster Analysis (HCA) have been employed for the data treatment of sites of Delhi region with different aims and objectives. Pearson’s correlation analysis was applied for identifying the correlation between PAH and total organic carbon in soils of different sites. The data have been subjected to PCA to ascertain the major sources of PAHs in soils of Delhi. PCA-MLR was performed to identify the profiles of PAH sources. HCA was performed for the assessment of risk associated with the selected sites using between groups linkage method and Euclidean distances as a measure of similarity. All the statistical analyses were performed using SPSS 17.0 software (SPSS Inc., USA) for Windows.

The accuracy of the method employed for the determination of PAHs was assured by analyzing the spiked standard samples. The agreement in the results is within ± 10%. The values reported are the average of triplicate runs and the variance observed is less than 10%. Reagent blanks were run, wherever necessary.

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INTRODUCTION

In the present scenario, the greatest threat posed to humanity, and to a great extent to the whole biosphere, is environmental contamination, a byproduct of man's advancement in industrialization, urbanization and modern domestic activities. Major activities responsible for environmental pollution in an urban area are plastic and metal production factories, power plants, petrochemical plants, pharmaceutical and chemical plants, paper and pulp manufacturing units, refining processes, waste incineration, heavy vehicular traffic. The said activities introduce a number of inorganic and organic pollutants in the environment. The environmental pollutants have a wide range of adverse effects on human health such as carcinogenicity, mutagenicity, neurotoxicity, immunotoxicity and endocrine disruption. Human exposure to small amounts of such pollutants is widespread due to ubiquity and high stability of these compounds. High exposure to pollutants may occur among people living near the polluted sites.

Soil in an urban area is affected by the pollutants released by the above mentioned activities. Majority of pollutants are organic in nature and persist for a longer duration. One such category of persistent organic pollutants is polycyclic aromatic hydrocarbons (PAHs) which are well known for their persistence and toxicity, thus posing a challenge to the ecologists and toxicologists. The anthropogenic sources of PAHs in the soil are industrial releases, domestic burning, vehicular exhaust, atmospheric deposition, oil spillage, improper disposal of waste materials and use of organic waste as soil fertilizer. Some natural activities like volcanic eruption, forest fire also contribute towards PAH contamination. Some PAHs present naturally in fuel deposits such as coal, diesel, petrol etc. are referred as petrogenic PAHs. PAHs mainly concentrate in industrial zones and urban areas due to heavy emissions from industries and dense vehicular traffic. In view of this, studies were planned to monitor the distribution of PAHs in the soils of Delhi region.

In the last decade, awareness about the presence of PAHs in the environment has increased and the studies have been focused to measure the levels of PAHs in different systems/segments such as indoor and outdoor dust [1], sewer effluent [2], sewage sludge [3], treatment plant [4], fish [5], edible oil [6], air [7], soil [8], marine organism [9], cigarette smoke [10], wastewater [11], lake water [12], alcohol drinks [13], coffee brew [14]. PAHs have a tendency to bioaccumulate in the food chain and thus pose a great threat to the human health. PAHs have been detected in the soils of China [8], Japan [15], Serbia [16], Poland [17], France [18, 19], Russia [20] including India [21]. In India, PAHs have been detected in almost all the segments like air [22-24], ground and drinking water [25-28], agricultural soil [29, 30], sediments [31, 32], food commodities [33-35], fish [36, 37], birds [38, 39], mothers' milk [40] and human blood [41]. A serious concern about the occurrence of PAHs in soils has arisen among the environmentalists world over and enormous literature is being published every year. It is not possible to compile all the existing literature here. Therefore, an overview of the contributions of various researchers for the monitoring of PAHs in the soils of different regions of the world in the last decade is given below.

A study from Serbia [16] reported monitoring of PAHs in surface soils of an urban area Novi Sad (Serbia) and in sediment sample of Danube River (Serbia). The total PAH concentrations in surface soils were in the range 0.307-1.452 µg/g and in sediment sample ∑PAHs value was 0.975 µg/g. Maximum ∑PAHs values were observed in soil near the industrial area. Carcinogenic PAH benzo[a]pyrene was 6-14% of ∑PAH content in all the samples. The results revealed that only one site which was in outskirts of the city had carcinogenic potency below the polluted level. Xing et al. [42] studied the distribution of PAHs in the valley of Yangte Delta region, China. The average concentration of PAHs was in the range 0-530 µg/Kg. Indeno[1,2,3-cd]pyrene and B[a]P were found in higher concentrations, whereas, pyrene and fluorene were observed in very low concentrations. The average concentrations of PAH homologues were in the order: 2-rings < 6-rings < 4-rings < 3-rings << 5-rings. The study further revealed that the south easterly winds during spring and winter seasons resulted in atmospheric deposition which led to higher PAH levels in the southern part of the valley. Higher PAH concentrations were also observed in soil samples which were from the area near the smelting furnaces.

A study [8] on PAH levels in urban soils of Beijing (China) indicated the dominance of 4-6 ring PAHs at all the sites. Correlation analysis further indicated that the sources of PAHs were similar. The isomer pair ratios suggested coal combustion and vehicular emission as the major sources of PAHs. Garcia-Falcon et al. [43] studied PAH levels in burnt woodland soils and found that the levels of PAHs were similar to those observed in the distant and periurban soil (unburnt) and were seven times higher than the rural soil (unburnt).

Morillo et al. [44] investigated PAH pollution in the urban soils of Torino (Italy), Glasgow (UK) and Ljubljana (Slovenia). The levels of PAHs were significant in Glasgow and in other two cities the levels were ten-fold lower than Glasgow. Pyrene, fluoranthene and phenanthrene were the predominant PAHs. The results suggested pyrogenic origin of PAHs and exhausts of motor vehicles were the major PAH source in all the cities.

Holoubek et al. [45] assessed background levels of some POP's in soils, needles, moss and sediments of Czech Republic (Kosetice observatory). The average PCB concentrations in soil or moss were in the range 2-7 ng/g. The DDT concentrations were higher in soil or sediment than needle or moss, whereas hexachlorocyclohexane (HCH) levels were higher in needle or moss than soil/sediment. ∑PAHs values were in the following order: soil > needles > moss > sediment. Results further indicated that the levels of PAHs, HCH and PCBs decreased over the years in water, sediment and soil, whereas, no such trend was observed for HCH and DDT.

Crnkovic and associates [46] examined surface soils of rural, urban and recreational areas of Belgrade (Serbia). ∑PAHs values in recreational areas (298 µg kg^{-1}) were comparable to urban areas (375 µg kg^{-1}), whereas, relatively low ∑PAHs values (18 µg kg^{-1}) were observed in rural areas. The isomer pair ratio indicated pyrogenic sources of PAHs. The results revealed high concentrations of pyrene, phenanthrene, benz[a]anthracene and fluoranthene, which were assigned to the use of non-catalyst vehicles in Serbia.

Presence of PAHs and PCBs in the urban soils of Kathmandu (Nepal) was observed by Aichner et al. [47]. ∑PAHs and ∑PCBs were in the range 1.84-10.279 µg g^{-1} and 3.56-44.71 µg kg^{-1}, respectively. Perylene, benzo[b,j,k]fluoranthene, phenanthrene and naphthalene were found as most abundant PAHs. At petrol stations, the PAH ratios indicated petrogenic origin of PAHs. The samples from gutter showed highest PAH and PCB levels.

The elevated levels of PAHs in the soils of banks of Mosel and Saar rivers (Germany) were detected by Pies et al. [48]. Results suggested that the upstream confluence of the rivers is dominated by pyrogenic sources of PAHs, whereas, the downstream confluence is dominated by both petrogenic and pyrogenic sources. Wang and co-workers [49] investigated the distribution and sources of PAHs in urban soils of Detroit and New Orleans. The average total PAHs concentration of Detroit soils was higher than the New Orleans soils. In both the cities, observed PAH concentrations followed the order open space soil < residential street soil < busy street soil. Isomer pair ratios indicated pyrogenic sources.

PAH levels in background soils of UK and Norway were determined by Nam and others [50]. The PAH concentrations were in the range 0.42-11.2 µg/g and 0.086-1.05 µg/g in UK and Norway soils, respectively. In Norwegian soils, PAH and TOC show significant correlation, but in UK soils, black carbon shows significant correlation with high molecular weight PAHs. The same group [51] monitored PAHs in background soils worldover. The observed levels of PAHs were in the order: South America > Africa > Oceania > Asia > North America > Europe. A strong positive correlation was observed between soil PAH concentrations and population density. The results also revealed significant correlation between PAHs and black carbon.

Surface soils and street dust of Dalian, an urban area in China were analysed to monitor PAH concentrations [52]. The total PAH levels in street dust and surface soils were in the range 1.89-17.07 µg g^{-1} and 0.65-28.9 µg g^{-1}, respectively. Industrial sites show much higher PAH concentrations than garden or residential/business sites. PAH concentrations were dominated by 4-6 ring PAHs in surface soils and street dust. PAH concentration and TOC showed insignificant correlation in case of street dust, whereas, a strong correlation was observed for surface soil. Torre-Roche et al. [53] monitored soil borne PAHs in US/Mexico border area, El Paso (Texas). ∑PAH values were in the range 0.1-2225.5 µg/Kg. Two ring PAH, naphthalene was observed in all the samples, whereas, 5-6 ring PAHs were detected only near industrial areas and traffic points.

The levels of PAHs were assessed in soils of natural reserve, Isola delle Femmine (Italy) located in front of cement production plant [54]. ∑PAHs in the area were in the range 35-45 µg kg^{-1}. The results suggested the presence of 4-5 ring PAHs in higher amount. Moreover, the percentage of 3-6 ring PAHs in the investigated samples were similar to those in reference rural sites. Therefore, it was concluded that cement plant had negligible effect on the levels of PAHs in the examined area.

Bandowe and associates [55] reported the levels of PAHs and their derivatives in the soils of an industrial area of Uzbekistan. The total PAHs concentrations were in the range 104-5913 ng/g. The total concentrations of carbonyl-oxygeneted PAHs (carbonyl-OPAH) and hydroxyl-oxygeneted PAHs (hydroxyl-OPAH) were in the range 54-1848 ng/g and 8-63 ng/g, respectively. The total concentrations of PAHs show positive correlation with carbonyl-OPAHs, hydroxyl-OPAHs and trace metals emitted industrially. This suggested, industrial emission is one of the common source for these pollutants. Same research group [56] analysed PAHs and their derivatives in soils collected from an urban site in Mainz (Germany), a gasworks site in Berlin (Germany) and a forest site in Manaus (Brazil). The ∑PAH values of 34 PAHs were 107, 3.5, 0.021 µg/g, carbonyl-OPAHs were 15.6, 0.17 and 0.007 µg/g and hydroxyl-PAHs were 0.518, 0.036 and 0.016 µg/g, in soils of Berlin, Mainz and Manaus, respectively. Several OPAHs were found in higher concentrations than their parent PAH, indicating the significance of OPAH levels in the assessment of potential risk due to PAHs. The researcher extended the study for the soils of Bratislava (Slovakia), an urban area [57]. The concentrations of 34 PAHs and 14 OPAHs were in the range 0.842-244.8 µg/g and 0.088-2.69 µg/g, respectively. The significant correlation between total concentrations of PAHs and OPAHs suggested close association between parent PAHs and OPAHs. Parent PAHs were observed in lower amounts than carbonyl-OPAHs at several sites but increase in ratio of OPAH to their parent PAH was observed with increasing soil depth, which indicates faster vertical transportation of OPAHs than parent PAHs.

Distribution of PAHs in soils near Songshan coking plant, Guangdong (China) was studied by Zhang et al. [58]. The total PAHs levels were in the range 2.36-1146.39 µg/g. The sites near the coking plant were dominated by 2-3 ring PAHs, whereas, sites distant from the coking plant showed abundance of 4-5 ring PAHs. The isomer pair ratios were evaluated which revealed pyrolytic processes as the source of PAHs in the soils near coking plant.

Rural terrain soils (Tlahuac and Milpa Alta) from Mexico city were monitored for PAH levels by Oritz and co-workers [59]. In Tlahuac, PAH contents were 9.13 µg/g and 11.22 µg/g, whereas in Milpa Alta, 11.43 µg/g and 35.77 µg/g in dry and wet seasons, respectively. The carcinogenic PAHs were in the permissible limits, but total PAH content was higher than the permissible limit, indicating probable risk to human health in Mexico city. Kaya et al. [60] investigated an industrial region (Izmir, Turkey) for the air-soil exchange of PAHs and PCBs. In soil samples, the most abundant PAH observed was phenanthrene and dominance of pyrene, fluoranthene and fluorene was observed at all the sites. The spatial distribution of PAHs in air suggested ship dismantling plants, petroleum refinery and iron-steel plants as major sources of PAHs. PAH levels were higher in winter, whereas, PCB levels were higher in summer. This was attributed to high emissions of PAHs due to residential heating in winters and increased volatilization of PCBs at high temperatures in summer. A significant correlation was observed between PAH and PCB concentration in air and soil, which indicated interaction between the two compartments.

PAH levels and sources in the urban irrigated agricultural soils of Accra (Ghana) have been reported by Tay and Biney [61]. The PAH levels were in the range 1.23-2.95 µg/g. The 2-4 ring PAHs dominated the soils. However, 5-6 ring, carcinogenic PAHs were also present in significant amounts at some sites indicating potential risk to public health. On the basis of isomer pair ratios incomplete combustion of petroleum products and automobile exhausts were suggested as sources of PAHs.

The effects of soil properties and climate on the concentrations of PAHs, OPAHs and azaarenes in topsoils and subsoils were studied in a 2100 Km long stretch in Argentina [62]. The total concentrations of 15 OPAHs, 29 PAHs and 4 azaarenes were in the range 0.05-124 ng/g, 2.4-38 and 0-0.97 ng/g, respectively. An increase in lower molecular weight PAHs and OPAHs was observed from north to south due to decrease in anthropogenic activities. The presence of azaarenes was found only in few soils with quinoline as major compound, which was preferentially observed in north indicating combustion sources.

Xiao and associates [63] studied the distribution of PAHs and identified their sources in forest soils of Pearl river delta (China). The PAHs values in different soils were in the order: rural < suburban < urban, suggesting anthropogenic activities as the sources of PAHs. Source diagnostics studies indicated coal/wood combustion, mixed sources and traffic emission as the major sources of PAHs in rural, suburban and urban areas, respectively.

In the developing countries, such as India, the advent of industrial revolution has resulted in the exploitation of resources in a non-judicious manner. Inspite of providing social benefits, industrialization has resulted in the release of a large number of pollutants such as PAHs, which accumulate in soil, transport in food chain and cause serious health effects on humans. Therefore, monitoring of PAHs in the developing countries such as India is of utmost importance. Several researchers in the last decade have focussed their studies on the monitoring of PAHs in the soils of various parts of India which is discussed in the following section.

Masih et al. [64] monitored the levels of PAHs in roadside soils at a major crossing in Agra city, India. The contribution of PAHs at this location is due to industrial processes, vehicular exhausts, refused burning and fossil fuel combustion. The total concentrations of PAHs were in the range 6.72-25.91 µg g^{-1}. The most abundant PAHs were benzo[ghi]perylene, benzo[b]fluoranthene, chrysene and fluoranthene. The research group also assessed the levels of PAHs in agricultural, roadside, residential and industrial soils of the city [65]. The ∑PAHs were in the range 3.1-28.5 µg g^{-1}. PAH concentrations in different seasons were in the order: winter > summer > monsoon. PAH concentrations at different sites were in the order: industrial > roadside > residential > agricultural. The results of factor analysis indicated mixed origin of sources at all the sites. They concluded that the carcinogenic potential due to PAHs in the soils is insignificant. Ray et al. [21] determined PAH levels in soils around Indira Gandhi International airport, Delhi and indicated maximum PAH contamination near the landing point of aircraft. The total PAH concentrations were in the range 2.39-7.53 µg g^{-1}. The results indicated the predominance of pyrene in the examined soils and pyrogenic sources of PAHs were suggested.

Predominance of low molecular weight PAHs in the agricultural soil of Delhi was reported by Agarwal et al. [30]. Total PAH concentrations were in the range 0.83-3.88 µg g^{-1}. Principal component analysis and isomer pair ratio indicated combustion of fossil fuel and biomass as the major sources of PAHs. On the basis of benzo[a]pyrene-equivalent concentration, it was suggested that urban agricultural soils have more carcinogenic potential than rural agricultural soils. The same group monitored the concentrations of PAHs at traffic sites of Delhi [66] and compared the data with rural sites. At traffic sites, the ∑PAHs concentrations were in the range 1.06-9.65 µg g^{-1}. The results suggested that the carcinogenic potential of traffic sites was 21 times higher than rural sites. At traffic sites, dominance of 5-6 ring PAH was observed, whereas, at rural sites, dominance of 2-3 ring PAH was observed. The results further revealed an insignificant correlation between total PAH concentration and total organic carbon at the traffic sites.

Kumar and Kothiyal [67, 68] investigated automobile generated PAHs in the roadside soil of Jalandhar (Punjab), a developing city of India. The average concentration for carcinogenic PAHs (5-6 ring PAHs) was 31.39 µg g^{-1}, and for non-carcinogenic PAHs (2-4 ring PAHs), 4.86 µg g^{-1} in autumn. The average concentration of PAHs in winter and autumn was 4.04 and 16.38 µg g^{-1}, respectively. Dibenzo[ah]anthracene and benzo[a]pyrene were the most abundant PAHs at all the traffic intercepts in both the seasons. At most of the intercepts total concentrations of carcinogenic PAHs were much higher (80%) than non-carcinogenic PAHs (20%). Bahuguna and others [69] analysed physicochemical properties of automobile contaminated soil near Rishikesh (Uttarakhand), India. The soil pH ranged from 6.8-8.1, temperature 38-43 °C, moisture content 472-1864 µg g^{-1}, inorganic phosphates 30-499 µg g^{-1}, and nitates 221-7112 µg g^{-1}. ∑PAHs, were in the range 21.81-75.25 µg g^{-1}. The results of the study suggested inverse relation between bacterial counts and PAH content of the soil. The study also indicated that high ∑PAHs in soil results in low moisture content and high temperature, which act as microbial growth inhibitor.

Distribution of PAHs and PCBs in the roadside soils of Kurukshetra (Haryana) was evaluated by Kumar and associates [70]. Total concentrations of PAHs and PCBs were in the range 0.016 to 2.53 µg g^{-1} and 0.0033-0.034 µg g^{-1}, respectively. The fractions of carcinogenic PAHs and PCBs were found to be 90.1 % and 34.6 %, respectively. Diagnostic ratios suggested pyrogenic origin of PAHs and group homolog pattern suggested higher concentration of low chlorinated PCBs than high chlorinated PCBs. Carcinogenic levels of some PAHs at major traffic intercepts of Jalandhar were determined by Kumar and Kothiyal [71]. The total PAH concentrations were in the range 0.008-28.4 µg g^{-1}. Dibenzo[ah]anthracene was present in highest concentration at all the intercepts. Carcinogenic and non-carcinogenic PAHs were 60-80 %, and 20-40 %, respectively. The same research group [72] determined toxic equivalency factors for some PAHs in the roadside soils in summer, autumn and winter seasons in Jalandhar. The average PAH levels were 18.17, 16.38 and 4.04 µg g^{-1} in summer, autumn and winter seasons, respectively. In all the seasons, benzo[a]pyrene and dibenzo[ah]anthracene were found as most abundant PAHs having highest toxic equivalency factors.

PAH profiles and carcinogenic potencies of 16 PAHs and their association with black carbon in the forest and urban soils of Delhi were investigated by Ray et al. [73]. Soil samples were collected from R.K. puram, an urban area and Bawana forest. Carcinogenic PAHs in the urban site were 11 times higher than the forest site. At both the sites the correlation between black carbon and PAH was found to be significant. The diagnostic ratios and principal component analysis indicated biomass combustion and vehicular emission as the major sources of PAHs at forest site and urban site, respectively.

The literature review thus reveals the presence of PAHs in the soils of different regions of India. The selection of Delhi region for the present study is based on the fact that Delhi, being the capital of India is densely populated and highly urbanised city having enormous traffic load and industrial areas in its vicinity. Public transport, private vehicles, small scale industries, crematoria, thermal power plants are the major contributors of PAHs in Delhi region. Inspite of the importance of the city as a centre for various international and national activities, only a few studies reporting levels of PAHs in soils of Delhi are available. Therefore, systematic studies on the distribution of PAHs in soils of Delhi were conducted in the pre-winter and the post-winter seasons. Seven PAHs were analysed, four low molecular weight PAHs namely Naphthalene, Fluorene, Phenanthrene, Anthracene and three high molecular weight PAH Fluoranthene, Pyrene and Benzo[a]pyrene (Fig 3.1). Out of these benzo[a]pyrene is considered as environmental indicator of PAH contamination [20].

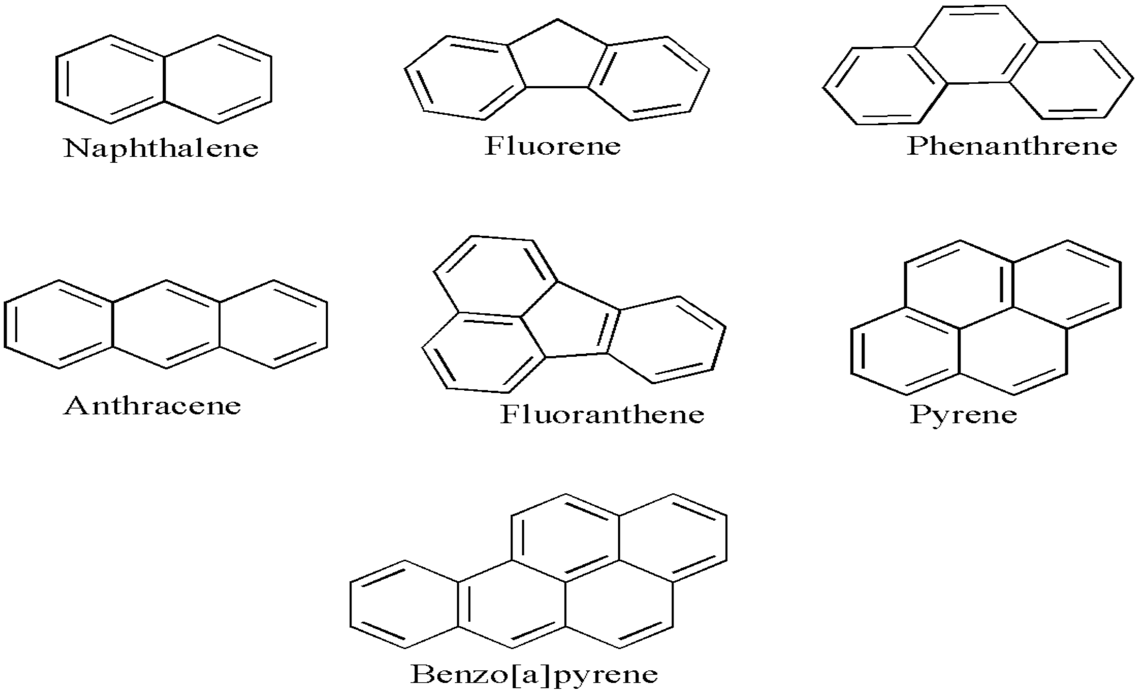


Fig. 3.1 Structures of studied polycyclic aromatic hydrocarbons.

Low molecular weight PAHs are more abundant and cause much more lethal toxicity than their higher counterparts [74]. The selected PAHs are from the list of sixteen PAHs categorised as priority organic pollutants by USEPA and EU. The study will reflect an overview of the distribution pattern of PAHs at various selected sites of Delhi which are susceptible to PAH contamination due to different anthropogenic activities. Source apportionment studies were carried out to indicate the origin of PAHs at these sites. The results might be helpful in suggesting some remedial measures or designing some environment related policies.

Distribution of PAHs in the soils of ten selected sites of Delhi region was studied. To assess the impact of season the samples were collected in pre-winter (October, 2012) and post-winter season (March, 2013). Source apportionment of PAHs was performed by isomer pair ratios. The data was subjected to principal component analysis-multiple linear regression (PCA-MLR) to identify the percentage contribution of various sources of PAHs. Hierarchical cluster analysis was performed to analyse the sites with potential environmental risk.

3.1 EXPERIMENTAL

The details regarding sample collection, sampling sites, extraction, cleanup and analysis of PAHs have been discussed in chapter II.

3.2 RESULTS AND DISCUSSION

3.2.1 Distribution of PAHs

The concentrations of seven PAHs in pre-winter and post-winter seasons were determined at ten selected sites of Delhi and are shown in Table 3.1(a&b). The total concentrations of seven PAHs ($\sum_7$PAHs) at various sites of Delhi were in the range 956-2348 µg kg^{-1} and 1230-2714 µg kg^{-1} for pre-winter and post-winter seasons, respectively. Results indicate slightly higher ∑PAHs values in winter. Only a few regulations exist regarding the concentrations of PAHs in soils worldwide and no such regulation till date exists in India. The levels of PAHs in soils of various sites were compared with Dutch and polish standards [16] given in Table 3.2 (a&b). The total PAH concentrations in the soils of various sites of Delhi were several times higher than the Dutch standards and fall under polluted category i.e. class III (1000-5000 µg kg^{-1}) with respect to polish standards of PAHs.

Table 3.1(a): PAH levels (μg kg^{-1}) at different sites in Delhi during pre-winter season

Site PAH	ITO	ITO flyover	NTPC	RG	PP	AV	KG	SKK	NG	NGYB
Naphthalene	103	158	463	580	197	bdl	bdl	138	364	269
Fluorene	254	220	346	210	112	140	121	122	205	185
Phenanthrene	411	238	317	285	215	307	276	417	508	436
Anthracene	269	166	282	291	098	182	114	202	326	274
Fluoranthene	491	221	464	445	196	266	162	225	523	349
Pyrene	331	239	225	255	171	163	129	195	326	209
Benzo[a]pyrene	315	154	234	124	134	142	154	331	96	74
$\sum_7$PAH	2174	1396	2331	2190	1123	1200	956	1630	2348	1796

bdl- below detection limit

Table 3.1(b): PAH levels (μg kg^{-1}) at different sites in Delhi during post-winter season

Site PAH	ITO	ITO flyover	NTPC	RG	PP	AV	KG	SKK	NG	NGYB
Naphthalene	154	284	433	862	121	bdl	108	147	313	286
Fluorene	318	247	184	280	188	168	154	104	213	198
Phenanthrene	476	309	264	390	285	410	339	496	510	548
Anthracene	174	116	110	182	84	215	80	152	336	285
Fluoranthene	509	242	377	469	251	241	207	358	587	365
Pyrene	440	349	309	351	255	198	195	257	386	221
Benzo[a]pyrene	383	174	312	179	159	166	147	260	137	87
$\sum_7$PAH	2454	1719	1989	2714	1343	1398	1230	1774	2482	1990

bdl- below detection limit

Benzo[a]pyrene is an environmental indicator of PAH contamination and a probable human carcinogen [20]. The concentration of B[a]P ranged from 74 to 331 μg kg^{-1} (mean 175 μg kg^{-1}) in pre-winter season and 90 to 380 μg kg^{-1} (mean 200 μgkg^{-1}) in post-winter season. Results suggest almost comparable concentrations of B[a]P in the two seasons with upward trend in post-winter season. Data further suggest that phenanthrene and fluoranthene are among the two most abundant PAHs at all the sites except the sites near thermal power plants

(NTPC, RG, PP). Similarly, abundance of phenanthrene and fluoranthene has been reported in soils of Tokushima (Japan) and Guangdong (China) [75, 76].

Table 3.2: Polish and Dutch standards for pollution of PAHs in soil

(a) Polish Standards

∑PAHs (µg/Kg)	Class	Soil Assessment
<200	0	Natural Content (unpolluted)
200-600	I	Increased Content (unpolluted)
600-1000	II	Slightly polluted
1000-5000	III	Polluted
5000-10000	IV	Heavily polluted
>10000	V	Very heavily polluted

(b) Dutch Standards

PAH	Target Value for Unpolluted Soil (µg/Kg)
Naphthalene	-
Fluorene	-
Phenanthrene	45
Anthracene	50
Fluoranthene	20
Pyrene	-
Benzo[a]pyrene	25

At coal based power plants (NTPC and RG) naphthalene is one of the most abundant PAH. This suggests higher emission of naphthalene through burning of coal. The $\sum_7$PAH concentrations are higher near the crematorium and coal based power plants followed by ITO sites and bus terminals in both the seasons. The $\sum_7$PAHs values are higher during post-winter season as compared to pre-winter season which may be attributed to the fact that PAHs degrade less efficiently in the winter season due to lower temperature. Increased use of heaters, wood and other substances for heating, lead to higher emission of PAHs in winters.

Besides, slow photochemical degradation in winter season is also responsible for higher PAH concentration in post-winter season than pre-winter season. Higher PAHs concentrations in winters in comparison to summers have been observed by various authors [77-81].

3.2.2 Ecotoxicological concern due to PAHs

The effect range low (ERL) and the effect range median (ERM) values are intended to define chemical concentration ranges that are rarely (<ERL), occasionally (≥ERL and <ERM) and frequently (≥ERM) associated with the adverse biological effects [82]. The measured concentrations of individual PAH and ∑PAHs at various sites [Tables 3.1(a) and Table 3.1(b)] have been compared with the ERL and ERM guideline values for sediments and the results are compiled in Tables 3.3.

Perusal of data suggests that fluorene concentrations at all the sites are between ERL and ERM, whereas, naphthalene and phenanthrene exceed ERL values at a majority of the sites. For anthracene, fluoranthene, pyrene and B[a]P individual PAH concentrations at all the sites are below ERL values. Thus, adverse biological effects due to these toxicants are occasionally possible in soils of Delhi.

3.2.3 PAH Profiles

Spatial profiles of ∑PAHs in pre-winter and post-winter seasons are shown in Fig. 3.2. The site ITO is more polluted than ITO flyover probably due to heavy congestion of traffic at ITO than ITO flyover where traffic moves smoothly. Among the power plants, the soil near Pragati Power Plant (PP) is least polluted. This may be due to the fact that PP is a gas based power plant. Among the bus terminals, soil of site SKK is most polluted. The soil near crematorium (NG) and Yamuna bank behind the crematorium (NGYB) are also significantly polluted due to the burning of wood and pyres on a regular basis.

Table 3.3: Comparison of individual and total PAH in soils of Delhi with effect range low (ERL) and effect range median (ERM) values[#] (µg/Kg)

	Naphthalene		Fluorene		Phenanthrene		Anthracene		Fluoranthene		Pyrene		B[a]P		∑PAH	
	ERL	ERM	ERL	ERM	ERL	ERM	ERL	ERM	ERL	ERM	ERL	ERM	ERL	ERM	ERL	ERM
Sampling sites	(160)	(2100)	(19)	(540)	(240)	(1500)	(853)	(1100)	(600)	(5100)	(665)	(2600)	(430)	(1600)	(4000)	(44792)
	$(P_1/P_2)^a$	(P_1/P_2)	(P_1/P_2)	(P_1/P_2)	(P_1/P_2)	(P_1/P_2)	(P_1/P_2)	(P_1/P_2)	(P_1/P_2)	(P_1/P_2)	(P_1/P_2)	(P_1/P_2)	(P_1/P_2)	(P_1/P_2)	(P_1/P_2)	(P_1/P_2)
ITO	-/-	-/-	+/+	-/-	+/+	-/-	-/-	-/-	-/-	-/-	-/-	-/-	-/-	-/-	-	-
ITO flyover	-/+	-/-	+/+	-/-	-/+	-/-	-/-	-/-	-/-	-/-	-/-	-/-	-/-	-/-	-	-
NTPC	+/+	-/-	+/+	-/-	+/+	-/-	-/-	-/-	-/-	-/-	-/-	-/-	-/-	-/-	-	-
RG	+/+	-/-	+/+	-/-	+/+	-/-	-/-	-/-	-/-	-/-	-/-	-/-	-/-	-/-	-	-
PP	+/-	-/-	+/+	-/-	-/+	-/-	-/-	-/-	-/-	-/-	-/-	-/-	-/-	-/-	-	-
AV	-/-	-/-	+/+	-/-	+/+	-/-	-/-	-/-	-/-	-/-	-/-	-/-	-/-	-/-	-	-
KG	-/-	-/-	+/+	-/-	+/+	-/-	-/-	-/-	-/-	-/-	-/-	-/-	-/-	-/-	-	-
SKK	-/-	-/-	+/+	-/-	+/+	-/-	-/-	-/-	-/-	-/-	-/-	-/-	-/-	-/-	-	-
NG	+/+	-/-	+/+	-/-	+/+	-/-	-/-	-/-	-/-	-/-	-/-	-/-	-/-	-/-	-	-
NGYB	+/+	-/-	+/+	-/-	+/+	-/-	-/-	-/-	-/-	-/-	-/-	-/-	-/-	-/-	-	-

[a] (P_1/P_2) = Pre-Winter/Post-Winter, + indicate exceeded level, - indicate below level.

[#] ERL and ERM values used for comparison are for sediments.

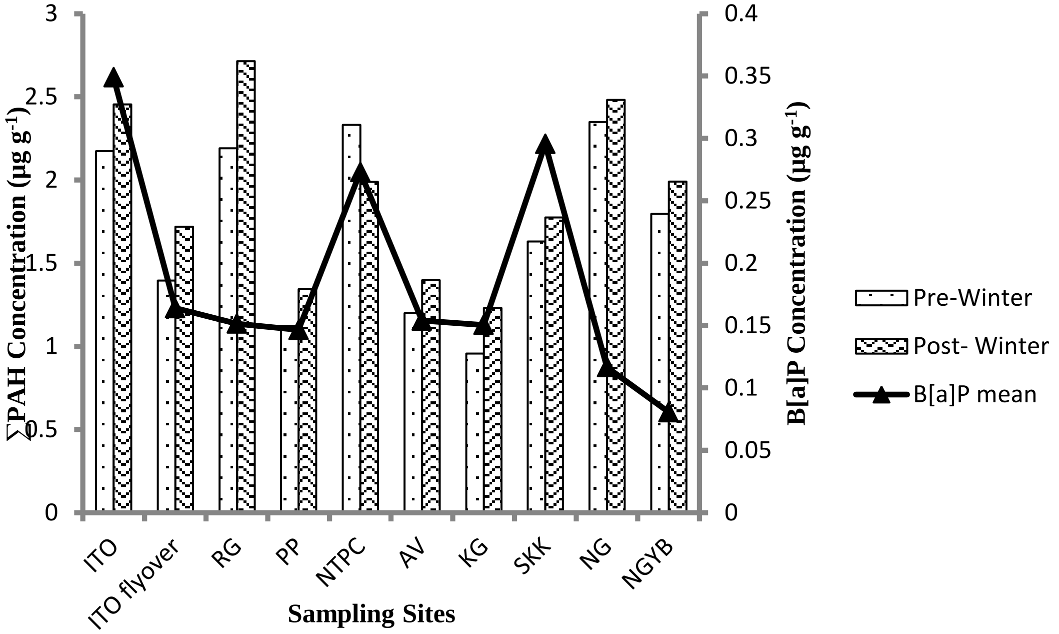
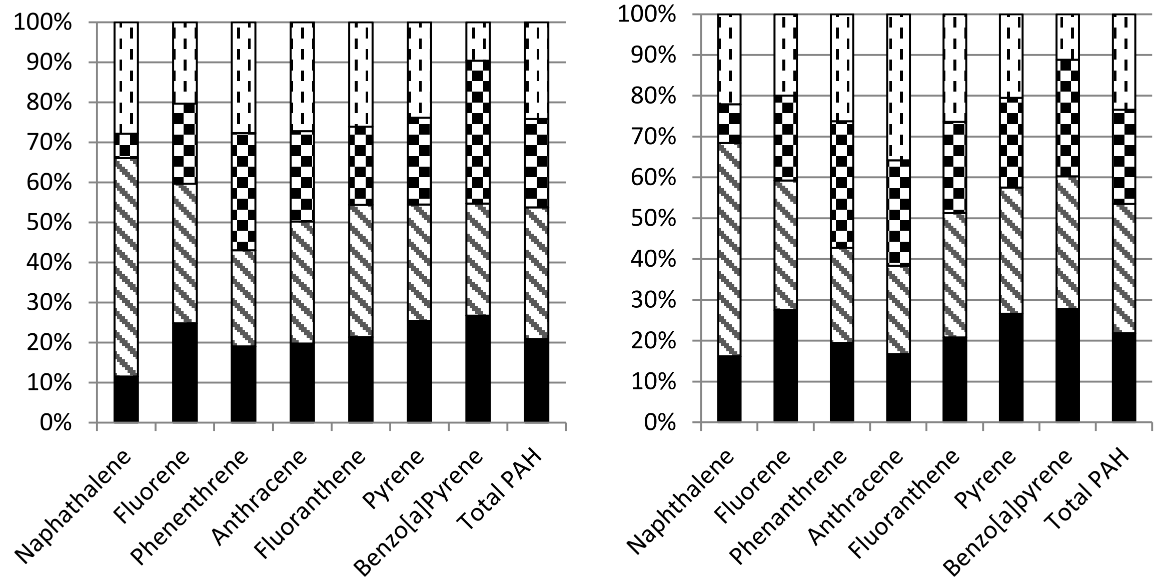


Fig. 3.2: Graph showing $\sum_7$PAHs concentration in pre-winter and post-winter seasons on primary Y-axis and mean B[a]P concentration on secondary Y-axis

The average benzo[a]pyrene concentration for the two seasons at various sites is shown on the secondary axis in Fig. 3.2. The results reveal that the B[a]P concentration is relatively high at the sites ITO, NTPC and SKK. It is noticeable that B[a]P concentration is relatively low at the sites where activity of wood burning is dominant i.e. NG and NGYB. Relatively low concentration of benzo[a]pyrene during combustion of wood at residential site and fireplace has also been reported by Mcdonald et al. [83] and Schauer et al. [84], respectively.

The profiles of individual PAHs at sites of similar anthropogenic activity in the two seasons are shown in Fig. 3.3. Data indicate that the concentration of naphthalene (two ring) is maximum near power plants and minimum near bus stops. Three and four ring PAHs are found in comparable amounts at all the sites. B[a]P, a five ring PAH has maximum concentration at sites near bus terminals and minimum near crematorium sites. The results thus reveal that burning of coal releases high naphthalene concentration while vehicular traffic contributes minimum naphthalene. On the other hand, benzo[a]pyrene is released more through vehicular traffic and less through burning of wood.



a) Pre-winter season **b) Post-winter season**

Fig. 3.3: Percentage composition of individual PAH at sites with similar anthropogenic activity in pre-winter and post-winter seasons

░	crematorium (NG + NGYB)	▩	bus stops (AV+KG+SKK)
▧	Power Plants (IP+PP+NTPC)	■	heavy traffic sites (ITO+ITO flyover)

3.2.4 Correlation between PAHs and total organic carbon

Individual PAH concentrations at various sites and total carbon content at the respective sites were taken and analysed by Pearson correlation method. Correlation coefficients are given in Table 3.4. All the PAHs show negative or insignificant correlation with TOC. Negative or insignificant correlation seems reasonable as the urban soils receive fresh PAHs continuously from vehicular traffic, power plants and wood burning, but organic carbon content does not change proportionately. Therefore, role of TOC in controlling PAH concentrations in surface soils is insignificant. Similar observation was reported by Agarwal in 2009 [66] in traffic soils of Delhi.

Table 3.4 Correlation coefficients for PAHs and TOC at various sites of Delhi in pre-winter and post-winter season

PAH	Correlation Coefficient	
	Pre-Winter	Post-Winter
Naphthalene	-0.204	-0.183
Fluorene	-0.585	-0.565
Phenanthrene	0.103	0.254
Anthracene	-0.306	-0.21
Fluoranthene	-0.463	-0.085
Pyrene	-0.328	-0.256
Benzo[a]pyrene	0.454	0.095
$\sum_7$PAH	-0.266	-0.186

3.2.5 Source diagnostics

Isomer pair ratios as well as principal component analysis (PCA) were used to evaluate the possible sources of PAHs at various sites of Delhi. Factor scores of PCA were used to evaluate percentage contribution of the sources using multiple linear regression (MLR).

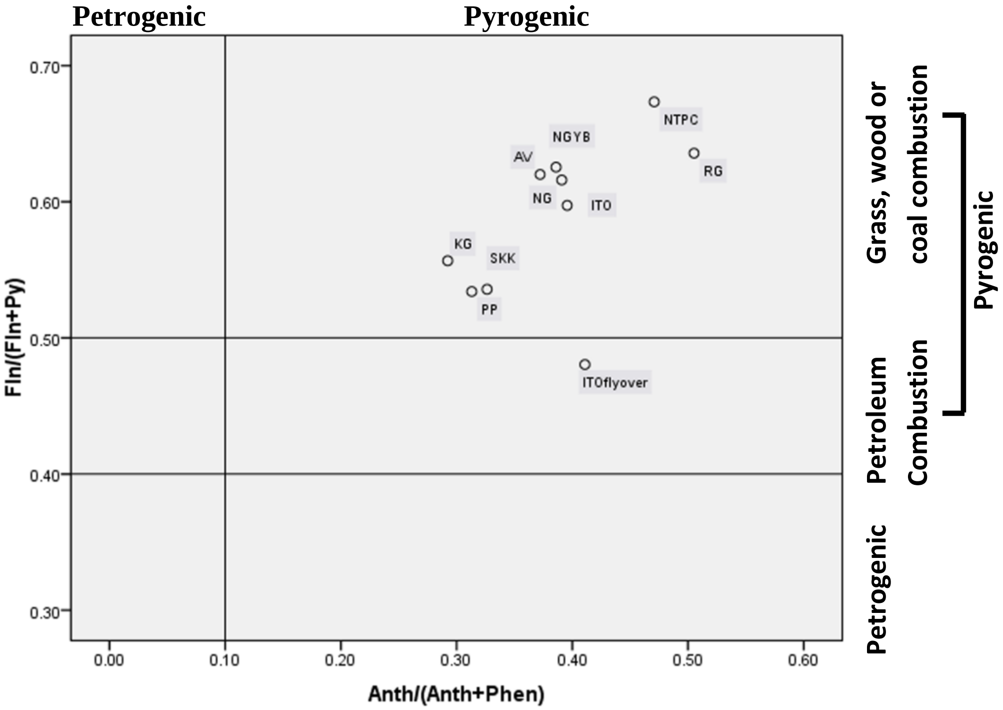
3.2.5.1 Isomer pair ratios

PAHs are categorized as petrogenic and pyrogenic. Most of the PAHs enter the environment through anthropogenic activities, for instance, vehicular exhaust, releases from thermal power plants and incomplete combustion of wood, coal etc. These are categorised as pyrogenic sources of PAHs. Petrogenic PAHs are present naturally in the fuel deposits, coal, crude oil coal tar and various refinery products [85, 86]. As all the selected sites are located in the urban city, Delhi, it can be assumed that the probability of solely petrogenic sources of PAH is low.

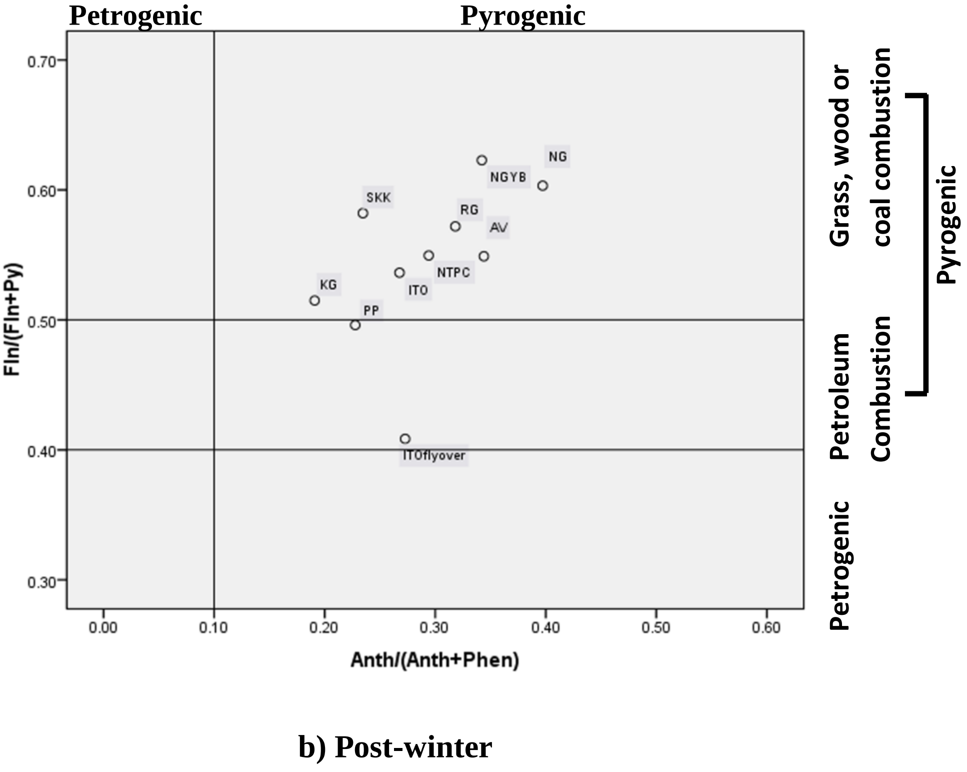
The identification of sources of PAHs is a complex exercise due to their dynamic existence in the environment and diversity of their sources. The thermodynamic stability and kinetic evolution of some PAHs are comparable. Therefore, isomer pair ratio has been used as an efficient method for the assignment of probable PAH sources [87]. In the present study, anthracene to anthracene plus phenanthrene (Ant/Ant+Phen) ratio and fluoranthene to fluoranthene plus pyrene (Fln/Fln+Py) ratio have been used to assign sources of PAHs. A value of Ant/Ant+Phen ratio less than 0.1 indicates petrogenic origin of PAHs while a ratio greater than 0.1 indicates pyrogenic origin. Similarly, a ratio of Fl/Fl+Py less than 0.4 suggest petrogenic sources, between 0.4 and 0.5 suggest petroleum combustion (liquid fossil fuel combustion) and greator than 0.5 represents biomass combustion (grass, wood or coal combustion) [88, 89].

During pre-winter season the ratio of Anth/(Anth + Phen) range from 0.29 to 0.50, indicating pyrogenic sources of PAHs at all the sites. The ratio of Fln/(Fln+Py) for all the sites except ITO range between 0.53 and 0.67 (Fig. 3.4a) indicating biomass combustion as a source of PAHs at these sites. Only at ITO flyover, the ratio is 0.48, indicating petroleum combustion as the source of PAHs.

During post-winter season, the ratio of Anth/(Anth + Phen) range from 0.22 to 0.39, indicating pyrogenic sources of PAHs at all the sites. The ratio of Fln/(Fln + Py) range between 0.40 and 0.62 for all the sites (Fig. 3.4b) indicating pyrolytic origin of PAHs at all the sites. During post-winter season Fln/(Fln+Py) ratio (0.40) at ITO flyover, suggest petroleum combustion as the source of PAHs. The data thus suggest that in both the seasons the levels of PAHs at various sites are different but the trend and nature of sources are similar.



a) Pre-winter



b) Post-winter

Fig. 3.4: Cross plots for the isomer ratio of Anth/(Anth + Phen) versus Fln/(Fln + Py) in the soil of Delhi during (a) pre-winter and (b) post-winter seasons

3.2.5.2 Principal Component Analysis with Multiple Linear Regression (PCA/MLR)

Principal Component Analysis (PCA) was used to determine the sources of PAHs at various sites of Delhi region. PCA is a widely used multivariate statistical technique. PCA transforms the original set of variables into a smaller set of linear combinations. The objective of PCA is to reduce the number of variables retaining the original information as much as possible. Thus variables having similar characteristics can be grouped into factors. The Statistical Package for the Social Sciences (SPSS), Version 17.0 was used to perform PCA and factors were analysed using varimax rotation. PCA was conducted on the individual PAH concentrations at various sites and principal components with eigen values greater than 1 were extracted.

Factor analysis score during pre-winter season shows 76.10% of the variance which is explained by two factors (Table 3.5a). Factor 1 accounts for 58.28 % of the total variance with significant loading for naphthalene, fluorene, phenanthrene, anthracene, fluoranthene and pyrene. Factor 2 accounts for only 17.82% of the total variance and has significant loading for B[a]P only. To illustrate the contribution of different sites to individual principal components, the score plots between PC1 and PC2 were drawn (Fig. 3.5). From score plot for pre-winter season, it is evident that sites ITO, NTPC, PP, NG, NGYB show positive values for PC1. This suggests that the six PAHs namely, naphthalene, fluorene, phenanthene, anthracene, fluoranthene and pyrene have mixed sources such as traffic, coal and wood combustion. The sites ITO, KG, AV and SKK show positive values for PC2, indicating vehicular emission as the major source of B[a]P. According to literature, significant loading of naphthalene, fluorene, phenanthrene, anthracene, fluoranthene and pyrene suggests mixed sources of PAHs and that of B[a]P suggest vehicular emission as the major source [89].

During post-winter season, 87.84% of variance is explained by three factors (Table 3.5b). Factor 1 explains only 44.76% of the total variance and has significant loading for phenanthrene, anthracene and fluoranthene. Factor 2 explains 28.11 % of total variance with significant loading of naphthalene, fluorene, fluoranthene and pyrene. Factor 3 accounts for 14.96% of the total variance with significant loading for B[a]P and pyrene.

Table 3.5: Factor analysis scores using Varimax rotation for PAHs (factor loadings >0.5 are shown in bold)

a) Pre-winter Season

Variable	Component 1	Component 2
Fln	**.97**	.01
Anth	**.96**	.01
Py	**.86**	.22
Flu	**.76**	-.04
Naph	**.71**	-.54
Phen	**.61**	.46
BaP	.05	**.84**
Eigen Value	4.08	1.25
% of Variance	58.28	17.82
Cumulative %	58.28	76.10
Probable sources	Mixed Sources	Vehicle

Extraction Method: Principal Component Analysis.

b) Post-Winter Season

Variable	Component 1	Component 2	Component 3
Phen	**.94**	-.12	.02
Anth	**.94**	.16	-.19
Fln	**.68**	**.53**	.40
Naph	-.02	**.91**	-.14
Flu	.09	**.74**	.42
BaP	-.16	-.01	**.94**
Py	.23	**.63**	**.68**
Eigen Values	3.13	1.97	1.05
% of Variance	44.76	28.11	14.96
Cumulative %	44.76	72.88	87.84
Probable Sources	Coal	Mixed Sources	Vehicle

Extraction Method: Principal Component Analysis.

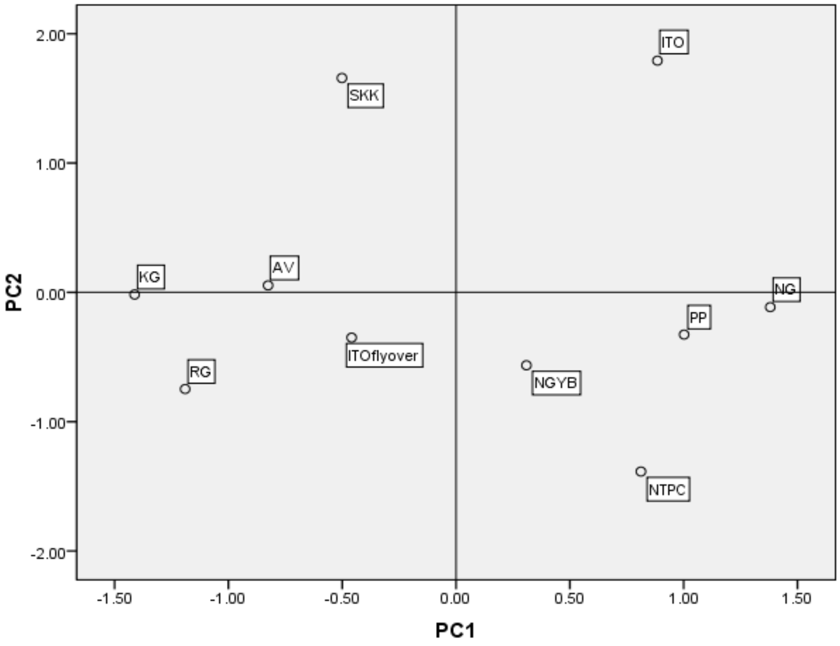


Fig. 3.5: Principal component score plot for pre-winter season

The score plots for post-winter season (Fig. 3.6) indicate that the sites ITO, AV, SKK, NG, NGYB show positive values for PC1. This suggests vehicular traffic and combustion of wood as the sources of phenanthrene, anthracene and fluoranthene. The sites NTPC, ITO flyover, ITO, PP and NG show positive values for PC2 suggesting mixed sources such as vehicular traffic and combustion of coal and wood as the sources of naphthalene, fluorene, fluoranthene and pyrene. The sites ITO, PP and SKK show positive values for PC3 (Fig. 3.6), indicating vehicular emission and burning of natural gas as major source of benzo[a]pyrene and pyrene, respectively [90]. Biomass combustion is considered as a major source of phenanthrene, anthracene and fluoranthene, whereas, phenanthrene and fluoranthene result from traffic emmission also [63].

PCA analysis in both the seasons indicate that the sources of B[a]P are different from other studied PAHs. The results of PCA for the two seasons reveal that PAH profiles are different in pre-winter and post-winter seasons. This may be due to the difference in temperature and environmental conditions in the two seasons.

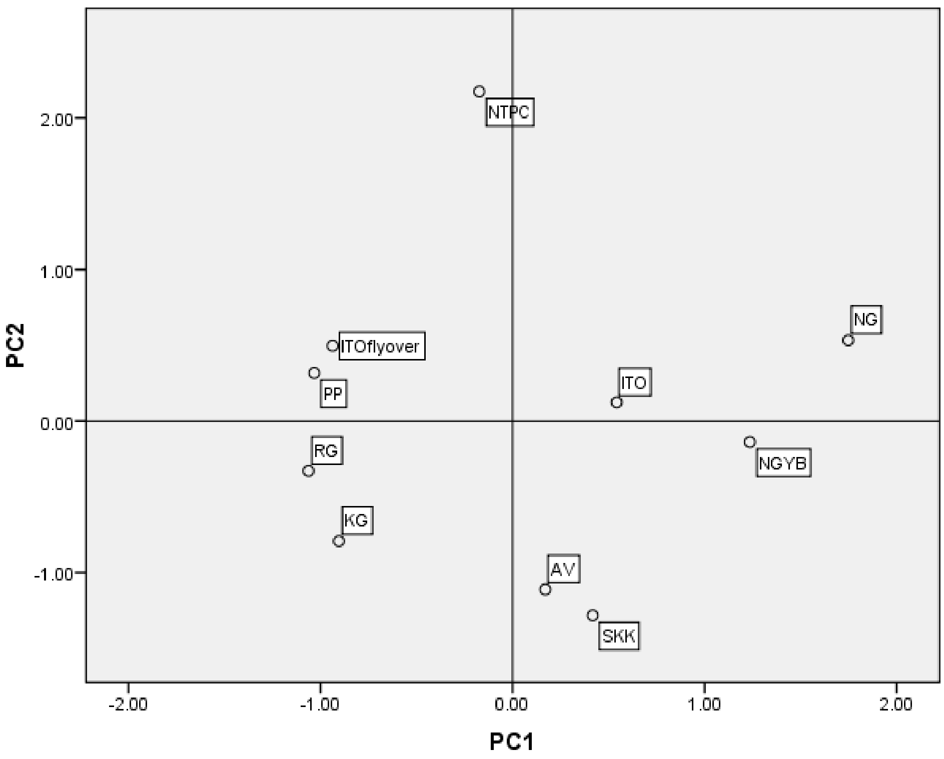
Qualitative assessment of PAH sources can be achieved using diagnostic ratios or PCA. To evaluate the PAH sources quantitatively more detailed information is required. PCA/MLR is a more suitable technique for further identification of profiles of PAH sources. PCA/MLR uses PCA to represent the total variability of original PAH data in a minimum number of factors. Factor scores of PCA for each sample are then used to calculate percent contribution of PAH sources using MLR [91, 92]. When the variables are normalised the multiple linear regression equation is given as:

$$Z = \sum B_i X_i$$

where Z is the standard normalized deviate of ∑PAH, B_i are the regression coefficients and X_i are the PCA factor scores.

In pre-winter season, factor score 1 (X_1) and factor score 2 (X_2) of PCA were regressed with Z (standard normalized deviate of ∑PAH). The multiple linear regression equation obtained for pre-winter season is:

$$Z = 0.986X_1 + 0.051X_2 \ (R^2 = 0.974)$$



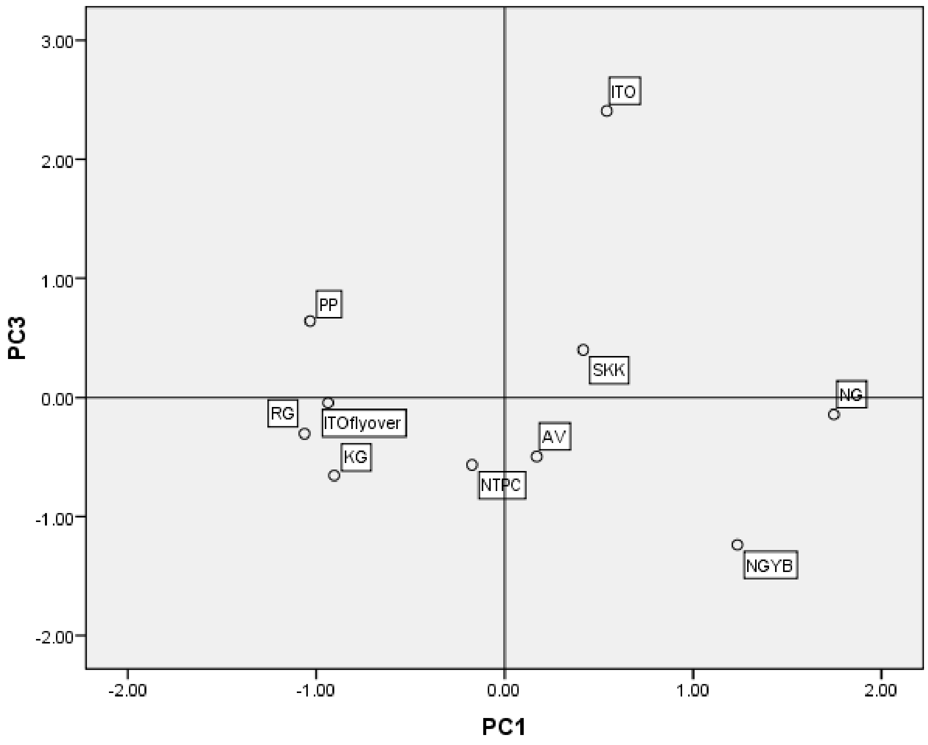


Fig. 3.6: Principal component score plots for post-winter season

Similarly, in the post winter season, factor score 1 (X_1), factor score 2 (X_2) and factor score 3 (X_3) of PCA were regressed with Z. The multiple linear regression equation obtained for post-winter season is :

$Z = 0.524X_1 + 0.757X_2 + 0.335X_3$ ($R^2 = 0.959$)

The percent contribution to the mean for all factors is calculated using the following equation:

$i(\%) = 100 \text{ X } B_i/\sum B_i$

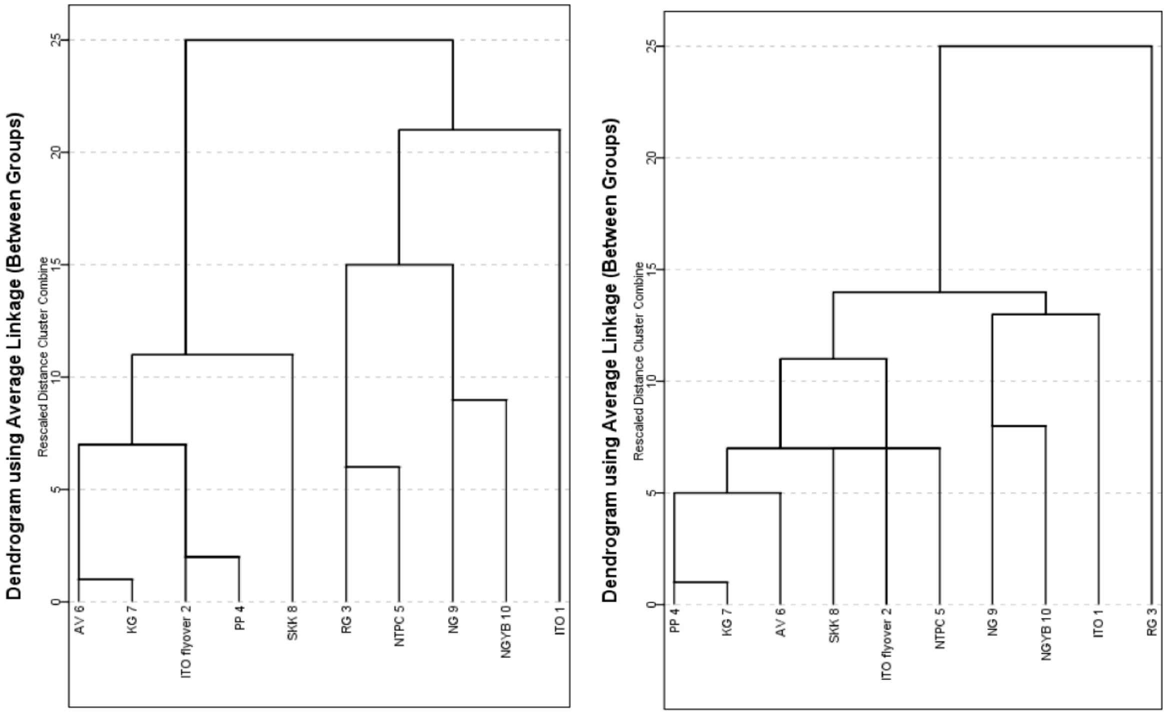
where i is the mean contribution of source and B_i are the regression coefficients.

The results indicated that in the pre-winter season most of the PAH burden was through mixed sources (95.08%) and only 4.92% was due to vehicular emission (4.92 %). In post-winter season, the contribution of coal combustion, mixed sources and vehicular emission to PAH load was 32.43%, 46.84% and 20.73%, respectively. Perusal of data clearly indicates that vehicular contribution of PAHs in post-winter season increases.

3.2.6 Hierarchical Cluster Analysis (HCA)

Hierarchical cluster analysis is a multivariate method to describe the relationships between variables. Initially, HCA forms the same number of clusters as the number of variables. Afterwards, new clusters are formed on the basis of similarities between the variables and the process is repeated until a single cluster is obtained. Hierarchical cluster analysis was performed in both pre-winter and post–winter seasons to analyse the sites with potential environmental risk. The concentrations of PAHs in soils were taken as objects and the sites were taken as variables. The dendrogram in pre-winter season (Fig. 3.7a) indicates the presence of three different clusters A, B and C. Cluster A includes sites ITO flyover, PP, AV, KG and SKK. At all the sites the major sources of PAH contamination are vehicular traffic and CNG. Cluster B includes sites RG, NTPC, NG and NGYB where major sources of pollution are burning of coal and wood, which release high concentrations of PAH naphthalene. Site ITO forms an independent cluster. The site has high traffic congestion, so traffic moves slowly in this region and emission of PAH is high. Moreover, the site is in the vicinity of power plants and receives significant PAH load from power plants. The site shows high concentration of carcinogenic PAH B[a]P and will pose potential risk to the environment.

The dendrogram in post-winter season (Fig. 3.7b) also indicates three clusters A, B and C, but the distribution of sites is slightly different. Cluster A consists of sites with relatively low PAH contamination namely, PP, KG, AV, SKK, ITO flyover and NTPC. Cluster B consists of sites NG, NGYB and ITO which are moderately contaminated and major sources of PAH emission are burning of wood and vehicular traffic. Cluster C consists of independent site RG which is the most contaminated site for post-winter season and major sources of PAHs are burning of coal and vehicular traffic.



a) Pre-winter **b) Post-winter**

Fig. 3.7 Dendrogram showing groups of sites of Delhi formed by cluster analysis

The site NTPC shows anomalous behaviour in the two seasons and falls in cluster B in pre-winter season and in less contaminated cluster A in post-winter season. This is probably due to the transport of low molecular weight PAHs to longer distances through smog in winters. The dendrograms support the observation drawn in section 4.4.2 that the pattern of PAH distribution is different in pre-winter and post-winter seasons.

3.2.7 Assessment of soil toxicity

The toxic equivalency factors (TEFs) were used to quantify the toxicity of PAHs and to estimate toxic equivalent concentrations. The toxic equivalent concentration (TEQ) of the individual PAH was calculated as

$$TEQ = \sum_i C_i \times TEF_i$$

where C_i is the concentration of individual PAH and TEF_i is the corresponding toxic equivalency factor. Nisbet and LaGoy [93] has calculated TEFs for naphthalene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene and B[a]P as 0.001, 0.001, 0.001, 0.01, 0.001, 0.001 and 1.00 respectively. B[a]P has been assigned a TEF value of one which is highest among all the PAHs. Total TEQ concentrations in pre-winter season at different sampling sites varied from 91.46 µg kg^{-1} to 386.63 µg kg^{-1}, with an average value of 179.33 µg kg^{-1} and during post-winter season from 78.18 µg kg^{-1} to 334.11 µg kg^{-1}, with an average of 203.67 µg kg^{-1}. An idea about the individual and total TEQ values at all the sites in pre-winter and post-winter seasons can be had from Table 3.6(a) and Table 3.6(b), respectively.

Table 3.6(a): Individual and total TEQ values during pre-winter season

	TEQ Values (µg Kg^{-1})									
Site / **PAH**	ITO	ITO flyover	NTPC	RG	PP	AV	KG	SKK	NG	NGYB
Naphthalene	0.103	0.158	0.463	0.58	0.197	0	0	0.138	0.364	0.269
Fluorene	0.254	0.22	0.346	0.21	0.112	0.14	0.121	0.122	0.205	0.185
Phenanthrene	0.411	0.238	0.317	0.285	0.215	0.307	0.276	0.417	0.508	0.436
Anthracene	2.69	1.66	2.82	2.91	0.98	1.82	1.14	2.02	3.26	2.74
Fluoranthene	0.491	0.221	0.464	0.445	0.196	0.266	0.162	0.225	0.523	0.349
Pyrene	0.331	0.239	0.225	0.255	0.171	0.163	0.129	0.195	0.326	0.209
Benzo[a]pyrene	315	154	234	124	134	142	154	331	96	74
Total TEQ	319.28	156.73	238.63	128.68	135.87	144.69	155.82	334.11	101.18	78.18

Table 3.6(b): Individual and total TEQ values during post-winter season

	TEQ Values (µg Kg^{-1})									
Site / **PAH**	ITO	ITO flyover	NTPC	RG	PP	AV	KG	SKK	NG	NGYB
Naphthalene	0.154	0.284	0.433	0.862	0.121	0	0.108	0.147	0.313	0.286
Fluorene	0.318	0.247	0.184	0.281	0.188	0.168	0.154	0.104	0.213	0.198
Phenanthrene	0.476	0.309	0.264	0.39	0.285	0.41	0.339	0.496	0.51	0.548
Anthracene	1.74	1.159	1.1	1.82	0.84	2.15	0.8	1.52	3.36	2.85
Fluoranthene	0.509	0.241	0.377	0.469	0.251	0.241	0.207	0.358	0.587	0.365
Pyrene	0.44	0.349	0.309	0.351	0.255	0.198	0.195	0.257	0.386	0.221
Benzo[a]pyrene	383	174	312	179	159	166	147	260	137	87
Total TEQ	386.63	176.58	314.66	183.17	160.94	169.16	148.80	262.88	142.37	91.47

According to the calculated toxic equivalent concentrations SKK and ITO are the two sites with high carcinogenic potency in pre-winter season. Though, $\sum_7$PAHs concentrations are high at NG and NTPC in this season (Table 3.1a). Similarly, in post-winter season, site ITO is found to have highest carcinogenic potency, though $\sum_7$PAHs is highest at site RG (Table 3.1b). At sites, SKK and ITO, the major contribution of PAHs is through vehicular load. This implies that carcinogenic potency of PAH load in soil due to traffic is very high.

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INTRODUCTION

PAHs enter in soil accidently or through the intended combustion of various kinds of fuels. Invariably after their release a large amount of the PAHs persist in the roadside and agricultural soils. They reach the soil mainly as atmospheric fallout after their release to the environment. The vehicular exhausts, domestic burning and cigarette smoke also contribute towards their entry into the open environment. Waste generated from the petroleum and coke manufacturing industries further adds to the pollution load into the environment. The presence and the persistence of PAHs in the soil affect the innocent biota and cause the unprecedented damage to the ecology of the area. The deleterious effects to a large extent will depend upon the decay rate and the toxicity of the PAHs and their metabolites. The persistence, no doubt, is primarily determined by the chemical nature but is significantly affected by the nature of the medium and the environmental factors like temperature, humidity and pH. The interaction of PAH with a medium like soil is more complicated than with water. The persistence of PAHs in the soil may vary from a few hours to many years depending on its type [1]. Fate and behaviour of PAHs in soil depends upon many factors like degradation rate, uptake by the soil microorganisms or plants, adsorption on the clay and organic matter, leaching with the downward percolation of water and volatilization (Fig. 4.1).

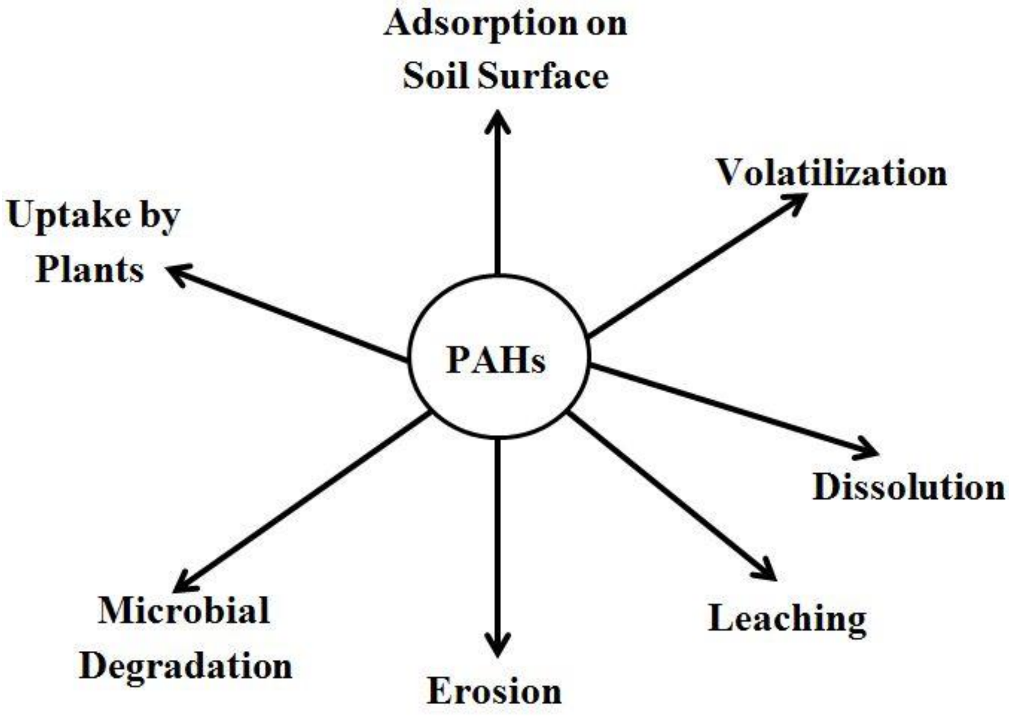


Figure 4.1: Fate of PAHs in soil environment

In a particular study, it may not be feasible to consider all the above factors leading to a decrease in the concentration of the PAH. Generally, the emphasis is laid on the chemical interaction. The degradation has been mainly reported as a first order or pseudo first order reaction. The persistence of a PAH is expressed in terms of half life or the rate constant of the reaction.

From the environment point of view, decay of PAHs in all the segments of the biosphere is of great concern but the decay in soil is of primary importance. It is the soil which is invariably directly used for the cultivation of crops, ultimately being consumed by the living beings. PAH residues are transported to various parts of the plant like root, stem, foliage and fruit in varying forms. It is ultimately important to know as to how much PAH remains in the soil with the passage of the time. In order to keep a proper track of the environmental impact of the release of these compounds, a comprehensive study on their decay profiles in the soil ecosystem under the varying environmental conditions is needed. The study should include both the dissipation rate and metabolic pathways. Dissipation rate of PAH in soil may be dependent on a number of environmental factors such as soil type, moisture, organic matter, microbial activity, sunlight intensity, amenability to aeration as well as weather conditions [2-7].

Amongst the priority PAHs, benzo[a]pyrene is carcinogenic in nature and treated as environmental indicator of PAH contamination, whereas, pyrene is mutagenic in nature [8]. Literature survey indicates that degradation studies on B[a]P and pyrene have been mainly carried out in the presence of micro-organisms or photocatalysts. In the following text recent literature on degradation of B[a]P and pyrene is presented.

Dean-Ross and Cernaglia [9] studied the degradation of pyrene by *Mycobacterium flavescens.* The products of ring oxidation and ring fission were identified and degradation pathway was proposed. Schneider et al. [8] studied decomposition of pyrene, Benz[a]anthracene (B[a]A) and B[a]P through Mycobacterium sp. strain RJGII-135, which was isolated from the soil of an abandoned coal gasification site. They reported that the bacterium is capable of degrading only a single site of pyrene molecule and different sites of B[a]A and B[a]P molecules. Kazunga and Aitken, [10] examined the degradation products of pyrene using different bacterial strains. The researchers observed more extensive PAH degradation in microbial consortia than pure cultures. Transient increases in toxicity of the soil were observed, which were explained by presence of metabolites. Vila et al., [11] investigated the degradation of pyrene using AP1 strain of Mycobacterium species and proposed degradation pathway. A new metabolite (biphenyl derivative) due to cleavage of central rings of pyrene was identified. Wasik et al. [12] investigated the benzo[a]pyrene photodegradation and biodegradation in different liquid media. They observed that the degradation was fastest in dichloromethane and slowest in methanol among the studied solvents. In the natural water systems degradation was fastest in pond water followed by river and sea water. They identified benzo[a]pyrene-4,5-dihydrodiol and an isomer of hydroxy-benzo[a]pyrene-diol as photodegradation products and benzo[a]pyrene-dione like compound as biodegradation products.

Yu et al. [13] investigated biodegradation of fluorene, phenanthrene and pyrene using bacterial consortium enriched from mangrove sediments. They concluded that pyrene requires longer time for complete biodegradation than fluorene and phenanthrene. Liang et al. [14] investigated the pyrene metabolism by KMS strain of *Mycobacterium* sp. and identified the key metabolites. Enzymes involved in the degradation process were studied by 2-D gel electrophoresis. A pathway for the degradation of pyrene was proposed and enzymes required during the initial steps of degradation were identified and confirmed by proteomic study. Kim et al. [15] employed genomic, proteomic and metabolic approaches to propose pathway for the degradation of pyrene by *Mycobacterium vanbaalenii* PYR-1. Genomic approach identified the genes involved in the degradation of pyrene. The proteins involved in pyrene degradation were identified by proteome analysis employing 1-D gel electrophoresis combined with LC-MS. Based on the results of genomic and proteomic analysis, 27 enzymes were found necessary for the complete degradation of pyrene. The results showed comprehensive metabolism of pyrene by *Mycobacterium vanbaalenii* PYR-1.

Decay of B[a]P by *Sphingomonas yanoikuyae* JAR02 was investigated by Rentz et al. [16]. The pathway for the degradation of B[a]P was proposed and formation of novel metabolites by ring cleavage was reported. The results showed that B[a]P degradation is biostimulated by water soluble and non-toxic substrate, salicylate. Lhoest [17] isolated new metabolites of B[a]P from microsomes of rat and human liver and proposed fragmentation pathways. The researcher observed metabolite 7,8-ketol, 9,10-epoxide bound with DNA and referred it as ultimate carcinogenic compound. Zeng et al. [18] studied benzo[a]pyrene degradation by laccase obtained from *Trametes versicolor* and *Mycobacterium* strains. The results indicated that B[a]P was oxidized to quinones and methoxy derivatives.

Wen et al., [19] studied the photodegradation of pyrene in aqueous solutions in presence of TiO_2. The results revealed the occurrence of Hydroxylation, ketolysis and ring-open reactions for the formation of intermediates. The pH of the solution had a little effect on the rate of photodegradation of pyrene. A study on photodegradation of pyrene adsorbed on microcrystalline cellulose and silica was conducted by Olivera et al. [20]. 1-Hydroxypyrene was detected as a major photoproduct on microcrystalline cellulose, but was not detected in case of silica. This was assigned to very slow oxidation of 1-hydroxypyrene on microcrystalline cellulose in the absence of oxygen and fast oxidation to other photoproducts on silica in the presence of oxygen. It was further observed that on both the substrates, the intermediate was pyrene radical cation. Garcia-Martinez et al. [21] investigated the photocatalytic degradation of naphthalene in aqueous solution by TiO_2 supported on glass Raschig rings. Photodegradation of naphthalene followed first order kinetics. Intermediate products were observed in trace amounts. Li-hong et al. [22] studied photodegradation of B[a]P on soil surfaces under UV irradiation and effect of various parameters on the photodegradation of B[a]P were examined. The results suggested that the degradation of B[a]P is not affected significantly by catalyst dose (TiO_2 or Fe_2O_3) and faster photocatalysis rate is achieved when irradiated with 254 nm wavelength. Zhang et al. [23] studied photodegradation of phenanthrene, pyrene and B[a]P on soil surfaces in presence of TiO_2 under UV irradiation. The effect of various parameters on the degradation was observed. The results suggested that photocatalytic degradation of phenanthrene, pyrene and B[a]P followed pseudo-first order kinetics with half-lives 130.77 h, 192.53 h and 103.26 h, respectively, when 0.5% TiO_2 was used as catalyst. The results further indicated faster photodegradation in acidic or alkaline soils than neutral soil. Carlo et al., [24] studied the photodegradation of B[a]P using DNA electrochemical sensors. The degradation of B[a]P under UV light follow first order kinetics with half-lives in the range 3-9.8 h and only four metabolities of benzo[a]pyrene were identified.

Photodegradation of pyrene on solid phase of iron oxide was investigated by Wang et al. [25]. The results revealed that the rate of photodegradation of pyrene is in the order, goethite > hematite > maghemite > lepidocrite. First order rate kinetics was observed for the degradation of pyrene. It was also observed that iron oxides in presence of oxalic acid can set up photo-Fenton like mechanism under UV irradiation in the absence of additional H_2O_2. An intermediate compound pyreno was identified during photodegradation of pyrene using GC-

MS. Dong et al. investigated degradation of phenanthrene and pyrene on soil surfaces using rutile TiO_2 [26] and anatase TiO_2 [27] as photocatalysts under UV irradiation. In both the cases, photodegradation rate followed pseudo-first order rate kinetics and the rate increased with the increasing concentration of H_2O_2 and humic acid and intensity of light. Zhang et al. [28, 29] studied the photodegradation of phenanthrene, pyrene and B[a]P under UV irradiation using hematite as photocatalyst, but did not identify the metabolites. The effect of various factors on photodegradation was examined and results revealed pseudo-first order rate kinetics. Results further indicated that humic acid significantly enhances the photocatalytic degradation of PAHs and rate of degradation is greater in acidic or alkaline soils than neutral soil.

It is apparent from the above discussion that most of the available information on metabolites of B[a]P and pyrene is for their microbial degradation. Detailed studies on the identification of metabolites of B[a]P and pyrene during their photodegradation in soil are still lacking. Only a few studies are available on metabolite identification during photodegradation of B[a]P and pyrene in different media. Moreover, microbial degradation of high molecular weight PAHs is slow due to their high stability [30, 31] and requires an effective maintenance of optimised conditions. Photodegradation using a photocatalyst is a favourable path for elimination of PAHs and other persistent organic pollutants [32, 33]. In view of this a systematic study was planned on photodegradation of benzo[a]pyrene and pyrene alongwith identification of metabolities in soils of varying pH. Five iron oxides were selected as photocatalyst for the present study.

Iron oxides are minerals found naturally in rocks, soils, hot brines, marine environments and formed in various organisms. There are sixteen types of iron oxides, hydroxides and oxide-hydroxides [34]. Out of these two oxide-hydroxides, namely, goethite (α-FeOOH), akaganeite (β-FeOOH) and three oxides, namely, magnetite (Fe_3O_4), maghemite (γ-Fe_2O_3) and haematite (α-Fe_2O_3) were selected for the photodegradation studies on B[a]P and pyrene. These can be synthesized readily in the laboratory. The photocatalytic dissipation of benzo[a]pyrene and pyrene was carried out on pure iron oxide surfaces as well as on soil surfaces in the presence of iron oxides. The effect of different parameters like soil pH, wavelength of UV radiation, amount of iron oxide and oxalic acid on the photocatalytic activity was evaluated. Metabolites of photodegradation in soils of various pH, in the presence of an iron oxide, goethite, were identified and possible pathways proposed.

4.1 EXPERIMENTAL

The details of extraction and clean up methods, operating conditions for HPLC and LC-MS, synthesis of iron oxides and methods for characterization of iron oxides are discussed in chapter II.

4.1.1 Photodegradation studies

To compare the efficiency of various synthesized iron oxides as photocatalyst the decay profile of B[a]P and pyrene was investigated on pure iron oxides. 0.1 g of each iron oxide was taken into a series of light proof petri dishes and spiked with 0.2 mL of 50 µg L^{-1} benzo[a]pyrene/pyrene. The spiked samples were irradiated with UV radiations for 1-10 h. Samples were removed periodically after every 60 min, extracted and analysed by HPLC. Photodegradation of B[a]P and pyrene was carried out in a UV cabinet at a selected wavelength of 254 nm unless mentioned otherwise. All the experiments were conducted in three replicates.

Detailed studies on photodegradation of B[a]P and pyrene on soil surfaces were carried out in presence of goethite, the selected iron oxide. 1 g soil samples were placed in petri dishes and spiked with 50 µg B[a]P/pyrene and placed in the UV chamber for 0-5 d. The samples were removed, extracted and analysed at regular intervals of 24 h. The effect of varying parameters such as soil pH, dose of goethite (0-5 wt%), oxalic acid dose (0-4 wt%) and wavelength of irradiation on the disintegration of B[a]P and pyrene was investigated. Controls and blanks were run wherever necessary. In the blank samples, the decay of PAHs was measured for 0-60 days at a regular interval of 5 days. It was observed that after an interval of 60 days, the degradation of benzo[a]pyrene and pyrene was <12 % and <10%, respectively.

4.2 RESULTS AND DISCUSSION

4.2.1 Characteristics of iron oxides

XRD spectra of all the synthesized forms of iron oxides are shown in Fig. 4.2. XRD data is concordant to the JCPDS-ICDD (1979). The crystallite sizes were calculated using

Scherrer's equation i.e. $D = (0.9\lambda) / (\beta \cos \theta)$, where λ is X-ray wavelength, β is line broadening measured at half-height of the most intense peak of XRD and θ is Bragg angle of the particles. Crystallite sizes were 9.83, 30.03, 13.05, 14.08 and 17.26 nm for goethite, akaganeite, haematite, magnetite and maghemite, respectively.

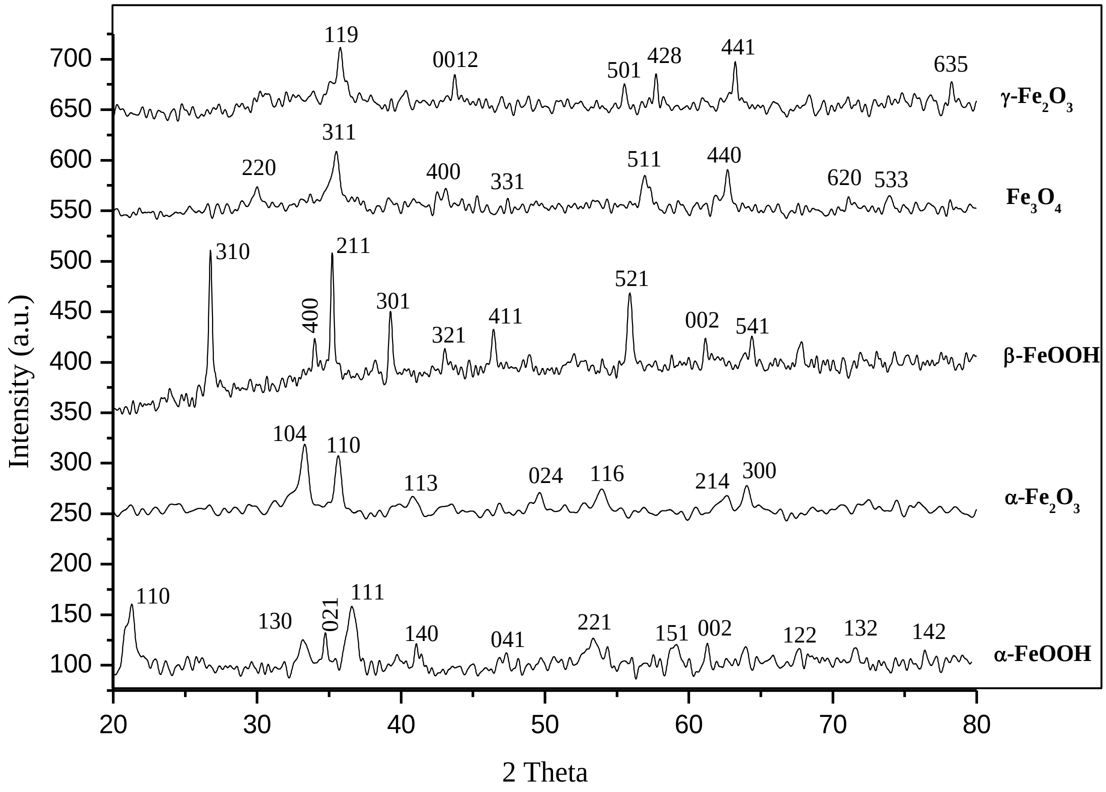
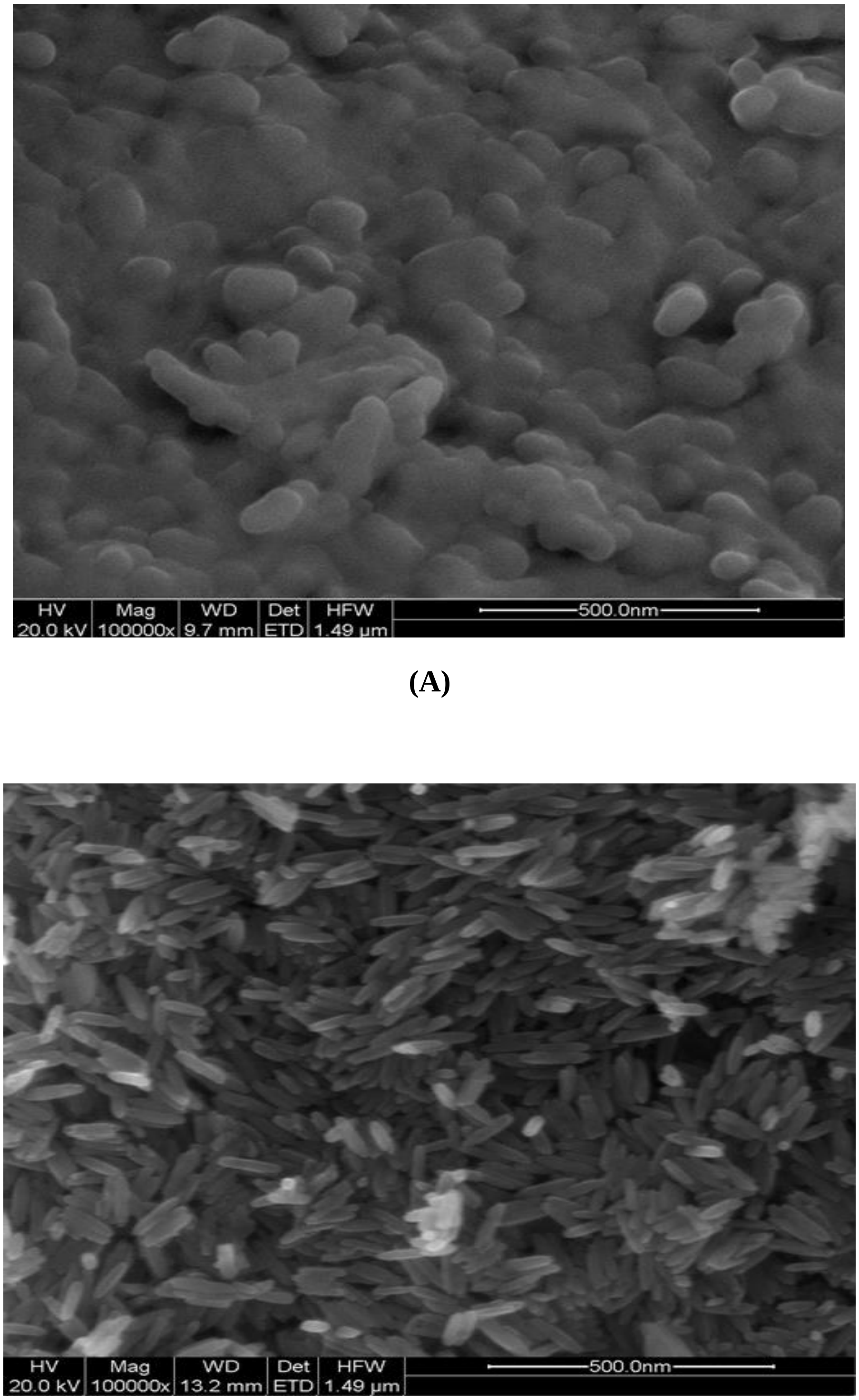


Fig. 4.2: XRD spectra of different iron oxides

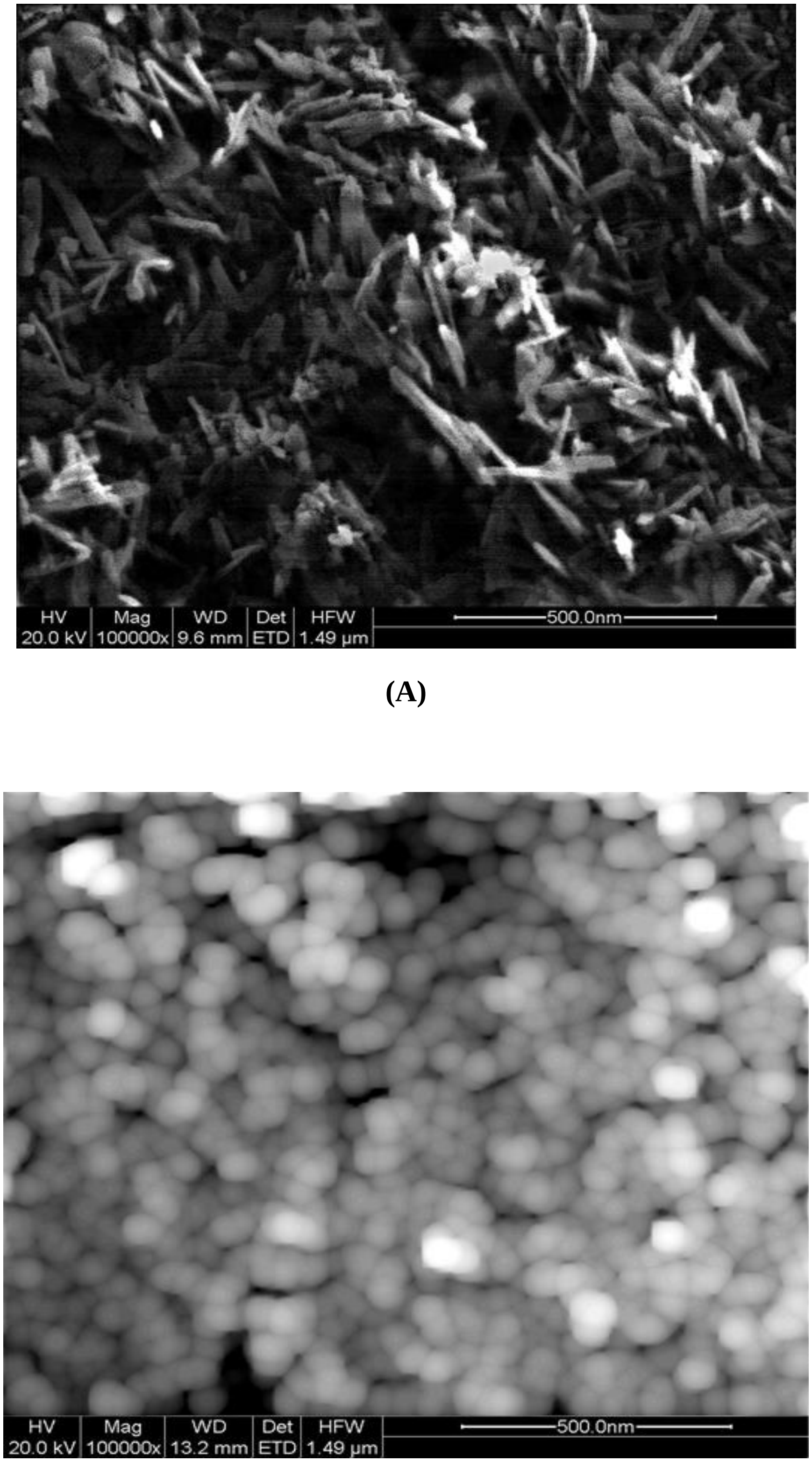
FE-SEM images (Fig. 4.3, 4.4 and 4.5) indicate that goethite, magnetite and maghemite were globular in structure with mean sizes 57.20, 39.67 and 64.70 nm, respectively. Hematite and akaganeite appear as rod shaped structures, 102.16, 85.93 nm long and 18.32, 18.07 nm thick, respectively.



(A)

(B)

Fig. 4.3: FE-SEM images of (A) Goethite (B) Akaganeite



(A)

Fig. 4.4: FE-SEM images of (A) Hematite (B) Magnetite

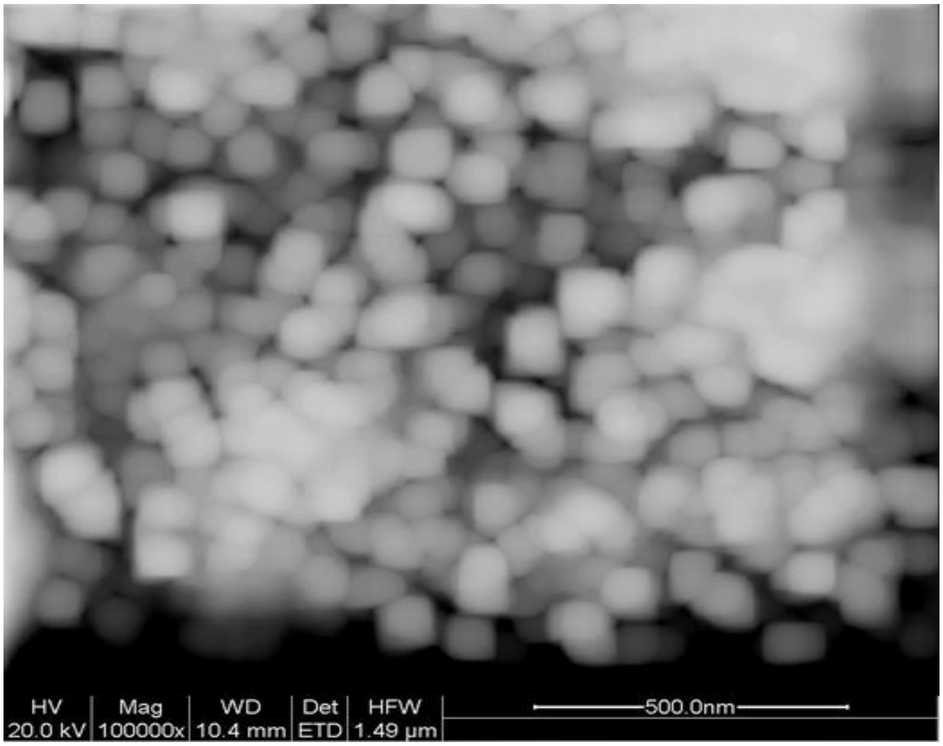


Fig. 4.5: FE-SEM image of Maghemite

4.2.2 Analysis with pure phase of iron oxides

All the five synthesized iron oxides were employed as photocatalyst for the degradation of benzo[a]pyrene and pyrene under UV light. Results indicate that all the five phases efficiently dissociate benzo[a]pyrene and pyrene at ambient temperature. Photodisintegration of B[a]P follows first order kinetics with rate constant (K) values of 2.38 x 10^{-1}, 2.04 x 10^{-1}, 1.96 x 10^{-1}, 1.95 x 10^{-1} and 1.80 x 10^{-1} h^{-1} in the presence of goethite, haematite, magnetite, akaganeite and maghemite, respectively. Degradation of pyrene also follows first order kinetics with rate constant (K) values 1.49 x 10^{-1}, 1.45 x 10^{-1}, 1.34 x 10^{-1}, 1.35 x 10^{-1} and 1.32 x 10^{-1} with goethite, hematite, magnetite, akaganeite and maghemite, respectively (Table 4.1). Results of the present study suggest fastest disintegration with goethite. Fastest degradation rate for various pollutants on goethite has been reported by different workers. Wang et al. [25] in their study on photodegradation of pyrene on different iron oxides also observed first order rate kinetics and fastest decay rate on goethite. He et al. [35] observed fastest photodegradation rate of Mordent Yellow 10 dye with goethite. Hu et al.

[36] observed better photocatalytic activity of goethite over hematite during photocatalytic degradation of atrazine under visible light.

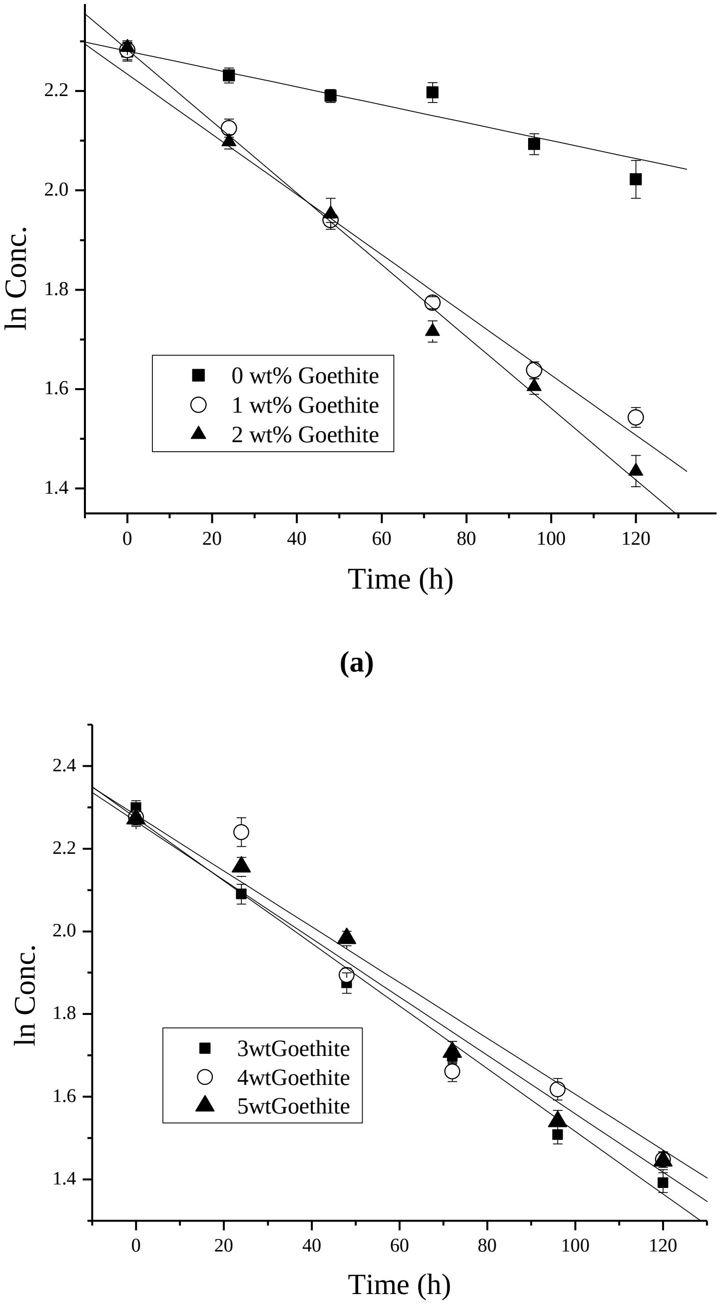
Detailed studies on disintegration of benzo[a]pyrene and pyrene on soil surfaces were thus carried out using goethite.

Table 4.1: Degradation rate constants and half lives of benzo[a]pyrene and pyrene on pure phase of iron oxides

Conditions	K (h^{-1})	$t_{1/2}$ (h)	r
Benzo[a]pyrene			
Goethite	2.38×10^{-1}	2.90	0.9721
Hematite	2.04×10^{-1}	3.39	0.9614
Magnetite	1.96×10^{-1}	3.53	0.9617
Akaganeite	1.95×10^{-1}	3.55	0.9623
Maghemite	1.80×10^{-1}	3.83	0.9593
Pyrene			
Goethite	1.49×10^{-1}	4.62	0.9899
Hematite	1.45×10^{-1}	4.77	0.9901
Magnetite	1.34×10^{-1}	5.15	0.9914
Akaganeite	1.35×10^{-1}	5.12	0.9829
Maghemite	1.32×10^{-1}	5.24	0.9657

4.2.3 Effect of Goethite (α-FeOOH) dose on degradation of B[a]P and pyrene

To study the effect of goethite dose on the photodegradation of benzo[a]pyrene and pyrene varying amounts (0-5 wt%) of goethite were added to the soil (pH 6.8) spiked with benzo[a]pyrene/pyrene and irradiated with radiations of wavelength 254 nm. The concentrations of benzo[a]pyrene/pyrene remaining after definite time intervals were determined and plots were drawn between natural logarithm of concentration and time. The results [Fig 4.6(a) and Fig. 4.6(b)] indicate that in all the cases disintegration of benzo[a]pyrene follows first order rate kinetics with rate constant values as 2.01 x 10^{-3}, 6.34 x 10^{-3}, 7.12 x 10^{-3}, 7.69 x 10^{-3}, 7.43 x 10^{-3} and 7.42 x 10^{-3} h^{-1} corresponding to a catalyst dose of 0, 1, 2, 3, 4 and 5 wt%, respectively.



(a)

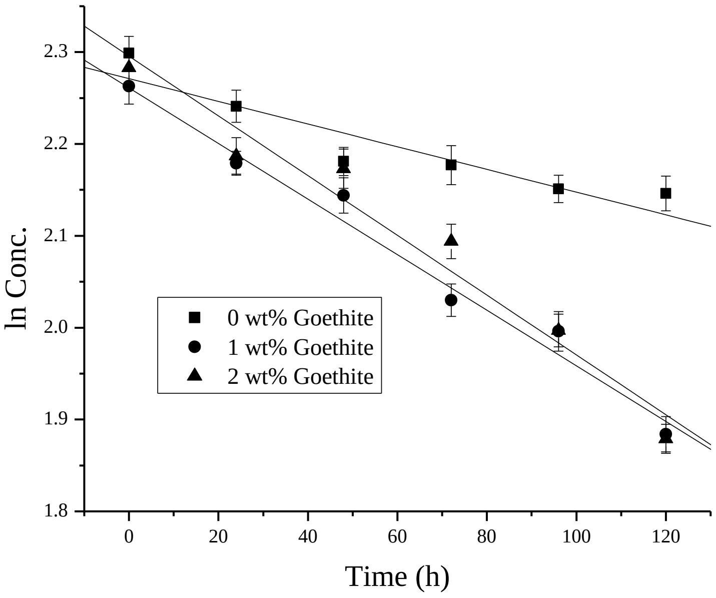
(b)

Fig. 4.6: Effect of dose of Goethite on photodegradation of benzo[a]pyrene

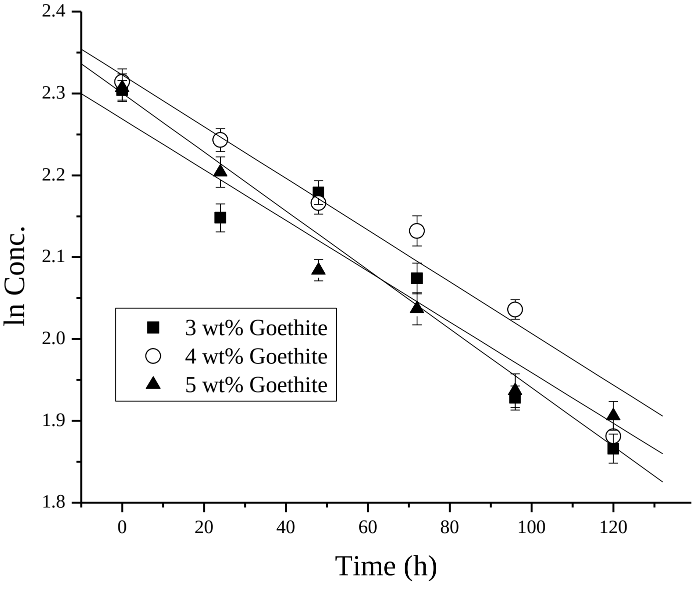
(a) 0-2 wt% Goethite, (b) 3-5 wt% Goethite

Conditions: pH: 6.8; wavelength: 254 nm; Time: 0-5 d

Similarly, in case of pyrene plots drawn between natural logarithm of pyrene concentration and time gave straight line, suggesting first order rate kinetics [Fig.4.7(a) and Fig. 4.7(b)].



(a)



(b)

Fig. 4.7: Effect of dose of Goethite on photodegradation of pyrene
(a) 0-2 wt% Goethite, (b) 3-5 wt% Goethite
Conditions: pH: 6.8; wavelength: 254 nm; Time: 0-5 d

The first order rate constant values for degradation of pyrene are 1.24 x 10^{-3}, 3.05 x 10^{-3}, 3.18 x 10^{-3}, 3.52 x 10^{-3}, 3.36 x 10^{-3} and 3.34 x 10^{-3} h^{-1} corresponding to catalyst dose of 0, 1, 2, 3, 4 and 5 wt%, respectively. It is evident from the results that the presence of goethite significantly enhances the photodegradation of benzo[a]pyrene and pyrene. In both the cases, the rate of degradation increases with increasing catalyst upto 3 wt% and is almost constant thereafter. This is probably due to the fact that low catalyst amount provides insufficient surface for disintegration of benzo[a]pyrene/pyrene.

4.2.4 Effect of soil pH on degradation of benzo[a]pyrene and pyrene

To evaluate the effect of pH on degradation efficiency, photocatalytic degradation of benzo[a]pyrene and pyrene was carried out in the soils of pH 5.4, 6.8 and 8.1 under UV irradiation (254 nm) in presence of optimum goethite concentration. Plots were drawn between natural logarithm of remaining PAH concentration and time. Fig. 4.8 shows the results of photodegradation of B[a]P at various soil pH. The first order rate constant values for B[a]P are 1.11 x 10^{-2}, 7.69 x 10^{-3} and 9.97 x 10^{-3} h^{-1} for acidic, neutral and basic soil, respectively.

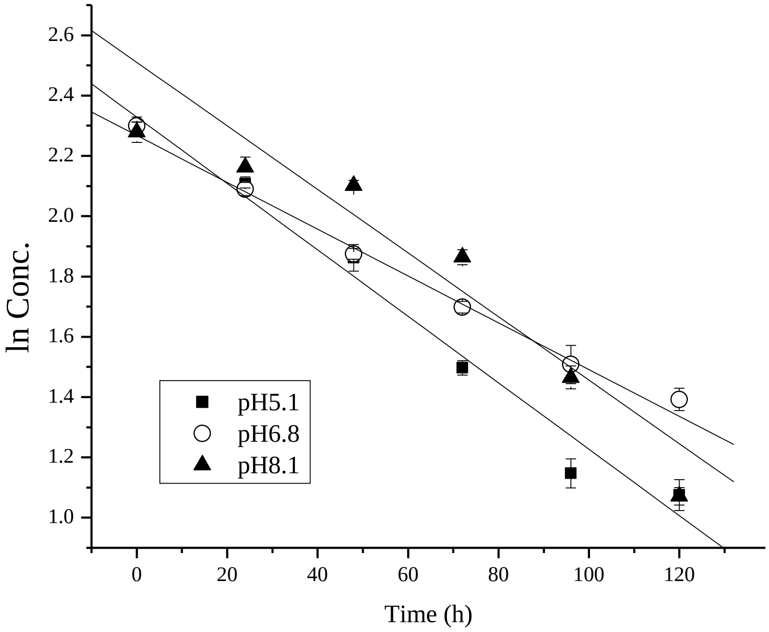


Fig. 4.8: Effect of soil pH on photodegradation of benzo[a]pyrene

Conditions: Goethite: 3wt%; wavelength: 254 nm; Time: 0-5 d

Fig. 4.9 shows the effect of pH on pyrene degradation. The first order rate constants calculated for pyrene are 1.03 x 10^{-2}, 3.52 x 10^{-3} and 8.99 x 10^{-3} h^{-1} corresponding to soils of pH 5.4, 6.8 and 8.1, respectively. It is evident from the results that rate of degradation of B[a]P and pyrene are faster in acidic and alkaline soils than neutral soil. This suggests that H^+/OH^- ions facilitate the degradation process. Similar trend was observed by Zhang et al. for the photocatalytic degradation of some PAHs [23, 29].

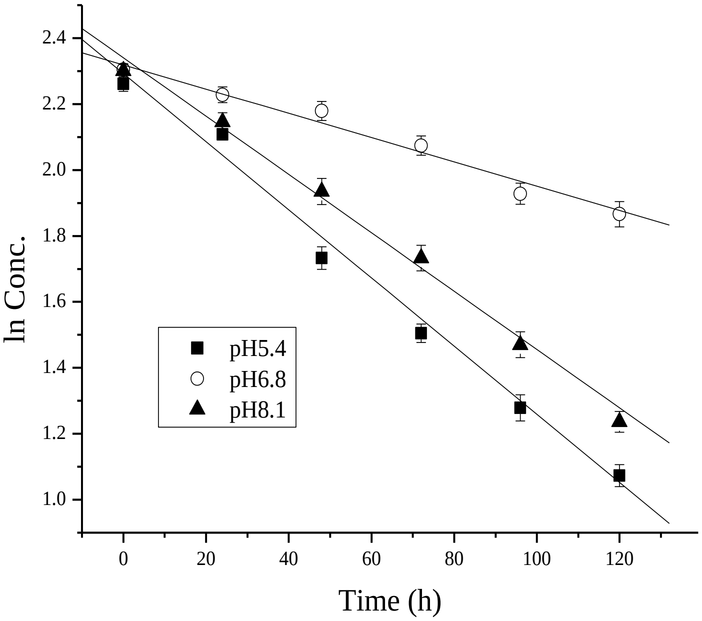


Fig. 4.9: Effect of soil pH on photocatalytic degradation of pyrene

Conditions: Goethite: 3wt%; wavelength: 254 nm; Time: 0-5 d

4.2.5 Effect of UV wavelength on the degradation of B[a]P and pyrene

It is well established that the photodegradation is influenced by the wavelength of the incident radiation. Disintegration of benzo[a]pyrene and pyrene was studied under three different wavelengths i.e. 254, 365 and 410 nm. Fig. 4.10 shows the photodegradation of benzo[a]pyrene at different wavelengths. The first order rate constants for B[a]P degradation are 7.69 x 10^{-3}, 4.76 x 10^{-3} and 2.69 x 10^{-3} at wavelengths 254, 365, and 410 nm, respectively. The values of rate constants for the degradation of pyrene are 3.52 x 10^{-3}, 3.10 x 10^{-3} and 2.01 x 10^{-3} h^{-1} at wavelengths 254, 365, and 410 nm, respectively (Fig. 4.11). The degradation rate of both, B[a]P and pyrene decreases with the increase in wavelength. Faster degradation at low wavelength can be explained on the basis of the fact that higher the energy of the incident radiation, greater is the degree of photodegradation.

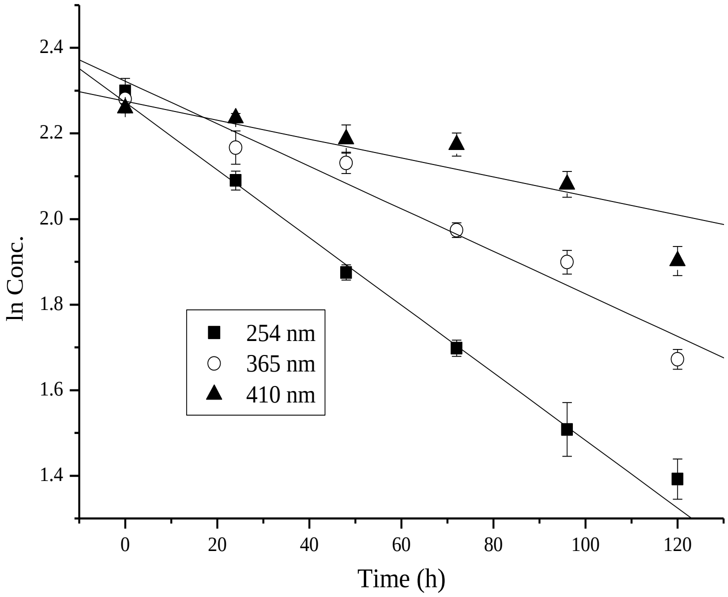


Fig. 4.10: Photodegradation of B[a]P at different wavelengths
Conditions: Goethite: 3wt%; pH: 6.8; Time: 0-5 d

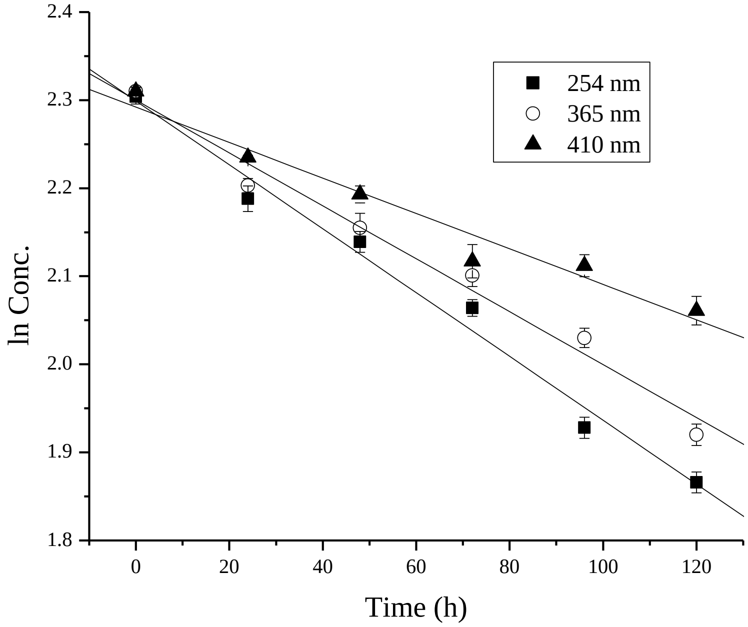


Fig. 4.11: Photodegradation of pyrene at different wavelengths
Conditions: Goethite: 3wt%; pH: 6.8; Time: 0-5 d

4.2.6 Mechanism of Photodegradation of PAHs

Iron oxides under UV irradiation catalyse the photodegradation of organic compounds due to their semiconducting properties. The band gap energies are 2.10, 2.20, 0.10, 2.12, and 2.03 eV for goethite, hematite, magnetite, akaganeite and maghemite, respectively [30]. The rate constants for the five iron oxides indicate that inspite of low band gap of magnetite, its photocatalytic activity is quite low. Beydoun and co-workers [37, 38] observed similar results and concluded that smaller band gap of magnetite and presence of both Fe^{II} and Fe^{III} in the lattice provides favourable environment for electron-hole recombination. Iron oxides when irradiated with UV light with energy greater than the band gap energy, generate electron (e^-) and hole (h^+) pairs, hole reacts with water molecule and generates hydroxyl radical and H^+, whereas, electron reacts with oxygen to form oxygen radical anion. The oxygen radical anion generated combines with H^+ to form $HOO^\bullet$ radical and two molecules of $HOO^\bullet$ radical may forms H_2O_2. H_2O_2 molecule dissociates to generate hydroxyl radicals responsible for the degradation of PAHs [25]. The recombination of hydroxyl radical and e^--h^+ pair may form H_2O_2 and regenerate iron oxide, respectively. A typical mechanism for the degradation of benzo[a]pyrene/pyrene employing iron oxides as photocatalyst under UV irradiation is given in Fig. 4.12.

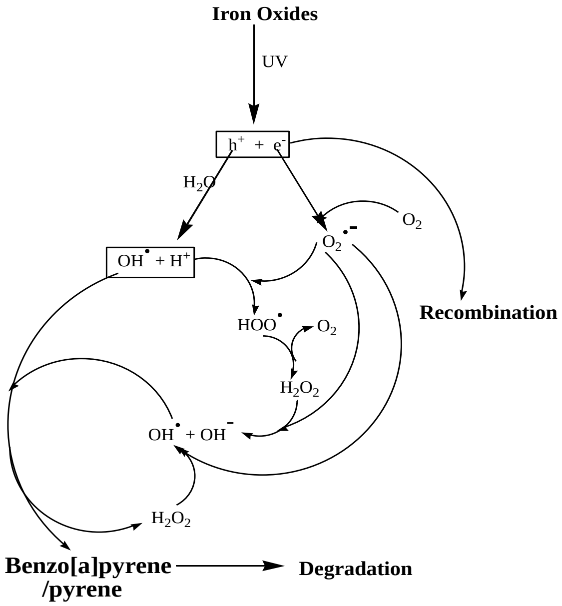


Fig. 4.12: A typical mechanism for the degradation of B[a]P/pyrene employing iron oxides as photocatalyst under UV irradiation

4.2.7 Effect of oxalic acid on the degradation of B[a]P and pyrene

Oxalic acids are organic molecules found naturally in soil due to secretion of plants [39]. In order to study the effect of oxalic acid on the degradation of B[a]P and pyrene, varying amounts of oxalic acid (0-4 wt%) were added to the soil spiked with B[a]P/pyrene and goethite (3 wt%). Degradation profiles of B[a]P and pyrene at different oxalic acid concentrations are shown in Fig. 4.13 and 4.14. The results indicate that both the PAHs disintegrate following first order kinetics and rate of photodegradation increases in the presence of oxalic acid. The rate increases with the increasing dose of oxalic acid. The faster kinetics in presence of oxalic acid can be attributed to the fact that oxalate reacts with goethite to form oxalate complex [40], which dissociates in presence of UV radiations to form different radicals and hydrogen peroxide. H_2O_2 undergoes fenton like process with Fe^{II} complex to form iron(III)–oxalate complex and $^{\cdot}OH$ radical. The $^{\cdot}OH$ radical facilitates the degradation of B[a]P or pyrene [25]. The mechanism of degradation of PAHs in presence of goethite along with oxalic acid is given in Fig. 4.15.

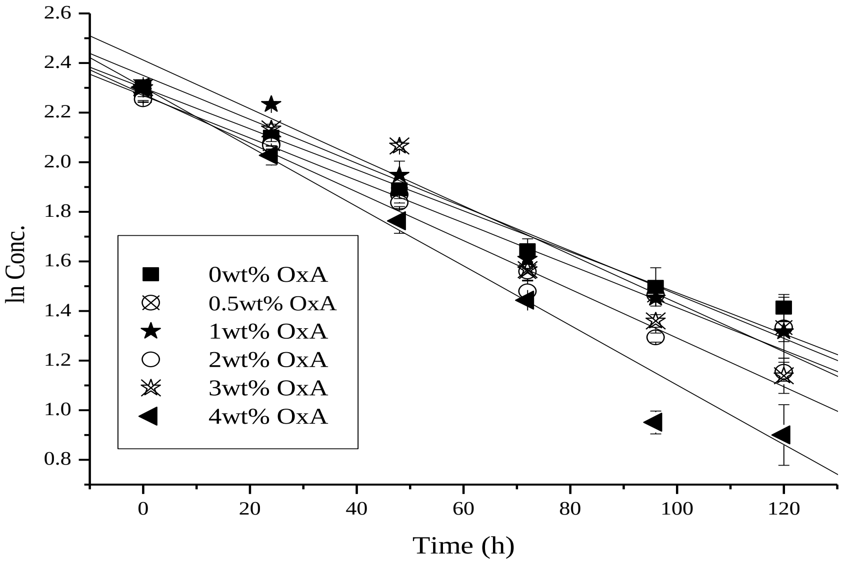


Fig. 4.13: Photodegradation of B[a]P with different oxalic acid concentrations
Conditions: Goethite: 3wt%; pH: 6.8; wavelength: 254 nm Time: 0-5 d

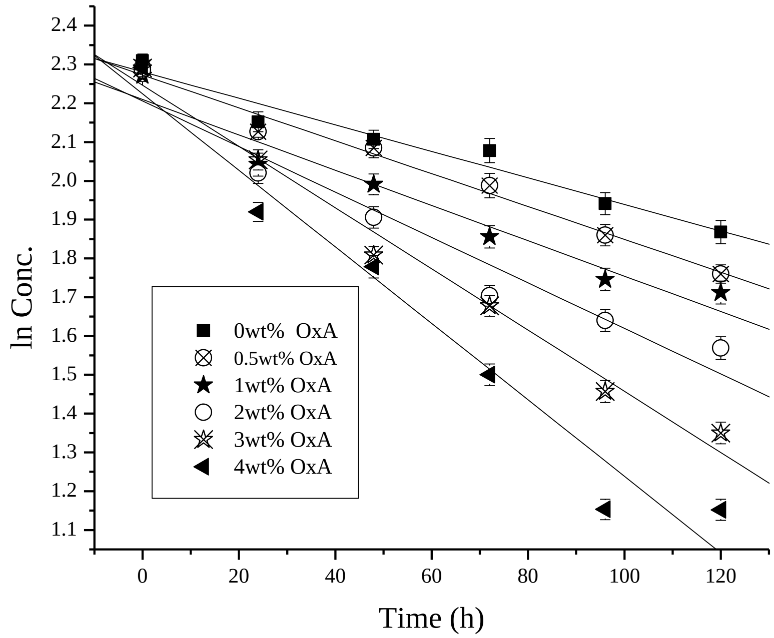


Fig. 4.14: Photodegradation of pyrene with different oxalic acid concentrations Conditions: Goethite: 3wt%; pH: 6.8; wavelength: 254 nm; Time: 0-5 d

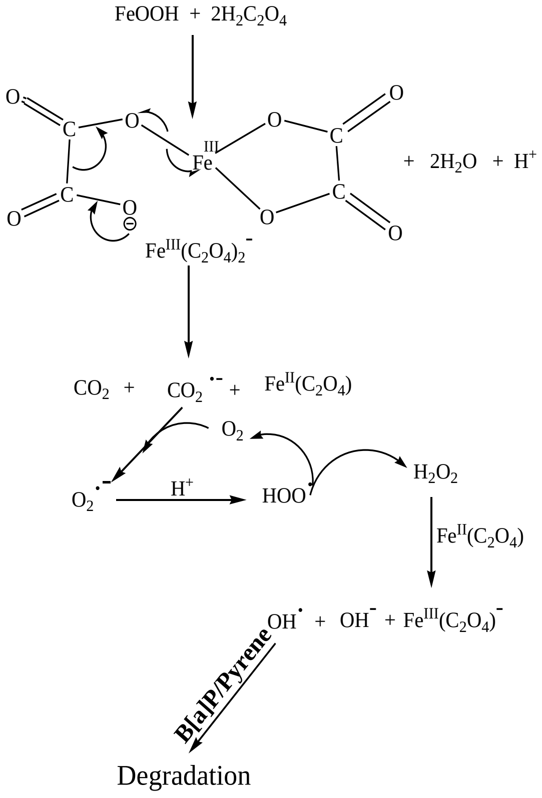
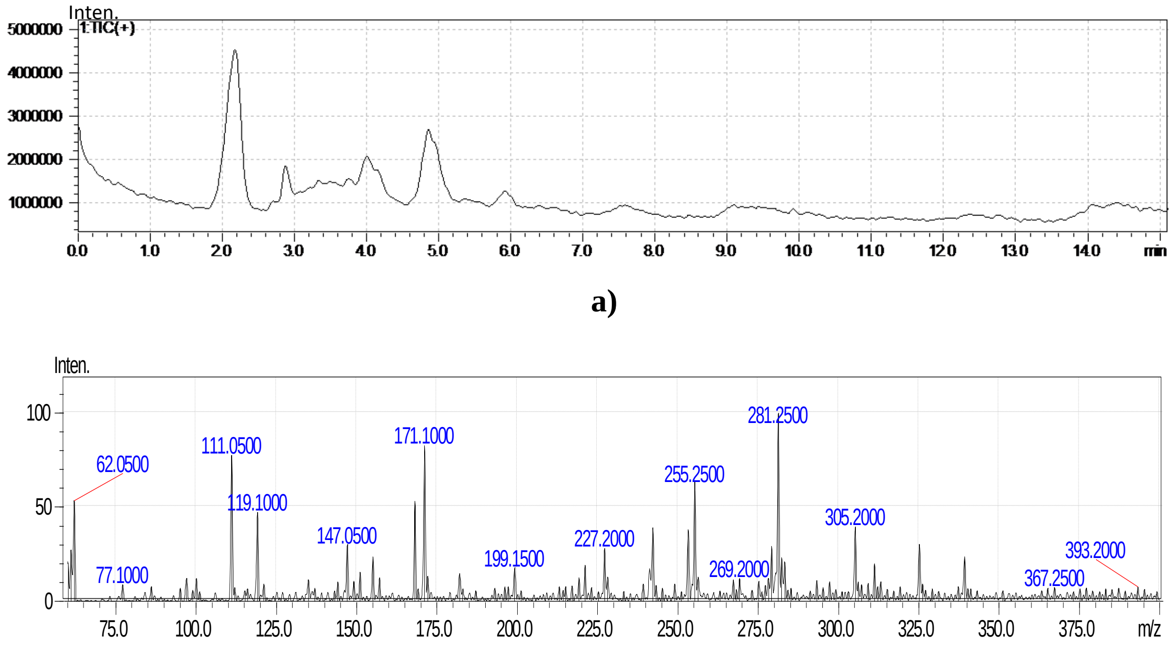


Fig. 4.15 Schematic representation of photocatalytic degradation of B[a]P/pyrene in presence of goethite and oxalic acid (OxA)

4.2.8 Degradation products of benzo[a]pyrene

Photodegradation of B[a]P was studied in soils of varying pH (5.4, 6.8, 8.1) with optimum goethite content (3 wt%) under UV irradiation of 254 nm for 120 h. The samples were extracted after different time intervals (0, 24 h, 48 h, 72 h, 96 h and 120 h) and analysed by LC-MS to identify the various metabolites. A typical total ion chromatogram and corresponding full scan mass spectrum of benzo[a]pyrene are shown in Fig. 4.16.



a)

b)

Fig. 4.16: Total ion chromatogram (a) and full scan mass spectrum (b) of metabolites of benzo[a]pyrene in soil (pH 6.8) after 24 h

The possible pathways for the formation of metabolites in neutral, basic and acidic soils in the presence of goethite are shown in Fig. 4.17, 4.18 and 4.19, respectively.

In case of neutral soil of pH 6.8, at zero h only a prominent molecular ion peak of the parent compound B[a]P at m/z 252 was observed. After 24 h, five metabolites with molecular ion peaks at m/z 217, 255, 269, 281 and 283 were observed. The metabolite with m/z 283 is obtained due to full oxidation of B[a]P and assigned to benzo[a]pyrene-4,5-dione [12] or benzo[a]pyrene-7,8-dione [24] which probably by loss of two hydrogen atoms yields a metabolite with m/z 281. Metabolites with m/z 269, 255 and 217 were assigned as 5-hydroxybenzo[a]pyrene [24], cyclopenta[d,e,f]chrysene-4-one [12] and 1,2-epoxypyrene, respectively. Metabolite with m/z 269 was observed due to loss of oxygen and m/z 255 was observed due to loss of CO group from m/z 283.

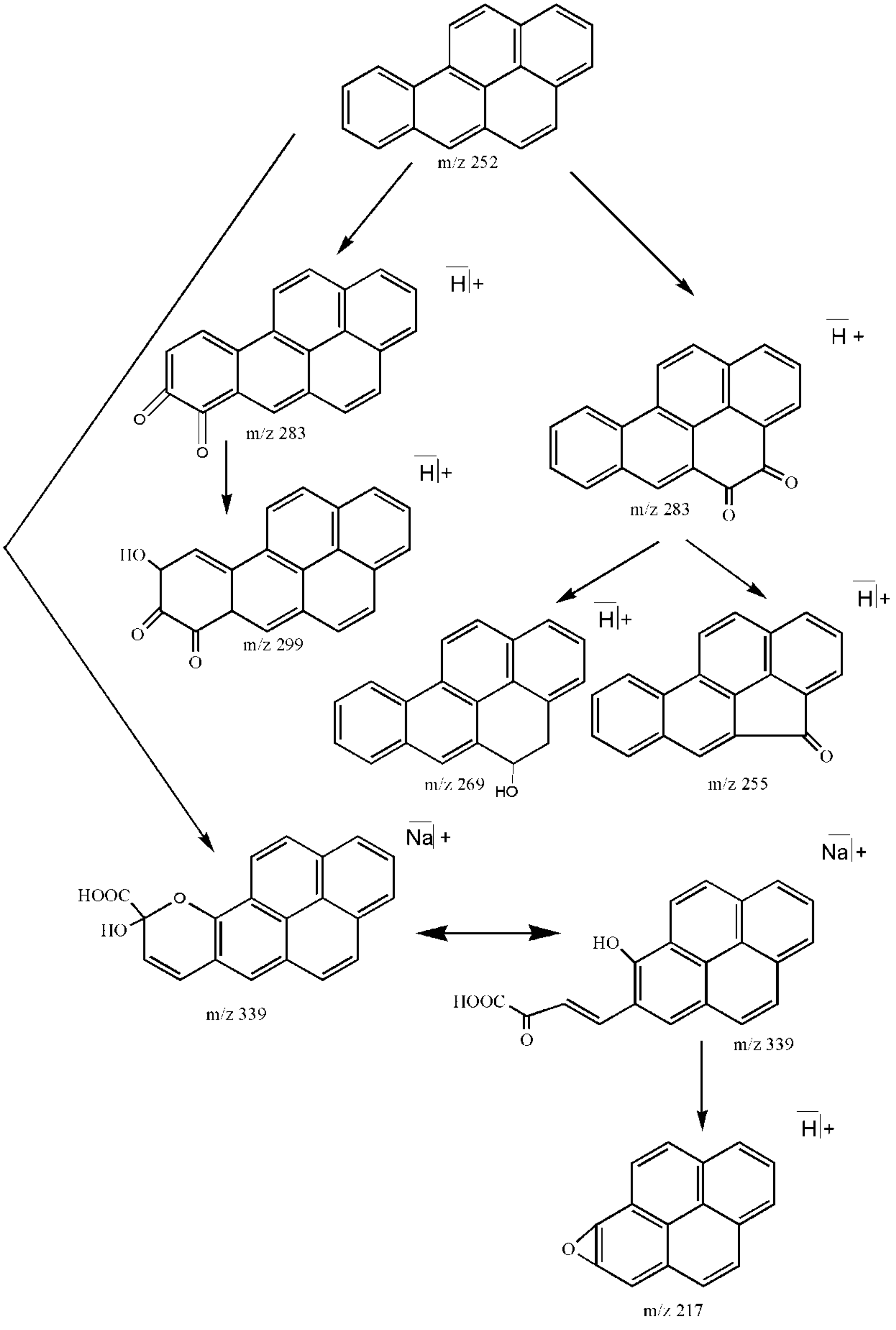


Fig. 4.17: Possible pathway for the degradation of B[a]P in neutral soil

After 48 and 72 h, an additional peak at m/z 339 was observed due to sodium adduct of 9-hydroxy-9H-phenaleno[1,9-gh]chromene-9-carboxylic acid or 4-(8-hydroxypyren-7-yl)-2-oxobut-3-enoic acid [8, 16]. After 96 h, the peaks at m/z 217, 255 and 283 disappeared and a new metabolite peak at m/z 299 appeared which is assigned to 9-hydoxybenzo[a]pyrene-7,8-dione [24]. After 120 h, above mentioned peaks disappeared and two prominent peaks at m/z 211 and 374 appeared which could not be assigned.

In case of basic soil (pH 8.1) also only a prominent molecular ion peak is observed at zero h. After 24 h, in addition to the parent compound peak, three metabolite peaks at m/z 269, 279 and 285 were observed. The peak at m/z 285 is due to partial oxidation of B[a]P and is assigned to 4,5-dihydroxybenzo[a]pyrene [16]. The metabolite at m/z 269 was due to loss of oxygen from metabolite with m/z 285. The metabolite peak at m/z 279 is assigned to sodium adduct of cyclopenta[d,e,f]chrysene-4-ol which is obtained by loss of CO group from m/z 285. Besides, the peaks at m/z 269 and 279, two additional peaks at m/z 217 and m/z 331 were observed after 48 h. The metabolite peak at m/z 331 was assigned to benzo[a]pyrene-4,5-ketol-7,8-dione-9,10-epoxide. A similar metabolite, benzo[a]pyrene-4,5-ketol-7,8-dihydrodiol-9,10-epoxide is reported elsewhere [18]. A metabolite peak at m/z 219 was observed after 72 h which was assigned to 1,2-dihydroepoxypyrene which by loss of two hydrogens gives metabolite with m/z 217. After 120 h, only metabolite peaks at m/z 255 and 269 were discernible. The metabolite peak at m/z 255 is probably due to protonated molecule derived from sodium adduct with m/z 279 after loss of two hydrogen atoms.

In the case of acidic soil of pH 5.4, three metabolites with molecular ion peaks at m/z 219, 255 and 281 were detected after 24 h. After 48 h, metabolite peaks at m/z 283 and m/z 311 were observed in addition to the peaks at m/z 219 and m/z 255. The metabolite peak at m/z 311 could not be explained. Metabolite peaks at m/z 331 and 279 were detected after 72 h. After 96 h, metabolite peaks at m/z 281 and 339 were discernible. New metabolites with peaks at m/z 203 and 319 along with a peak at m/z 269 were observed after 120 h. Metabolite peak at m/z 203 was assigned to pyrene, whereas metabolite peak at m/z 319 was probably due to the protonated molecule derived from sodium adduct with m/z 339 after addition of two hydrogen atoms. The metabolite with m/z 319 further fragments to give metabolite with m/z 219 which looses oxygen in presence of H^+ to give smaller hydrocarbon pyrene (m/z 203), which is more persistent and is observed after 120 h.

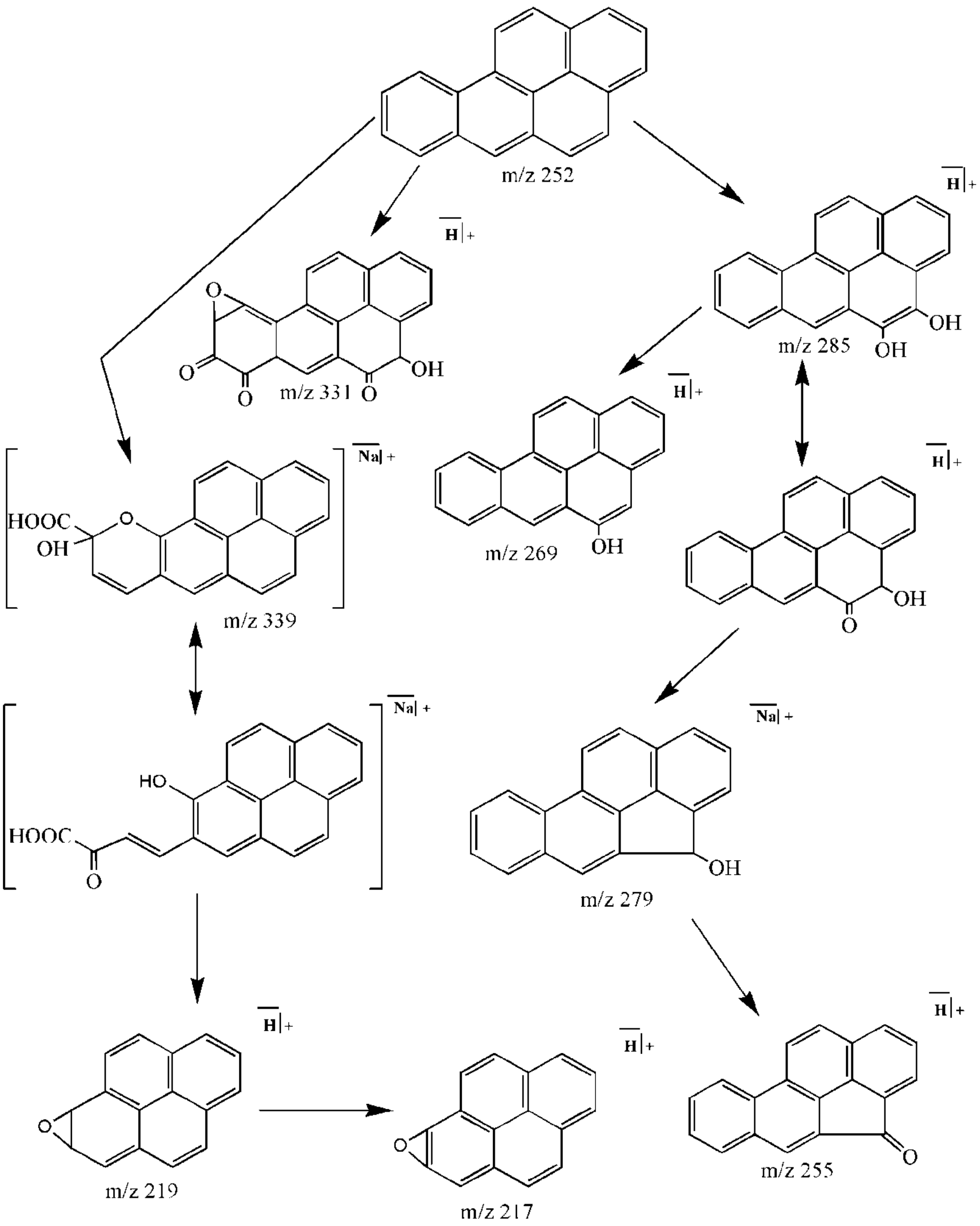


Fig. 4.18: Possible pathway for the degradation of B[a]P in basic soil. Structures in brackets are hypothetical intermediates.

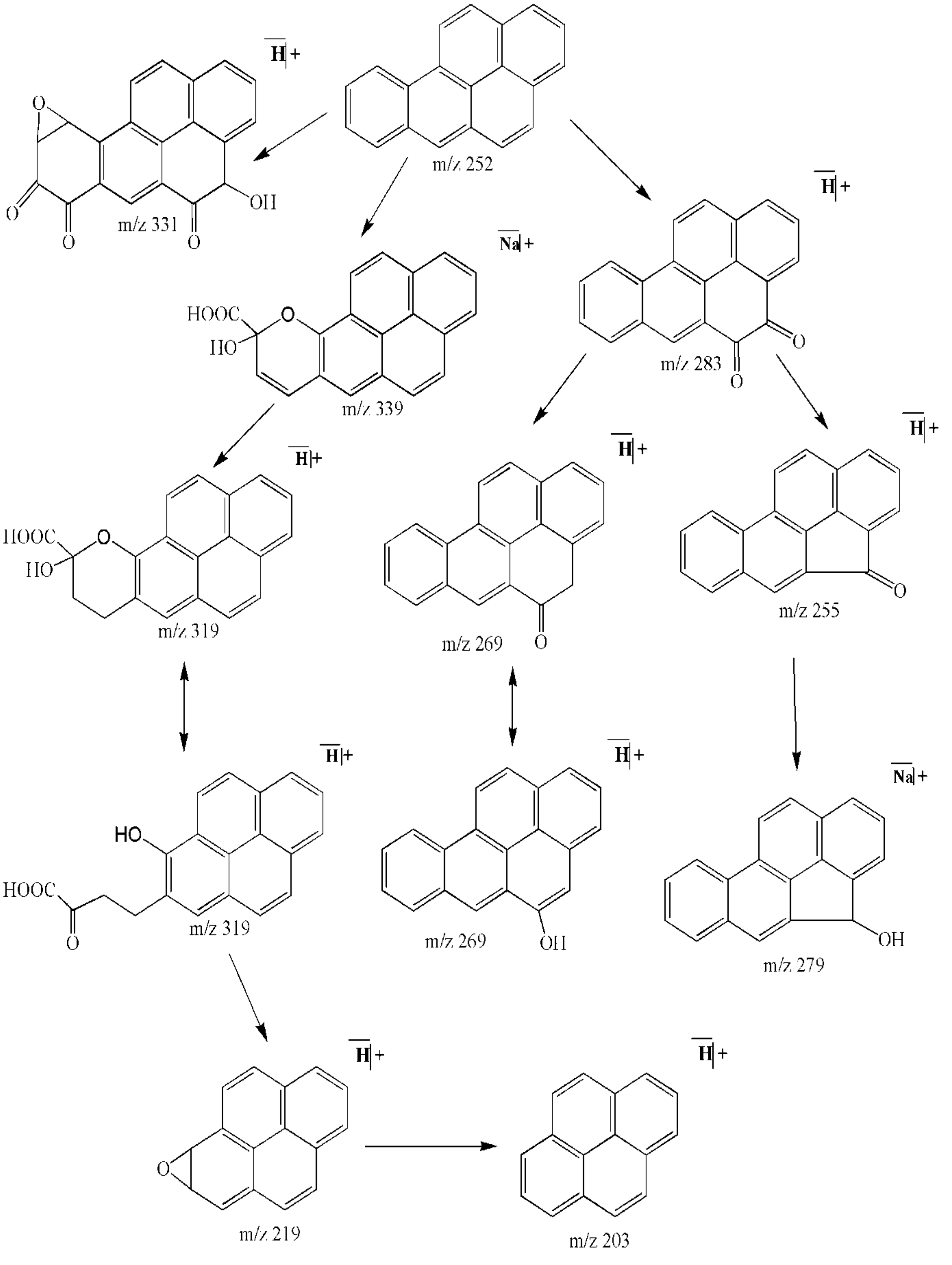


Fig. 4.19: Possible pathway for the degradation of B[a]P in acidic soil.

Blank experiments for the photodegradation of B[a]P in the absence of catalyst were conducted for 0, 24, 48, 72, 96 and 120 h. A prominent peak due to B[a]P was observed and none of the identified metabolite peaks were detected upto 72 h. After 96 and 120 h small peak at m/z 269 appears. Thus indicating a slow degradation of B[a]P in the absence of goethite.

It is clear from the observed metabolites that the degradation of B[a]P occurs through oxidative mechanism. The metabolites were confirmed by selective ion monitoring (SIM) and product ion scan. The metabolite peaks were detected at $[M + H]^+$ or $[M + Na]^+$. The structures of the metabolites are probable structures as these are not confirmed by NMR or other techniques. The oxygen containing structures could be drawn in various positions with high uncertainty. Therefore, these structures should be treated as representative structures for all possible isomers.

In soils of varying pH, the nature and persistence of the metabolites formed is different due to dissimilar chemical environment. In case of acidic and neutral soil m/z 283 was observed whereas in alkaline soils, m/z 285 was observed. This can be attributed to the full oxidation taking place in acidic and neutral medium and partial oxidation in alkaline medium. The metabolite with m/z 299 was observed in neutral soil only and in acidic and alkaline soils, it was further oxidised to m/z 331. Metabolite with m/z 269 was persistent after 120 h in both, basic and acidic soils, whereas this was not observed in neutral soil after 120 h. In acidic soil appearance of a metabolite peak at m/z 203 after 120 h indicates the conversion of carcinogen benzo[a]pyrene to smaller PAH, pyrene.

4.2.9 Degradation products of pyrene

Pyrene was degraded photochemically in acidic (pH 5.4), neutral (pH 6.8) and alkaline (pH 8.1) soils under optimised conditions (3 wt% goethite, 254 nm wavelength) for 120 h. The samples were extracted at regular time intervals (0, 24, 48, 72, 96 and 120 h) and analysed through LC-MS for the identification of different degradation products. The degradation products and their possible pathways in the three soils are shown in Fig. 4.20, 4.21 and 4.22, respectively. In all the three cases, unirradiated samples (zero h) gave a prominent peak of pyrene (parent compound) only.

In case of neutral soil, two metabolite peaks at m/z 219 and 100 were observed in addition to the molecular ion peak after 24 h. The metabolite at m/z 219 is due to 1-hydroxypyrene [20] or pyrene-4,5-epoxide [14] and the peak at m/z 100 could not be identified. After 48 h additional peaks at m/z 224 and 256 were observed which are assigned

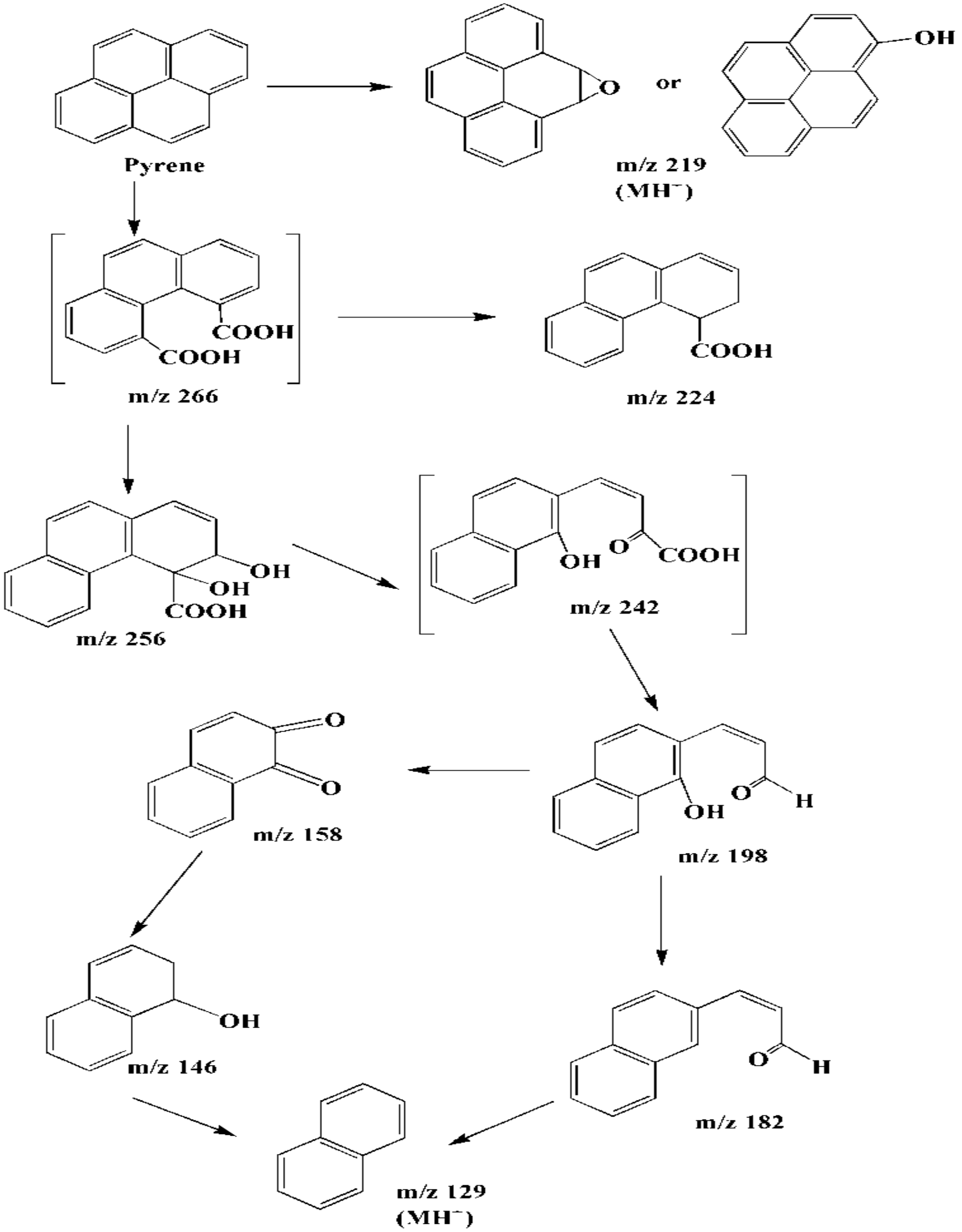


Fig. 4.20: Possible pathway for the degradation of pyrene in neutral soil. Structures in brackets are hypothetical intermediates.

to 3,4-dihydrophenanthrene-4-carboxylic acid and 3,4-dihydroxy-3,4-dihydrophenanthrene-4-carboxylic acid [9, 15]. After 72 h, peaks at m/z 224 and 256 disappeared and new peaks at m/z 105 and 198 appeared. The molecular ion peak at m/z 105 could not be identified and the peak at m/z 198 was assigned to 3-(1-hydroxy-2-naphthalenyl)-2- propenal [9]. After 96 h, the metabolite peaks were observed at m/z 105, 182 and 158. The metabolite peaks at m/z 182 and 158 have been assigned to 3-(2-naphthalenyl)-2-propenal and 1,2-naphthalenedione, respectively. After 120 h, peaks at m/z 146, 129 and 158 persist which are due to 1,2-dihydronaphthalene-1-ol, naphthalene and 1,2-naphthalenedione, respectively.

In basic soil, a metabolite peak at m/z 100 was observed in addition to the parent ion peak after 24 h. After 48 h, additional peaks at m/z 219 and 198 were observed. After 72 h, the metabolite peaks observed were at m/z 100, 105, 222, 219 and 158. The metabolite peaks at m/z 222 was assigned to phenenanthrene-4-carboxylic acid [9, 11, 14, 15]. Metabolite peaks at m/z 105, 182 and 158 were observed after 96 h. After 120 h, only the metabolites with m/z 100 and 146 were discernible.

In case of acidic soil, after 24 h, two metabolite peaks were observed at m/z 105 and 219, in addition to the parent ion peak. After 48 h, new metabolite peaks at m/z 248 and 220 appeared which were assigned to 2-hydroxypyrene-4,5-dione and 6-hydroxy-4H-cyclopenta[def]phenanthrene-4-one, respectively. After 72 h, the metabolites with m/z 219, 248 and 220 disappeared and new peaks at m/z 235, 225 and 206 appeared which were assigned to 4,5-dihydroxypyrene [9-11, 14, 15] , 3,4-dihydrophenanthrene-4-carboxylic acid and 4H-cyclopenta[def]phenanthrene-4-ol, respectively. After 96 h, the detected peaks were at m/z 100, 105, 182, 225 and 122. The metabolite peak at m/z 122 was assigned to benzoic acid. Only the metabolite peaks at m/z 100 and 182 were found persistent after 120 h.

Blank experiments for the photodegradation of pyrene in soil in the absence of catalyst were conducted for 0, 24, 48, 72, 96 and 120 h. A prominent peak due to pyrene was observed in all the samples and a few of the identified metabolite peaks (m/z 224, 182, 105 and 102) were detected till 120 h, which indicates that the degradation of pyrene is slow in the absence of the catalyst and may involve mechanism similar to the degradation occurring in presence of the catalyst. A typical total ion chromatogram and corresponding full scan mass spectrum of pyrene are shown in Fig. 4.23(a) and 4.23(b), respectively. On the basis of the observed metabolites, it can be concluded that the degradation of pyrene occurs through oxidative mechanism. The degradation products may also appear in the form of other possible isomers, in addition to the metabolites shown in the degradation pathways. In different soils, the nature and persistence of the degradation products are different due to dissimilar chemical environment.

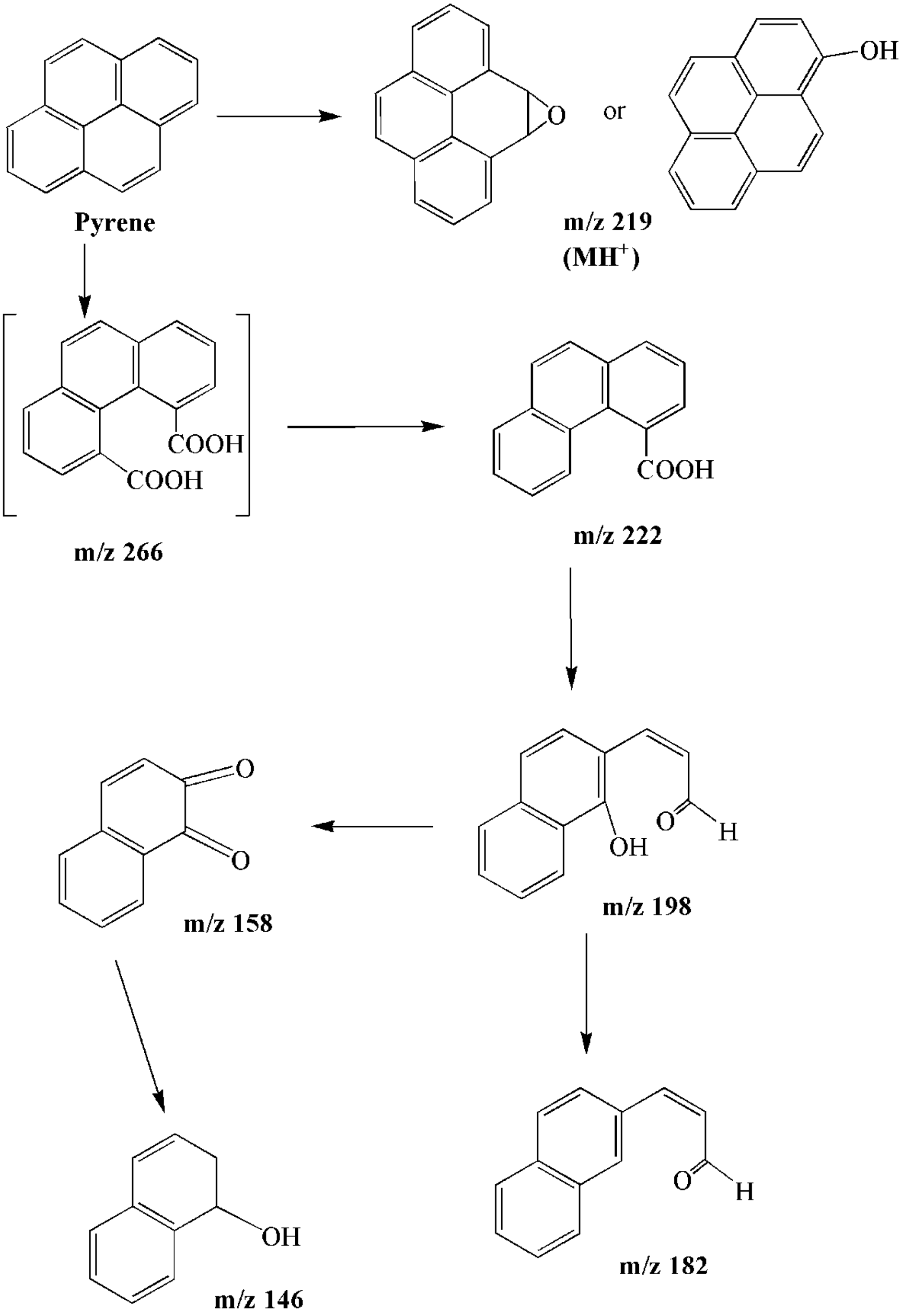


Fig. 4.21: Possible pathway for the degradation of pyrene in basic soil. Structures in brackets are hypothetical intermediates.

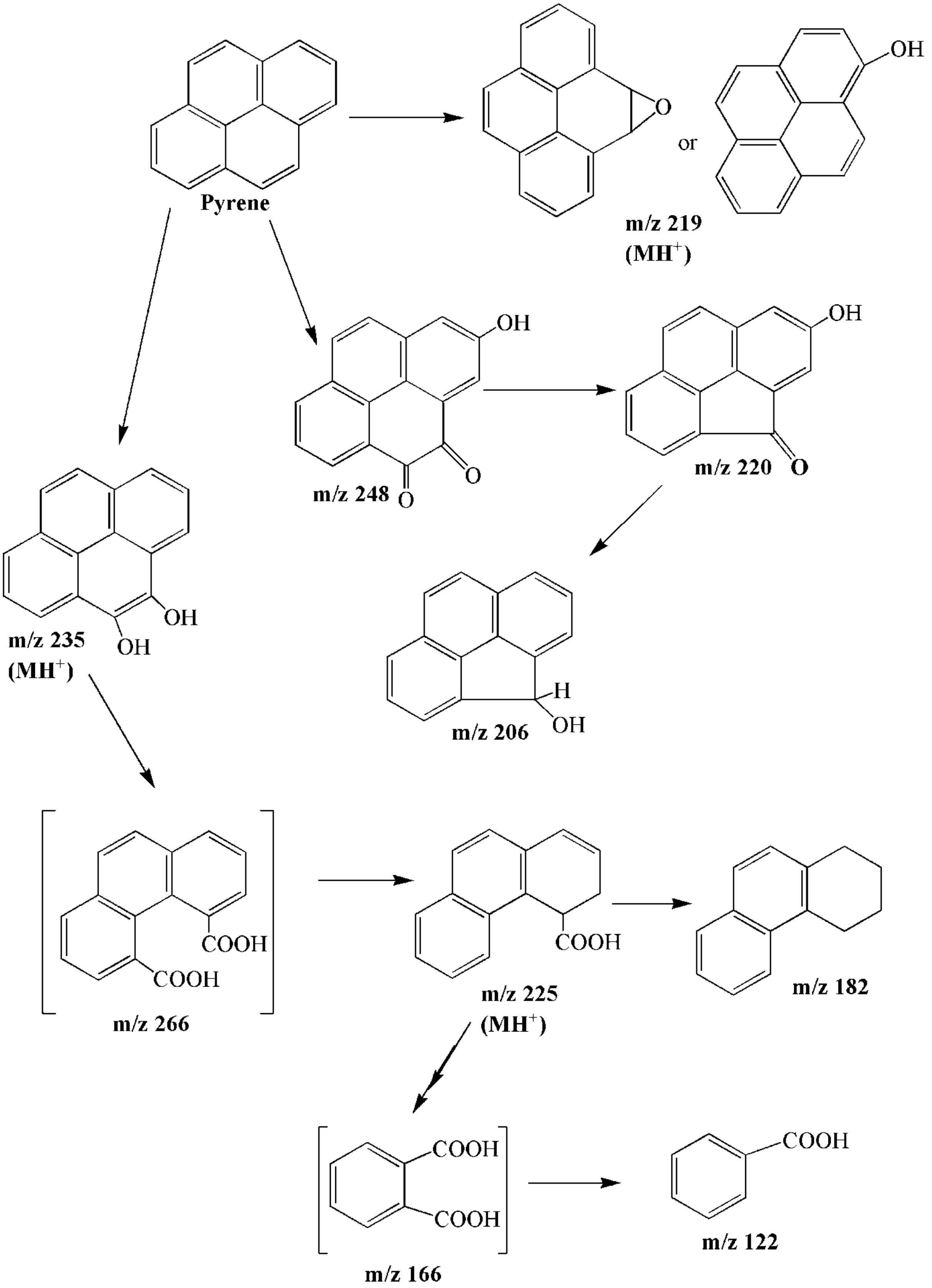


Fig. 4.22: Possible pathway for the degradation of pyrene in acidic soil. Structures in brackets are hypothetical intermediates.

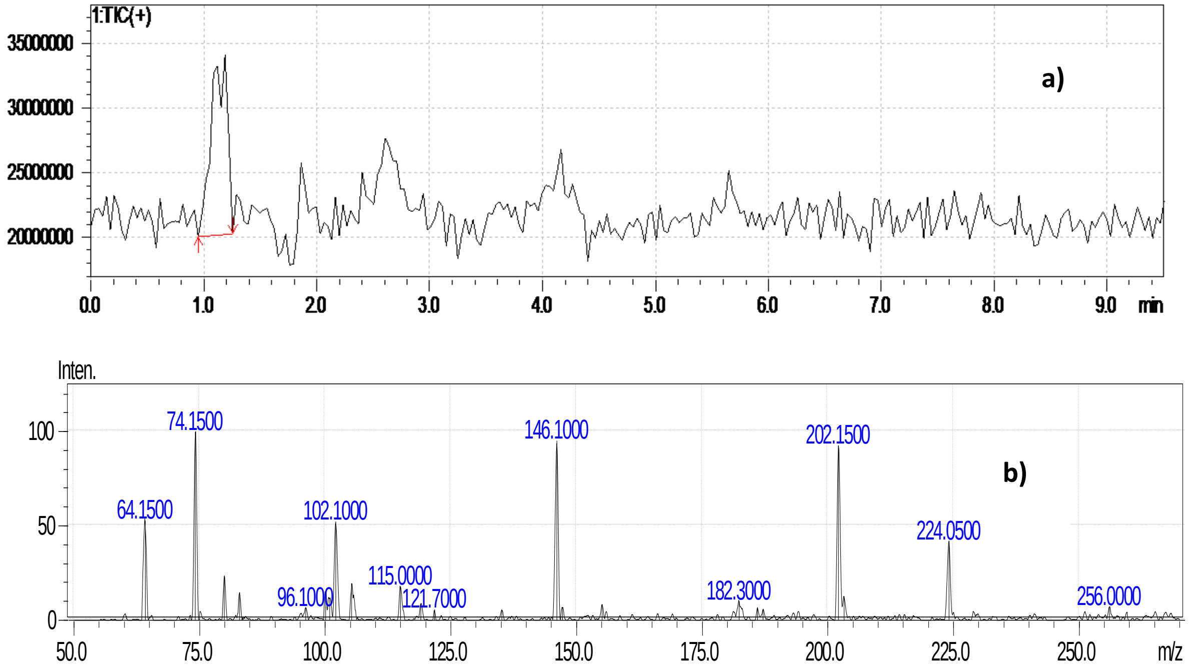


Fig. 4.23: Total ion chromatogram (a) and full scan mass spectrum (b) of metabolites of pyrene in soil (pH 6.8) after 48 h

In neutral and basic soils, the metabolites follow the similar pathway for the photodegradation of pyrene, while in acidic soil, a different metabolic pathway is followed. The metabolites were confirmed by selective ion monitoring (SIM) and product ion scan. The metabolite peaks were detected at $[M]^+$ or $[M + H]^+$. Several identified metabolites have been reported earlier under different experimental conditions [9-11, 14, 15, 20]. Metabolites with m/z 158, 146, 129 and m/z 100, 146 which correspond to naphthalene and its derivatives were found to be persistent in basic and neutral soil, respectively after 120 h. In case of acidic soil, metabolites with m/z 100 and 182 (hydrogenated phenanthrene) were persistent after 120 h. The degradation pathways indicated that the mutagen pyrene is degraded efficiently in presence of goethite into smaller non-carcinogenic/non-mutagenic hydrocarbons, naphthalene, phenanthrene and their derivatives after 120 h.

The content of this chapter have been published in the form of two research papers in the journals “**Chemosphere**” and “**International Journal of Environment Science and Development**”.

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INTRODUCTION

Water is an essential environmental resource, which is necessary for life on the planet, Earth. Besides sustaining life, water is required for irrigation, personal hygiene, bathing, washing of clothes etc. Almost, 70% of the earth is covered with water, but only approximately 2.5 % of the total water content is freshwater. From the freshwater content, more than 68% is present in glaciers and ice caps, 30% is present as ground water and only 0.3% is present in the form of surface water such as lakes, rivers etc. Moreover, rapid industrialization has resulted in utilization of a large amount of freshwater and generation of huge quantities of wastewater. Due to indiscrete discharge of pollutants, the water bodies are suffering irreversible damage and it is feared that in near future the water may not even remain appropriate for bathing, washing clothes and agricultural purposes. The unwanted release of pollutants can be counteracted, by the proper treatment of effluents in the treatment plants. Environmental awareness and concern has grown in the developing as well as the developed countries. In the developing country, like India, conservation of water has become a cause of concern due to lack of availability of freshwater in various parts of India. As a result of this, the need of removal of various pollutants from water has assumed paramount importance. Major sources of PAHs in the environment are atmospheric fallouts, oil spills, petroleum industry, coking plants, paper industry, municipal wastewater treatment plants etc. The petroleum industry releases large amounts of effluents containing PAHs produced during the refining of the crude oils, [1,2]. Chalbot et al. [3] reported the use of excessive chemicals, heat and pressure during paper production as a source of PAHs. The presence of PAHs in the municipal wastewaters [4, 5] and sewage sludge [6] has been reported by various authors. Production of coke is another major source of PAHs in surface waters [7, 8]. The treated coke industry wastewater containing PAHs is released in to the water systems or used for coke quenching. Coke quenching leads to PAHs release in the atmospheric air. In view of this, development of suitable methods for the removal of PAHs from surface waters as well as industrial wastewaters is required.

In a treatment plant, the wastewater is treated in three steps, primary, secondary and tertiary treatment. In primary treatment, preliminary purification of water is carried out using screening, grinding, filtration, coagulation, flotation, grit removal and sedimentation. The secondary treatment process involves biological treatment of wastewater through microbes (bacterial and fungal strains), which convert the organic content to water, carbon dioxide, methane and ammonia. Limitation of secondary treatment is the generation of large amounts of biosolids which require further management involving high cost. Tertiary treatment process converts the treated wastewater of secondary step to the recycled water which can be used for industrial or drinking purposes [9]. The techniques involved in the tertiary treatment are crystallization, solvent extraction, ion-exchange [10], distillation [11], sonolysis [12], chemical oxidation involving chlorine [13], hydrogen peroxide, ozone [14, 15] or Fenton's reagent [16, 17], photocatalysis using iron oxide [18], titanium oxide [19] or zinc oxide [20], microfiltration, ultafiltration [21], electrolysis [22] and adsorption [23]. Based on the type of pollutants a number of treatment methods are adopted in series to ensure removal of all the pollutants. Inspite of availability of several technologies, any satisfactory solution for the remediation of wastewaters is still not achieved. Moreover, their applications are limited by many factors, such as operational method, energy requirements, processing efficiency and economic benefit. Different physical, chemical or biological methods have been used for the wastewater treatment process, but these are limited to a certain extent. Physiochemical methods such as chemical precipitation, coagulation, flocculation, membrane filtration, reverse osmosis, ion exchange and electrodialysis have limitations such as high costs, less efficiency, energy requirement or limited versatility [24]. Biological treatment methods are limited to low removal yields. For selecting a proper treatment process different aspects such as cost, eco-friendly nature, versatility and recycling ability are considered. For this purpose, adsorption is considered more suitable due to its simplicity, convenience, easy operation and universality in use. Furthermore, adsorption can minimize a large variety of pollutants and thus has a wide applicability in environmental pollution control.

The phenomenon of adsorption is known from ancient times. However, in 1773 C. W. Scheele and in 1777 A. F. Fontana observed the adsorption of gases on charcoal. In 1785, Lowitz discovered the effective removal of organic colouring matter using charcoal [25]. E. du Bois-Reymond proposed the term adsorption and H. Kayser introduced it to the literature [26]. Since then the process of adsorption has gained acceptance for the removal of various pollutants from aqueous media and a variety of adsorbents have been introduced by various research groups. The important characteristics of a good adsorbent are porous structure, high surface area, short equilibration time, large adsorption capacity, easy recycling ability and low cost. Out of several adsorbents, silica gel, activated alumina, zeolites and ion-exchange resins have been widely explored, but their use is limited due to high cost. Inspite of a large variety of adsorbents available, activated carbon is most acceptable and widely used adsorbent due to its applicability for the removal of broad range of pollutants, high adsorption capacity and less equilibration time. In 1913, activated carbon was produced commercially for the first time [27]. Since then activated carbon has become a standard adsorbent for the removal of different kinds of pollutants. According to Bailey et al., “a sorbent is considered a low cost adsorbent if it is abundant, by product or waste product of any other industry and requires a little processing” [28]. Different types of agricultural, industrial and municipal wastes have been used as low cost adsorbents in their natural form or after physical or chemical modifications for the removal of various pollutants. Agricultural wastes include peanuts hull [29, 30], groundnuts shell [31], coconut husk [32], rice straw [33], maize tassels [34], corn wastes [35], wheat straw [36], sugarcane bagasse [37], coir pith [38], vegetable waste [39], plant bark [40], plant material [41, 42] and banana peel [43] etc. Industrial wastes include fly ash [44], bottom ash [45, 46], red mud [47], carbon slurry [48], industrial sludge [49], leather industry wastes [50], paper industry wastes [51] and battery industry waste [52]. Natural biosorbents such as peat [53], chitin [54], chitosan [55], hen feathers [56, 57], yeast [58], fungi [59], bacteria [60] and organic polymers [61-65] have also been explored for the removal of pollutants from water and wastewater systems. Survey of the literature reveals that a variety of substances have been used for the removal of PAHs from different media. As the amount of literature available is enormous and it is not possible to include all the reports in the present study. Therefore, literature review for adsorptive removal of PAHs from water has been confined to last 10 years.

Adsorption of naphthalene on zeolite from aqueous systems was assessed by Chang et al., [66]. Different kinetic models were applied and the results suggested the applicability of pseudo-second order rate equation for adsorption of naphthalene on zeolite. The equilibration time was greater than 200 min. Boving and Zhang [67] investigated the adsorption of aqueous phase PAHs (naphthalene, fluorene, anthracene and pyrene) on aspen wood fibres. The results suggested the adsorption process as linear, whereas, desorption as non-linear. The adsorption efficiency increased with the increase in hydrophobic character and molecular weight of the PAH. The use of aspen wood fibres have the limitation of very long equilibration time (upto 12.5 d).

Jung et al. [68] studied the adsorption of aqueous aromatic hydrocarbons using fibrous adsorbent (p-phenylene-2,6-benzobisoxazole (PBO). The adsorption efficiency for

PAHs and di-(2-ethyl hexyl)phthalate (DEHP) were 72.5-99 % and 95%, respectively. The desorption of DEHP was achieved using methanol, whereas, effective desorption of PAHs did not occur with organic solvents. Khan et al. [69] reported the adsorption of PAHs from water using natural fiber (kapok and cattail fiber) and a polyester fiber. Polyester fibre showed poor adsorption of naphthalene, whereas, Cattail fibre showed high adsorption for all the studied PAHs. Kapok fiber showed lowest PAH adsorption capacity among the three fibres. Valderrama and others [70] investigated PAH adsorption kinetics onto granular activated carbon (GAC) and Macronet hyper-cross-linked polymers (MN200). The adsorption was described by pseudo-first order and pseudo-second order kinetics. The result suggested that the adsorption of PAHs was more complex for GAC than MN200.

Karapanagioti [71] studied phenanthrene adsorption on activated carbon from saltwater solutions and demonstrated the effect of salinity on the adsorption of organic compound. It was observed that at low phenanthrene concentration, the removal of phenanthrene is more efficient from freshwater than the salt water but reverse is true at high phenanthrene concentration. Zeledon-Toruno and coworkers [72] studied the removal of PAHs from aqueous media through an immature coal (leonardite). The effects of various experimental parameters were investigated and the results suggested higher adsorption of fluorene at low pH values. The data fitted well to Freundlich adsorption isotherm. It was further observed that the polarity of humic substances present in leonardite may influence the adsorption capacity.

Ania et al. [73] investigated the role of porous and chemical heterogeneities of activated carbons in the adsorption of naphthalene. The results suggested that adsorption of naphthalene depended on pore size and adsorbents with high non-polar character (low oxygen content) were found more efficient for naphthalene adsorption. Same group of researchers [74] carried out study to correlate the textural and chemical features of carbonaceous adsorbents with adsorption capacity of naphthalene. The results suggested that the adsorption capacity of activated carbons depended on both, textural characteristics as well as functional groups. Ania et al. [75] again in 2008 studied adsorption of naphthalene on activated carbon from solvents of different polarity. The results revealed higher uptake of naphthalene from aqueous medium than organic media (heptane and cyclohexane) due to higher solubility of naphthalene in organic media.

Crisafully and associates [76] investigated the removal of PAHs from petrochemical wastewater through naturally occurring low cost adsorbents. The PAHs uptake capacity was in the order green coconut shell > sugarcane bagasse > chitin > chitosan. Adsorption properties of green coconut shells were comparable with that of Amberlite T. The commercial application of the studied adsorbents is limited due to low adsorption capacities. Gok et al. [77] reported naphthalene adsorption from aqueous media on a natural clay mineral organo-sepiolite. The natural sepiolite was modified by dodecyltrimethylammonium (DTMA) bromide. The effect of various experimental factors adsorbent dose, contact time, temperature and pH were investigated. The adsorption of naphthalene on DTMA-sepiolite increased with the increase in temperature, which suggested endothermic nature of the adsorption process.

Adsorption of acenaphthene from water using silica gel as an adsorbent has been described by Hall et al. [78]. Both Langmuir and Freundlich models fitted well with the equilibrium data. The pseudo-first order model described the adsorption kinetics. The mechanism of adsorption was controlled by intra-particle adsorption model. The adsorption capacity of silica gel for acenaphthene was found to be low. Cabal et al. [79] prepared activated carbons from bean pods through chemical and physical activation and observed that activated carbon obtained after chemical activation was more porous than the physically activated carbon. The study reveals that the adsorption process requires long equilibration time (72 h). Anbia and Moradi [80] synthesized ordered mesoporous carbon (OMC) using ordered mesoporous silica (MCM-48) and employed for the removal of naphthalene from petrochemical wastewater. The uptake of naphthalene on OMC, MCM-48 and commercial activated carbon was in the following order: OMC > commercial activated carbon > MCM-48. The equilibration time for the adsorption of naphthalene was observed to be 4 h.

Adsorption efficiency of fly ash obtained from power plant was investigated for the removal of PAH from water by Sasithorn et al. [81]. Naphthalene was treated as representative PAH. Coal fly ash, rice husk fly ash and silica from rice husk fly ash were utilized for adsorption of PAH for decontamination of water. Adsorbent surface was modified using surface treating agent, Cethyltrimethylammoniumbromide (CTAB). The work demonstrated that removal of PAHs can be achieved using all types of fly ash, with or without surface treatment. Adsorption of naphthalene was studied under diverse conditions of contact time, shaking speed, pH and adsorbent dose. Fastest PAH adsorption was achieved with silica modified with CTAB.

Yaun and associates [82] used porous carbon prepared from petroleum coke for the adsorption of PAHs from aqueous medium. The adsorption capacity followed the order: naphthalene > fluorene > phenanthrene > pyrene. The equilibration time was long (18 h). Sener and Ozyilmaz [83] investigated the use of sonicated talc for the adsorption of naphthalene from water. The results indicated that the adsorption of naphthalene was not influenced by the change in pH indicating that the main driving force for the adsorption of naphthalene was hydrophobic binding rather than electrostatic force.

Owabor and Audu [84] employed ripe orange peels as adsorbent for the removal of naphthalene and pyrene from water. The results indicated higher adsorption of naphthalene than pyrene on ripe orange peel. Freundlich isotherm model better fitted with the equilibrium data than the Langmuir model. Maximum adsorption of naphthalene and pyrene was achieved with 5-7 g and 6-8 g of the adsorbent, respectively. Mesoporous silica after modification was used for the adsorption of PAHs from aqueous media by Vidal et al. [85]. Pseudo-first order kinetic model was best fitted to naphthalene adsorption, whereas, pseudo-second order kinetic model to Acenaphthene, fluorene, fluoranthene and pyrene adsorption.

Lightweight expanded clay aggregates (LECA) have also been explored for the removal of PAHs from water [86]. The data obtained was fitted to linear, Langmuir and Freundlich models to determine water-LECA partition coefficients. The adsorption of studied PAHs was in the order pyrene > fluorene > phenanthrene. Owabor et al. [87] reported the use of unripe orange peels for the adsorption of naphthalene from aqueous medium and studied the effect of various operating variable on the adsorption. The adsorption efficiency increased with the increase in contact time, adsorbent dose, initial concentration, but decreased with the increase in particle size of the adsorbent. Alade and co-workers [88] employed flamboyant pod (FB) and milk bush kernel shell (MB) to obtain activated carbon for the removal of naphthalene from simulated wastewater. Activated carbons were obtained at different carbonisation temperature in the range 300-600 °C. The removal efficiency of the activated carbon obtained from FB was higher than the activated carbon obtained from MB. The adsorption of naphthalene on MB and FB was described by Langmuir and Freundlich adsorption isotherms. Zhang and others [89] reported adsorption and desorption of phenanthrene on coconut shell activated carbon. The effect of contact time and type of solvent was investigated on phenanthrene desorption, with or without ultrasonic treatment. The results suggested that maximum desorption was observed with ethanol as a solvent with ultrasonic treatment. The maximum adsorption capacity was 20.22 mg/g, which is quiet low for an efficient adsorption process.

Abu-Elella et al. [90] studied the adsorption of naphthalene from industrial wastewater on synthesized boehmite nanopowder. The effect of various factors such as initial concentration, operating time, pH and amount of adsorbent on the adsorption of naphthalene was investigated. The data was analysed by Langmuir, Freundlich and Redlich-Peterson models and found to be best fitted with Freundlich model. The negative values of free energy and enthalpy indicated that the adsorption of naphthalene on boehmite nanopowder is spontaneous and exothermic. Shi and others [91] prepared high surface area carbon by KOH activation of waste polystyrene based ion exchange resins. The adsorption of naphthalene was slightly affected by the variation in pH. The equilibrium time for the adsorption process was 5 h. The spent carbon was regenerated through alcohol treatment. Adsorption of naphthalene and toluene on commercial activated carbon in single and binary systems was investigated by Iovino et al. [92]. The study revealed that adsorption of toluene was higher than naphthalene in both, single and binary systems. Saad et al. [93] studied the adsorption of anthracene on commercial activated carbon and on *Posidonia Oceania* balls. The effect of contact time and pH on the adsorption of anthracene was examined. The results indicated that in both the cases anthracene adsorption was unaffected in the pH range 2-12 and the data fitted well to Langmuir adsorption isotherm. The adsorption capacities of both the adsorbents were low (8.35 and 0.14 mg/g for commercial activated carbon and Posidonia oceania, respectively).

The adsorption of PAHs (naphthalene, phenanthrene and pyrene) from water using activated carbon prepared from rice husk was assessed by Yakout and associates [94]. The adsorption of PAHs followed the order: naphthalene < phenanthrene < pyrene. Freundlich, Redlich-Peterson and Langmuir adsorption isotherms were best fitted for naphthalene, phenanthrene and pyrene, respectively. Canzano et al. [95] investigated the adsorption of some aromatic compounds (naphthalene, toluene, ethylbenzene and o-xylene) from groundwater using commercial activated carbon. It was observed that adsorption capacities for toluene and naphthalene were higher and comparable. The study revealed a longer equilibration time for the adsorption of all the aromatic compounds. Smol et al. [96] reported the adsorption of PAHs on different sorbents (quartz sand, mineral sorbent and activated carbon). The highest adsorption efficiency (>98%) was achieved with activated carbon. The adsorption of individual hydrocarbons on activated carbon was in the range 94.7-100 %. Adsorption of four heavy metals, namely, lead, zinc, copper and zinc as well as two PAHs, namely, phenanthrene and pyrene was investigated on rectorite based composite adsorbent by Tang et al. [97]. The adsorption capacities were in the order: $Pb^{2+} > Cd^{2+} > Zn^{2+} > Cu^{2+}$ > phenanthrene > pyrene. The mechanism of adsorption for heavy metal ions was complexation or ion exchange, whereas, for PAHs, the mechanism was partition. The adsorption capacity for phenanthrene and pyrene were only 18.45 and 3.3 mg g^{-1}, respectively.

Li and associates [98] reported the adsorption of phenanthrene from water using different types of zeolites modified by different amounts of surfactant, cetylpyridinium bromide. The results indicated that monolayer and bilayer modified zeolites were effective for the adsorption of phenanthrene. The equilibrium data followed linear and Freundlich adsorption models and pseudo second order kinetic model. Adsorption of phenanthrene on surfactant modified zeolites was exothermic and spontaneous. Rasheed and associates [99] used powdered activated carbon (PAC) for the adsorption of anthracene and pyrene. The results indicated that adsorption of pyrene was slower than anthracene. Pseudo-first order and intra-particle diffusion model fitted well for the adsorption of PAHs on activated carbon. Ge et al. [100] modified coal based $_{\text{activated}}$ carbon with microwave induction and used for the adsorption of naphthalene from aqueous systems. The adsorption of naphthalene was exothermic and spontaneous. Modified activated carbon had high adsorption capacity than the unmodified activated carbon.

Torabian and others [101] synthesized magnetic nanoparticles (NPs) and modified with 3-Mercaptopropytrimethoxysiline and the material was grafted using allyl glycidyl ether, so as to couple with beta naphthol. The nano-adsorbent prepared was employed for the removal of PAHs from contaminated water. The results revealed that the modification of magnetic NPs enhances the adsorption process. The equilibration time for the adsorption of PAHs on grafted magnetic NPs was 10 min and the maximum adsorption capacity was 4.15 mg/g, which is quiet low.

The literature cited above clearly indicates that different types of waste materials, before or after activation have been explored as adsorbents for the removal of PAHs. But many of these adsorbents suffer from limitations such as longer equilibration time or low adsorption capacity or the starting materials are costly or are not readily regenerated. So, the studies are continuously being focussed to develop novel, highly effective activated carbons from low cost raw materials. One of the low cost and highly abundant waste materials is banana peel. Banana peels have a number of useful applications such as livestock feed, fertilizer and compost preparation, cosmetics, wart and dental remedies. In spite of the usefulness of banana peels a huge number of banana peels are wasted every year. In U. S., 780 million pounds of banana peels are sent to the landfill every year [102]. In Thialand, 200 tons of the banana peels were thrown away everyday in 2006 and the number is continuously increasing every year [103]. India, the largest producer of banana, contributes about 27% of the total production of banana in the world [104] and hence the largest producer of banana peel waste. In view of this, banana peel has been selected as a low cost and highly abundant raw material for the preparation of activated carbon for the removal of PAHs from aqueous systems. The advantages of converting banana peel into activated carbon are, increased surface area and porosity. The synthesized activated carbon has been used for the removal of naphthalene (Naph), fluorene (Flu) and phenanthrene (Phen) from aqueous system. The three PAHs with less than four rings were chosen for the study due to their high availability in different water and wastewater systems. The adsorption data was subjected to Freundlich and Langmuir isotherms. The effect of various parameters such as contact time, adsorbent dose, pH and temperature on the adsorption was evaluated. Different thermodynamic parameters were calculated to ascertain the nature and spontaneity of the adsorption. The main objective of the work is to develop an efficient activated carbon from highly available waste which can be used for the treatment of different industrial effluents such as petroleum and coke industry wastewater. The resulting data will also serves as a base for the removal of other PAHs/pollutants.

5.1 EXPERIMENTAL

The details of synthesis and characterization of banana peel activated carbon (BPAC) and adsorption studies are discussed in chapter II.

5.2 RESULT AND DISCUSSION

5.2.1 Characteristics of adsorbent

XRD spectrum of the adsorbent BPAC is shown in Fig. 5.1. Two broad peaks around 24° and 42° in the spectrum show the formation of amorphous activated carbon [105]. The specific surface area of the adsorbent BPAC assessed using Micrometics instrument was 984.51 m^2/g.

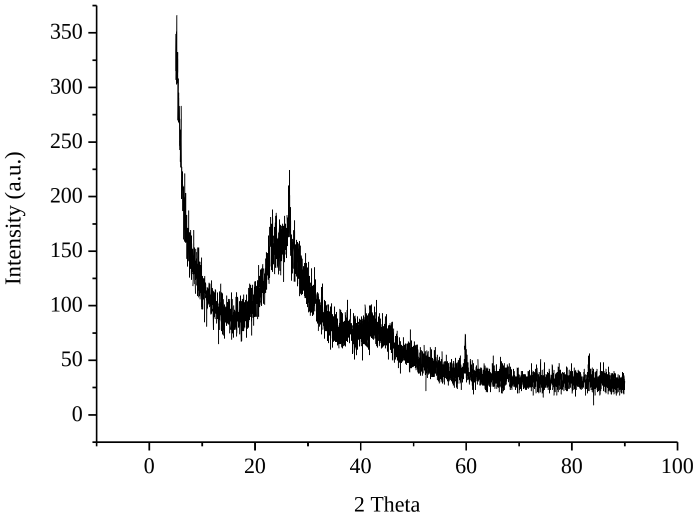

Fig. 5.1: XRD Spectrum of banana peel activated carbon

FE-SEM images of banana peel activated carbon depicting the surface morphology of the activated carbon, before and after adsorption of PAHs are shown in Fig. 5.2, 5.3, 5.4 and 5.5. FE-SEM image of BPAC before adsorption shows porous surface, whereas, after adsorption of PAHs smooth surfaces with agglomeration were observed. The dissimilar surface after adsorption may be due to the adsorption of PAHs in the pores of the adsorbent.

FT-IR spectra of BPAC before and after adsorption of PAHs are shown in Fig. 5.6. In FT-IR spectrum of the adsorbent major bands appeared at the peak positions 3413, 1599, 1387, 1212 and 1072 cm^{-1}. The peak at 3413 cm^{-1} is due to –OH group stretching and the band at 1599 cm^{-1} is due to C=C stretching vibration. The peaks at 1387 and 1212 cm^{-1} are due to P=O stretch or O-H bending vibration and P-O-C stretch, respectively. The presence of oxy-phosphorus groups on BPAC is due to the use of phosphoric acid in the preparation of BPAC. The peak at 1072 cm^{-1} is attributed to the phosphate group stretching. The FT-IR spectrum of BPAC clearly indicates that the major groups on the surface of BPAC are P=O and –OH groups. FT-IR spectra of BPAC obtained after adsorption of PAHs clearly indicate shifting of peaks and appearance of some new peaks after adsorption of naphthalene, fluorene and phenanthrene on the adsorbent. A new peak in the range 958-946 cm^{-1} after adsorption is due to the attachment of aromatic ring with P-O group. The peaks due to P=O, –OH, and PO_4^{3-} groups are shifted on adsorption of all the three PAHs. Additional peaks around 1500 cm^{-1} are due to aromatic ring stretch. Several new peaks in the reason 900-700 cm^{-1} are due to out of plane bending vibration of aromatic C-H which confirms the adsorption of aromatic compounds on BPAC in all the

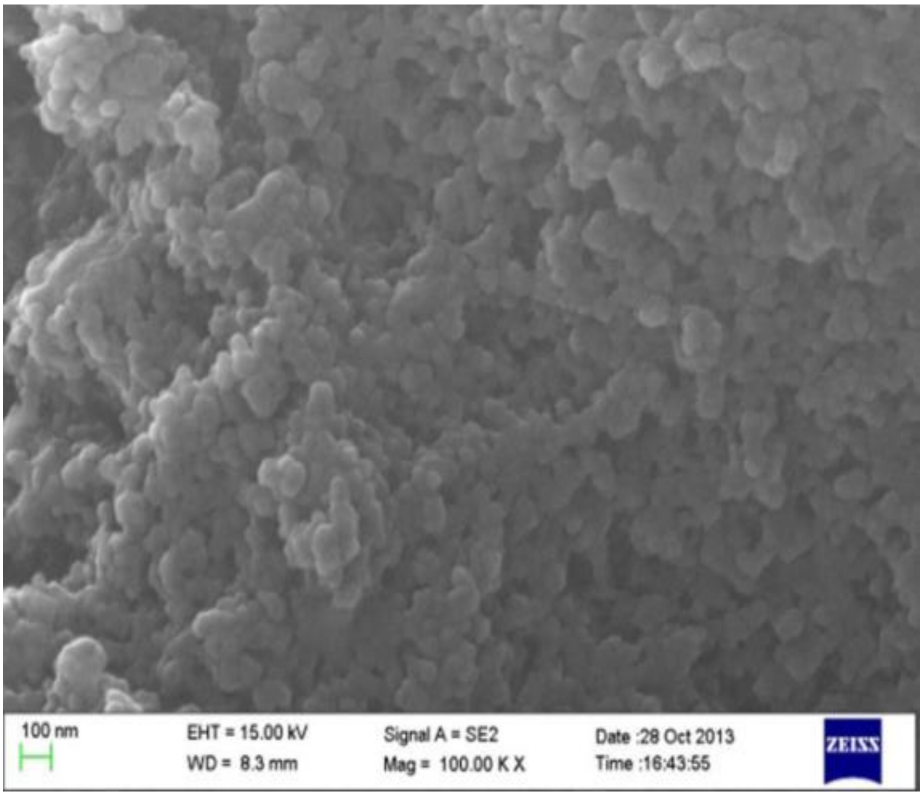

Fig. 5.2: FE-SEM image of activated carbon before adsorption of PAH

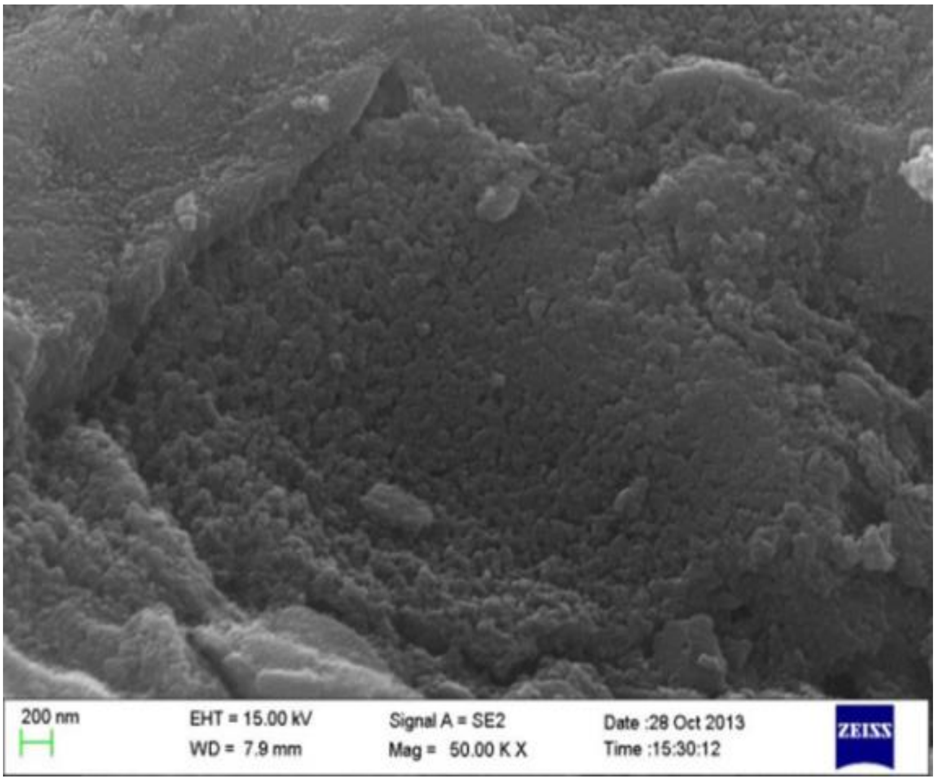

Fig. 5.3: FE-SEM image of activated carbon after adsorption of naphthalene

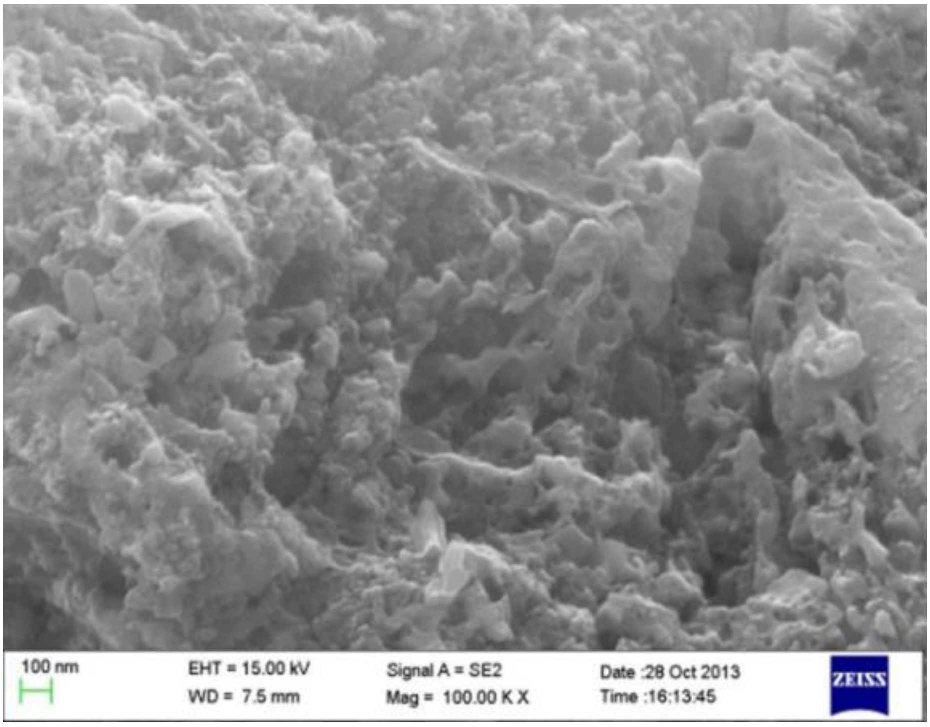

Fig. 5.4: FE-SEM image of activated carbon after adsorption of fluorene

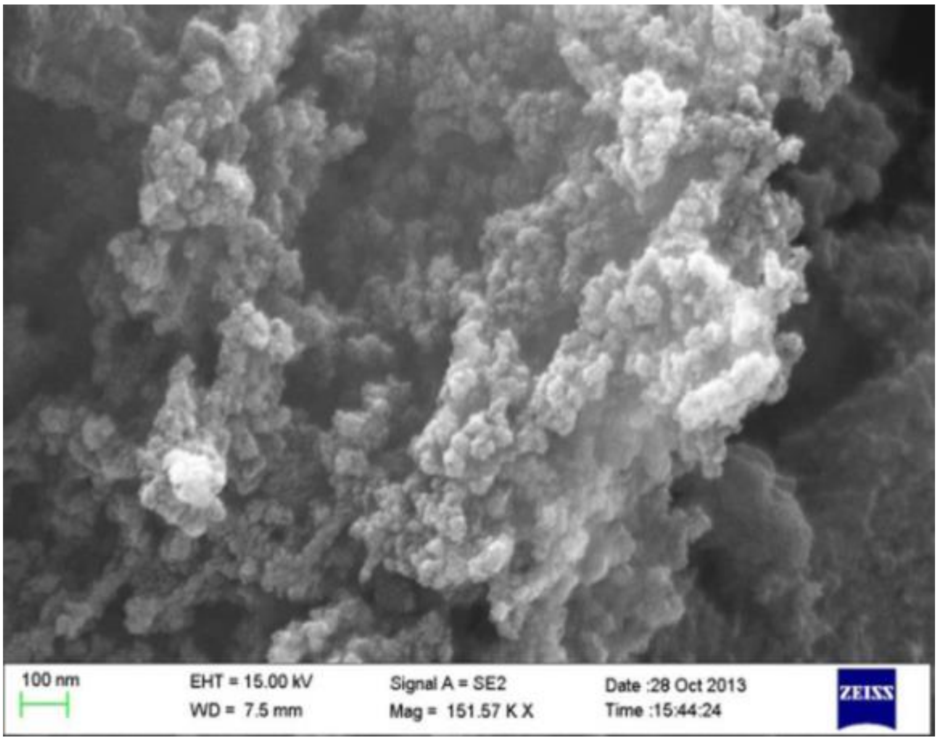

Fig. 5.5: FE-SEM image of activated carbon after adsorption of naphthalene

cases. The additional peaks at 2916, 1442 and 1301 cm^{-1} in case of fluorene adsorption are due to stretching and bending C-H vibration of methylene group and stretching of C-C single bond, respectively. The assignments of IR peaks before and after adsorption of PAHs on BPAC are given in Table 5.1.

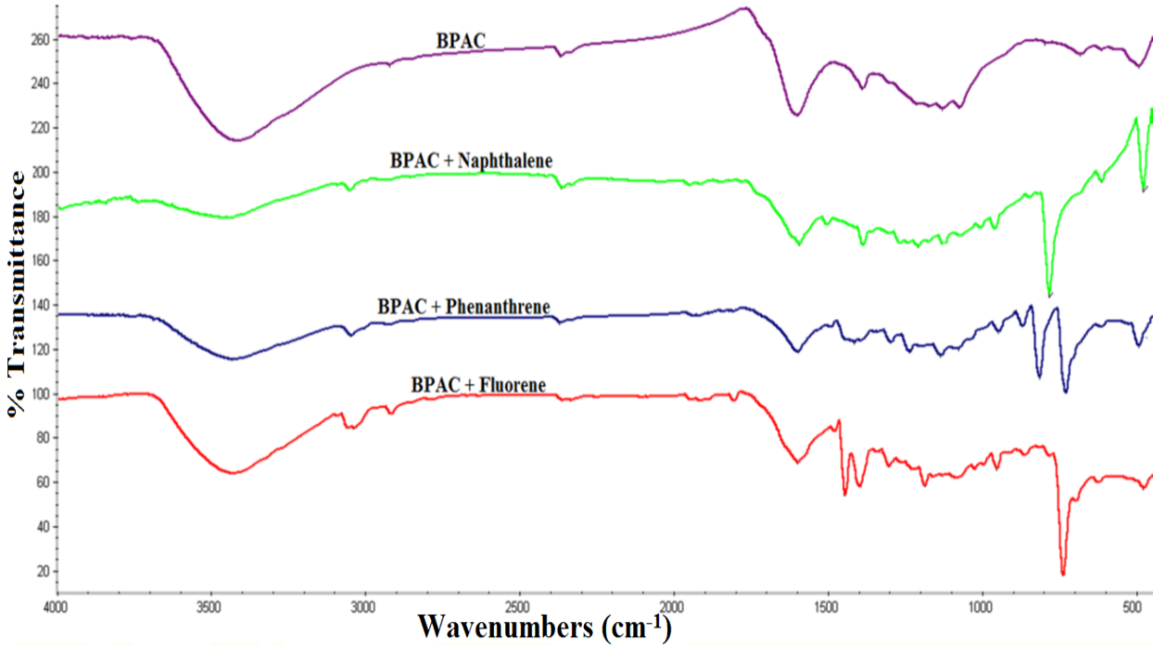

Fig. 5.6: FT-IR spectra of BPAC, before and after adsorption of PAHs

Table 5.1: IR frequencies of BPAC and BPAC + PAH (cm^{-1})

BPAC	BPAC + Naph	BPAC + Flu	BPAC + Phen	Assignments
3413	3439	3431	3432	U (O-H)
	3055	3036	3046	U(Aromatic C-H)
		2916		U (C-H)
1599	1592	1597	1595	U (C=C-C)
	1500	1474	1486	U (C=C-C)
		1442		δ (C-H)
1387	1385	1396		U(P=O)/δ (O-H)
		1301		U (C-C)
1212	1207	1184	1234	U(P-O-C)
1072	1065	1082	1074	U (PO_4^{3-})
	958	951	946	U (P-O-C)
	850	865	867	γ (C-H)
			813	γ (C-H)
	781	735	726	γ (C-H)

U = stretching; δ = bending; β = in plane bending; γ = out of plane bending

5.2.2 Effect of contact time

To study the effect of contact time on the adsorption of naphthalene, fluorene and phenanthrene on BPAC, a solution of individual PAH containing adsorbent was shaken mechanically for varying time (15-120 min). For all the three PAHs, adsorption increases upto 60 min and becomes constant thereafter (Fig. 5.7). For all subsequent studies a shaking time of 80 min was observed. It was checked that prolonged shaking had no adverse effect on the adsorption. The results suggest that the adsorption of naphthalene is slightly lower compared to fluorene and phenanthrene. This may be due to the most hydrophilic nature of naphthalene among the studied PAHs (log K_{ow} values: Naph – 3.30, Flu – 4.18, Phen – 4.57). Yakout et al. [94] also found higher adsorption of phenanthrene than naphthalene on activated carbon derived from agricultural wastes. Data further reveal that fluorene inspite of having low K_{ow} than phenanthrene shows slightly higher adsorption than phenanthrene. This observation may be attributed to the smaller diameter of fluorene than phenanthrene (Flu – 1.14 nm, Phen – 1.17 nm, [82]). The absence of any particular trend in the adsorption of the studied PAHs is probably due to fact that various factors such as hydrophobic character, solubility, molecular size, chemical properties of adsorbate and nature of adsorbent influence the adsorption process [95].

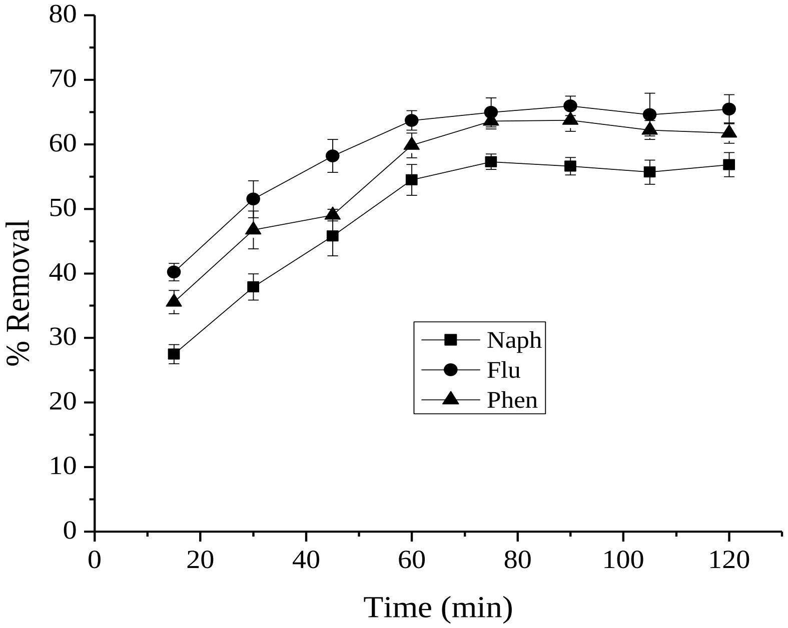

Fig. 5.7: Effect of contact time on adsorption of PAHs
[PAH] = 20 mg/L; pH = 7; adsorbent = 2 mg; temperature = 25±2°C

5.2.3 Effect of adsorbent dose

Figure 5.8 shows the results of adsorption study carried out with varying amounts of BPAC (0.5-10 mg). The results reveal that adsorption of PAHs increases with the increase in adsorbent dose initially and attains a quantitative value (>98 %) at 8 mg for fluorene and phenanthrene and 10 mg for naphthalene.

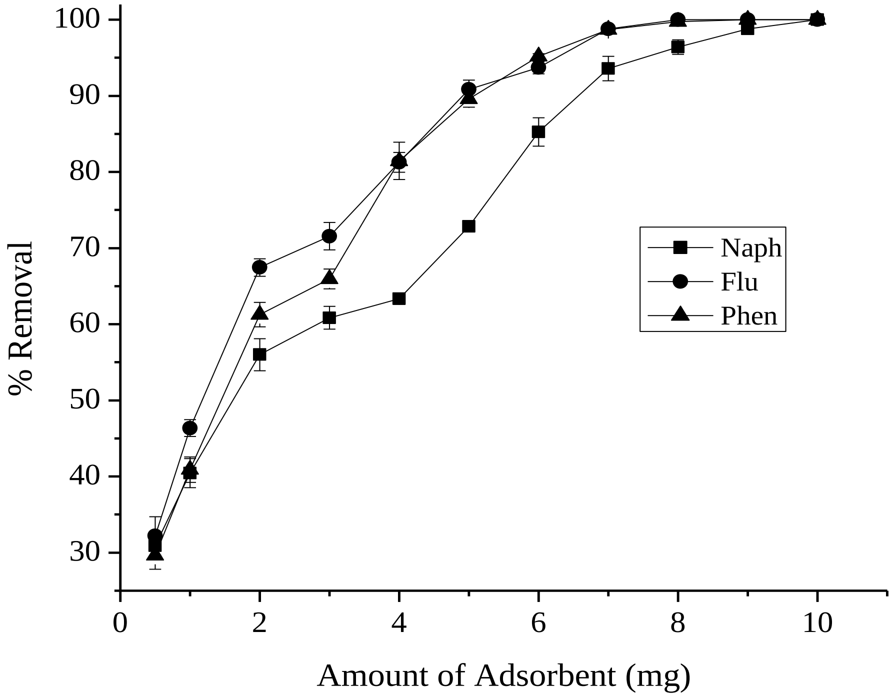

Fig. 5.8: Effect of adsorbent dose on adsorption of PAHs
[PAH] = 20 mg/L; pH = 7; shaking time = 80 min; temperature = 25±2°C

5.2.4 Effect of pH

The influence of pH on the adsorption of PAHs on BPAC was investigated in the pH range 2–12. The results are shown in Fig. 5.9 which indicate that the adsorption of all the three PAHs decrease with the increase in pH. The results further suggest that the adsorption of PAHs is higher at low pH due to the presence of positive charge on the surface of the adsorbent. Thus, at low pH, electrostatic attractions are higher between the positively charged adsorbent surface and PAH, accounting for higher adsorption. As the pH increases, the adsorption of PAHs decreases due to decrease in positive charge on the surface, followed by decrease in electrostatic attraction between the adsorbate and adsorbent. At higher pH, the competition between OH^- ions and PAH for adsorption sites may also lead to lower adsorption. Similar behaviour was observed by Owabor et al. [87] during removal of naphthalene using unripe orange peel.

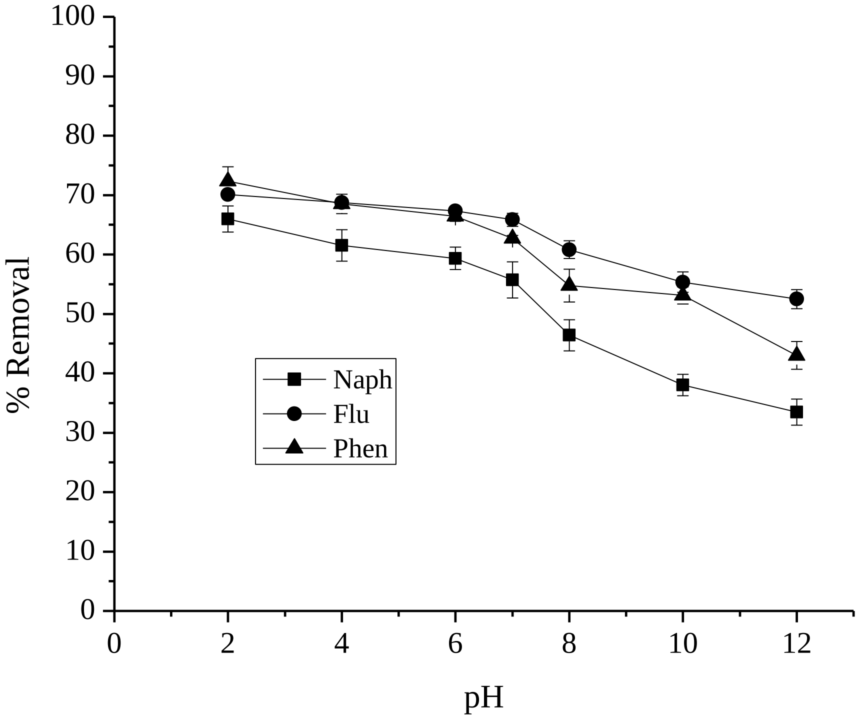

Fig. 5.9: Effect of pH on the adsorption of PAHs onto BPAC
[PAH] = 20 mg/L; adsorbent = 2 mg; shaking time = 80 min; temperature = 25±2°C

5.2.5 Effect of temperature

To discern the effect of temperature on the adsorption of PAHs, studies were carried out at 20, 30, 40 and 50 °C. The results indicate that adsorption of all the three PAHs increase with rise in temperature (Fig. 5.10, 5.11 and 5.12). The trend suggests that adsorption of PAHs on banana peel activated carbon is endothermic in nature. Endothermic adsorption of basic dyes and tartarazine on activated carbon was observed by Baseri et al. [40] and Mittal et al. [106], respectively.

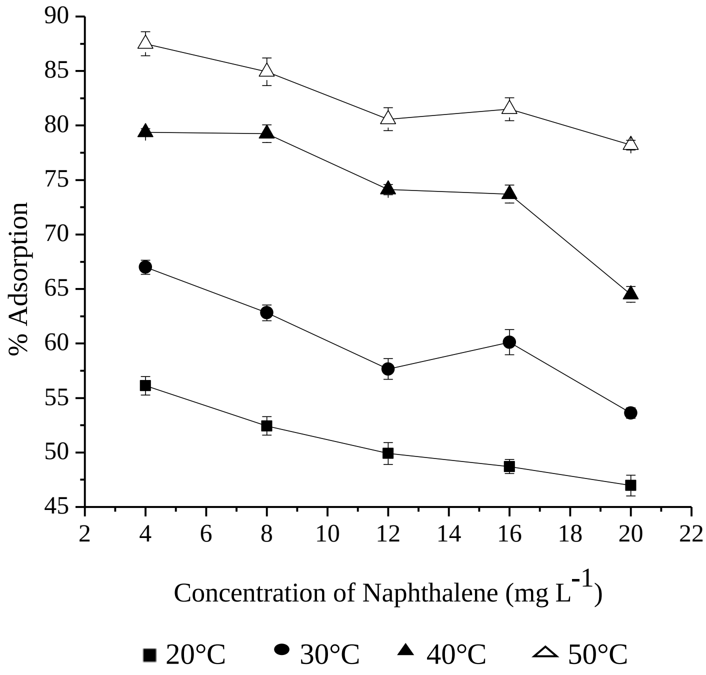

Fig. 5.10: Effect of temperature on adsorption of naphthalene on BPAC

[PAH] = 20 mg/L; pH = 7; adsorbent = 2 mg; shaking time = 80 min

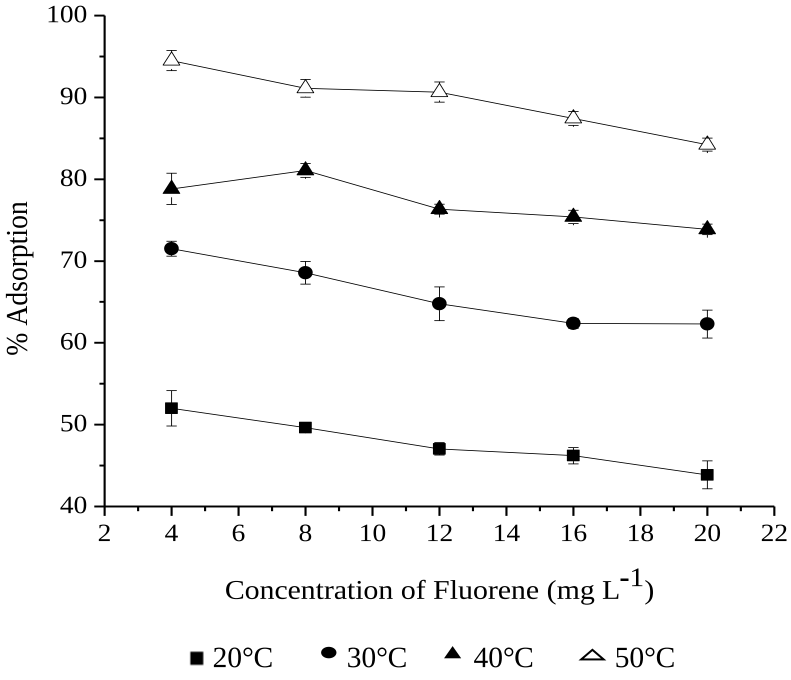

Fig. 5.11: Effect of temperature on adsorption of fluorene on BPAC

[PAH] = 20 mg/L; pH = 7; adsorbent = 2 mg; shaking time = 80 min

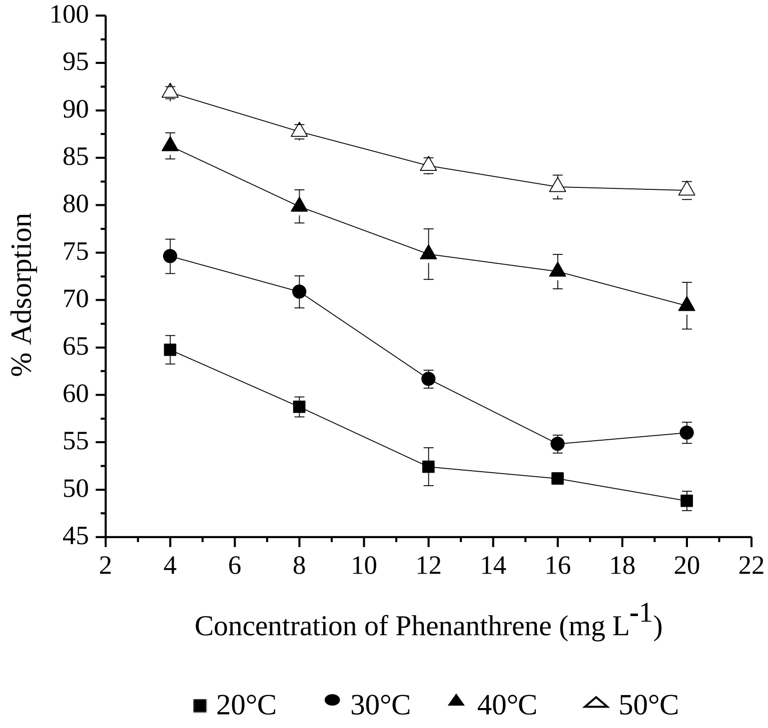

Fig. 5.12: Effect of temperature on adsorption of phenanthrene on BPAC

[PAH] = 20 mg/L; pH = 7; adsorbent = 2 mg; shaking time = 80 min

5.2.6 Modeling of adsorption isotherm

The plots between $1/q_e$ and $1/ C_e$ are straight line as shown in Fig. 5.13, 5.14 and 5.15. Langmuir adsorption constants Q^o and b were calculated using the slope and intercept values. Similarly, Freundlich adsorption isotherm plots were drawn between log q_e and log C_e (Fig. 5.16, 5.17 and 5.18). The straight line obtained was used to calculate Freundlich constants n and K_f. Langmuir and Freundlich constants along with R^2 values for adsorption of PAHs at different temperatures are presented in Table 5.2. The R^2 values suggest that the data is better fitted to Freundlich isotherm.

The calculated R_L values were in the range 0.0625 to 0.7974 for all the three PAHs which suggest the adsorption process to be favorable ($R_L>1$ Unfavorable, $R_L =1$ Linear, $0 < R_L<1$ Favorable, $R_L=0$ Irreversible) [106].

The synthesized adsorbent BPAC was compared with some other activated carbons used for PAHs adsorption with respect to adsorption capacity, equilibration time and temperature range (Table 5.3). The perusal of data suggests that the developed adsorbent has high adsorption capacity than several other reported adsorbents. Data shows that wherever adsorption capacity of BPAC is comparable (chemical activation of bean pods and activated carbon from flamboyant pod) or lower (zeolite) than the reported adsorbents, the equilibration time required for the BPAC is much less than the time required for the reported ones.

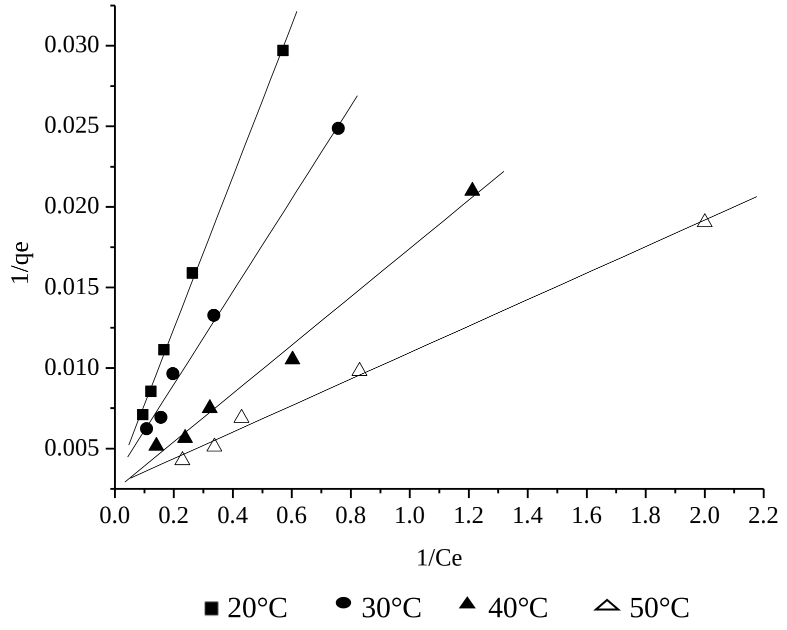

Fig. 5.13: Langmuir adsorption isotherm for naphthalene-BPAC system at different temperatures

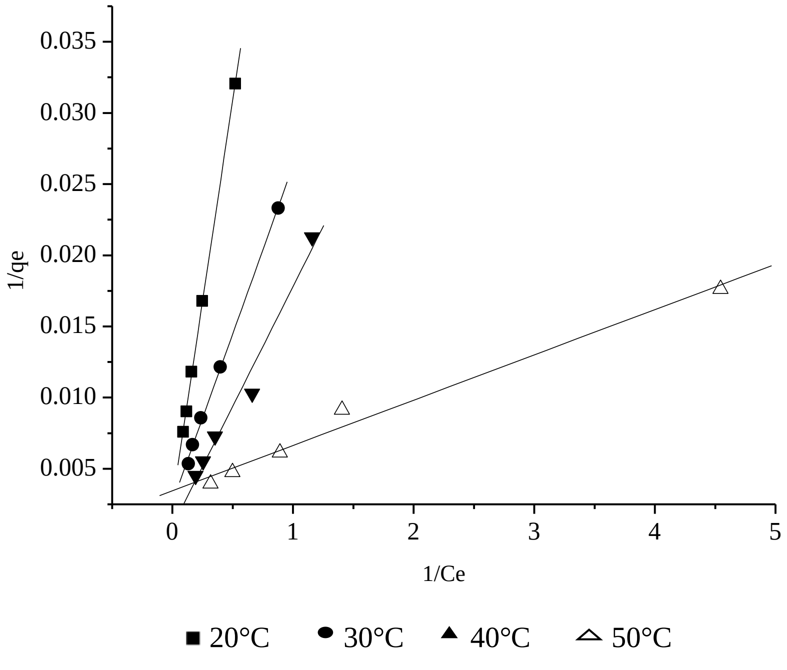

Fig. 5.14: Langmuir adsorption isotherm for fluorene-BPAC system at different temperatures

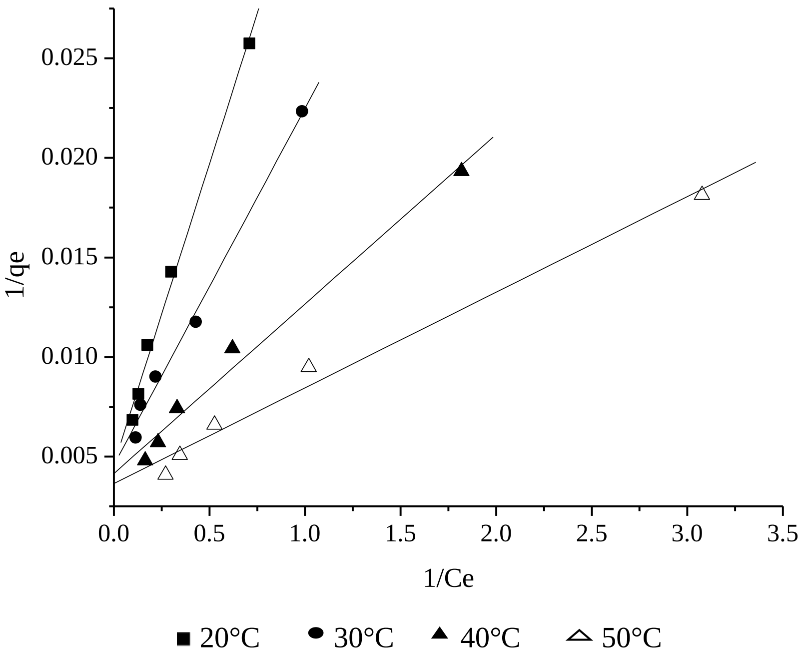

Fig. 5.15: Langmuir adsorption isotherm for phenanthrene-BPAC system at different temperatures

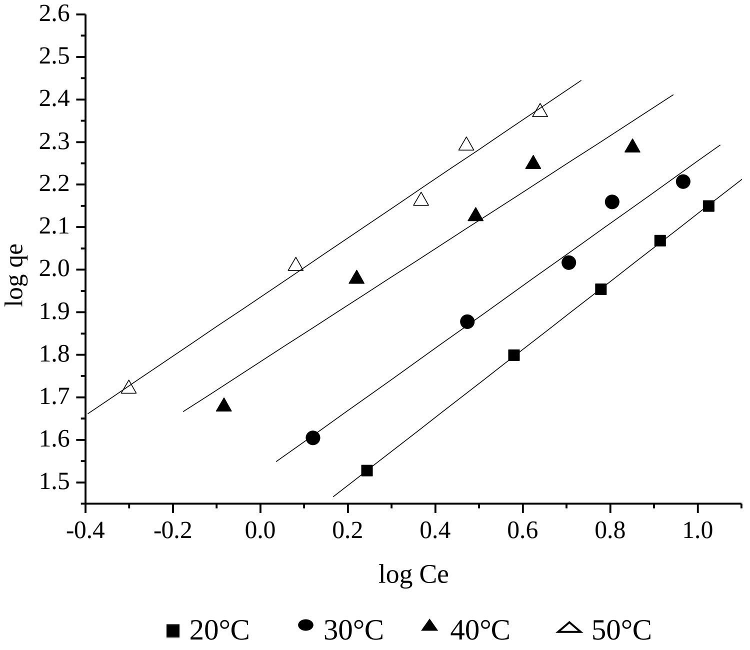

Fig. 5.16: Freundlich adsorption isotherm for naphthalene-BPAC system at different temperatures

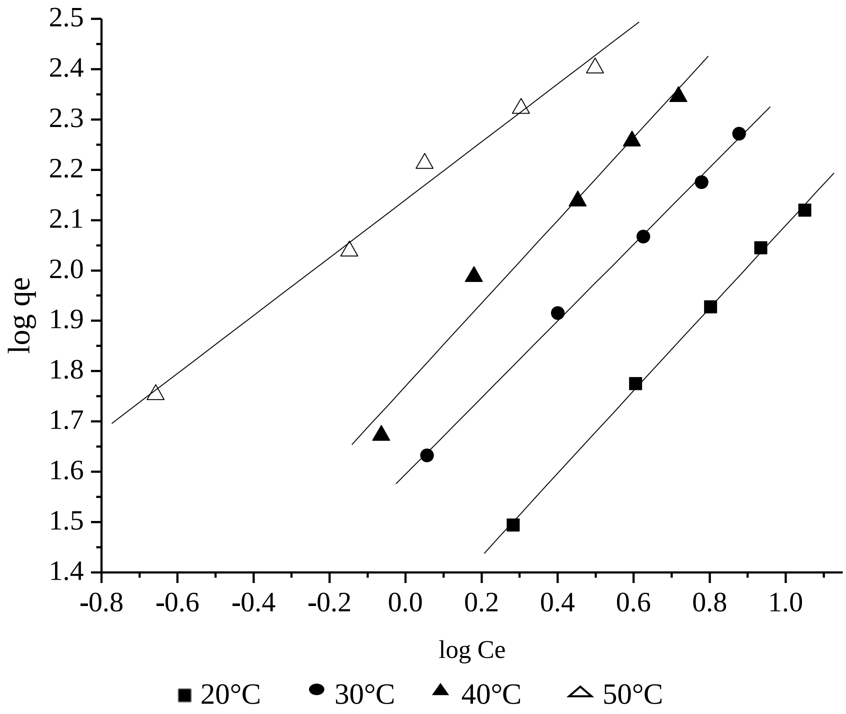

Fig. 5.17: Freundlich adsorption isotherm for fluorene-BPAC system at different temperatures

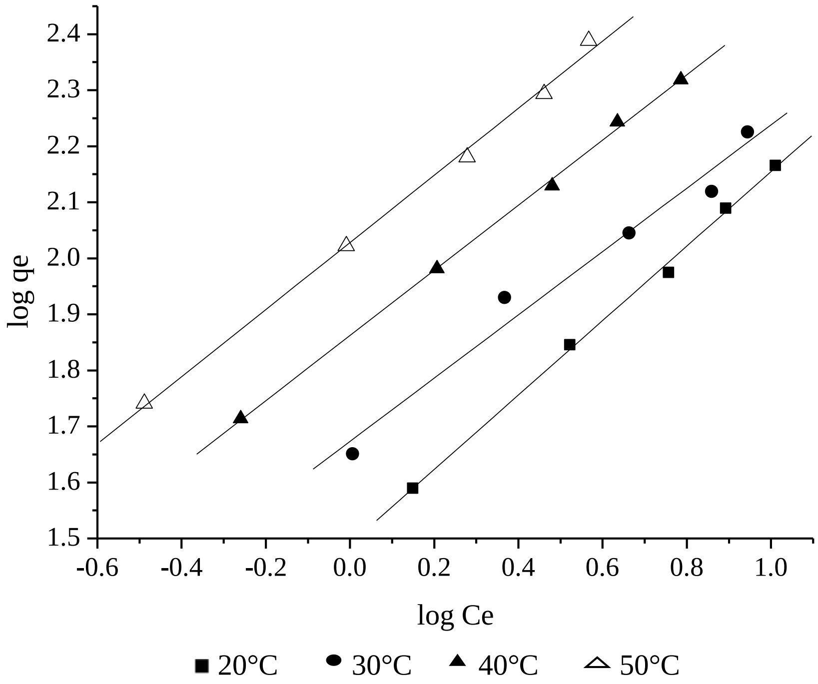

Fig. 5.18: Freundlich adsorption isotherm for phenanthrene-BPAC system at different temperatures

Table 5.2: Langmuir and Freundlich constants and R^2 values for adsorption of PAHs on BPAC at different temperature

	Naphthalene				**Fluorene**				**Phenanthrene**			
Langmuir Parameters												
	20°C	**30°C**	**40°C**	**50°C**	**20°C**	**30°C**	**40°C**	**50°C**	**20°C**	**30°C**	**40°C**	**50°C**
Q^o(mg/g)	333.33	344.82	370	416	285.71	370.37	384.61	476.19	217.39	222.22	243.90	277.77
b(L/mg)	0.0635	0.1006	0.18	0.2926	0.0762	0.1144	0.1538	0.2560	0.1523	0.2513	0.4823	0.75
R^2	0.9658	0.8918	0.9530	0.9228	0.9841	0.9371	0.8893	0.9804	0.9425	0.9359	0.9556	0.9218
Freundlich Parameters												
n	1.2521	1.3636	1.44	1.5055	1.217	1.2325	1.3131	1.7382	1.5053	1.5767	1.6329	1.7705
K_f	21.54	33.28	60.77	86.21	18.54	39.34	58.92	138.22	30.92	47.11	72.84	106.73
R^2	0.9998	0.9852	0.9905	0.9922	0.9986	0.9978	0.9743	0.9892	0.9978	0.9743	0.9987	0.9969

Table 5.3: Adsorption Capacities, equilibration time and temperature range of various adsorbents reported in literature

Adsorbent	Adsorbate	Adsorption Capacity (mg/g)	Temperature	Equilibrium Time	Reference
1. Activated Carbon(Coconut Shell)	Phenanthrene	20.22	25°C	1h	[89]
2. Activated Carbon(Commercial)	Naphthalene	271.72	20°C	NA	[92]
3. Activated Carbon (Bean Pods)	Naphthalene				[79]
a) Chemical activation		300	NA	72 h	
b) Physical Activation		85	NA	72 h	
4. Zeolite	Naphthalene	769.23	NA	>200 min	[66]
5. Activated Carbon	Naphthalene				[88]
a) Milk bush kernel shell		21	28±2°C	2 h	
b) Flamboyant pod		294.118	28±2°C	2 h	
6. Boehmite nanopowder	Naphthalene	200	Room Temp.	1 h	[90]
7. a) Activated Carbon(Commercial)	Anthracene	8.35	25°C	20 min	[93]
b) Posidonia oceanica		0.14	25°C	20 min	
8. a) BPAC	Naphthalene	333.33	20°C	80 min	Present Study
b) BPAC	Fluorene	285.71	20°C	80min	Present Study
c) BPAC	Phenanthrene	217.39	20°C	80 min	Present Study

NA- Not Available

5.2.7 Kinetics of adsorption

Lagergren pseudo-first order [107] and pseudo-second order model given by Ho and McKay [108] were applied to study rate constants for the adsorption of PAHs on BPAC. The expressions for pseudo-first order and pseudo-second order are given as eqs. (1) and (2), respectively.

$$\log (q_e - q_t) = \log q_e - (K_1/2.303)\, t \quad (1)$$

$$t/q_t = (1/K_2 q_e^2) + (1/q_e)t \quad (2)$$

where q_e and q_t denote amount of PAH adsorbed per gram of adsorbent at equilibrium and at time t. K_1 and K_2 are rate constants for pseudo-first order and pseudo-second order adsorption models. The plots for pseudo-first order model were drawn between log (q_e - q_t) and t for the adsorption of all the three PAHs. The plots were straight lines (Fig. 5.19), with R^2 values >0.95. Similarly, the pseudo-second order plots between t/q_t and t were also straight line (Fig. 5.20) with R^2 values <0.90. The rate constants K_1 and K_2 evaluated from the pseudo first order and pseudo-second order plots along with R^2 values for each PAH are given in Table 5.4. High values of correlation coefficients suggest better applicability of pseudo-first order kinetic model for PAH adsorption on BPAC.

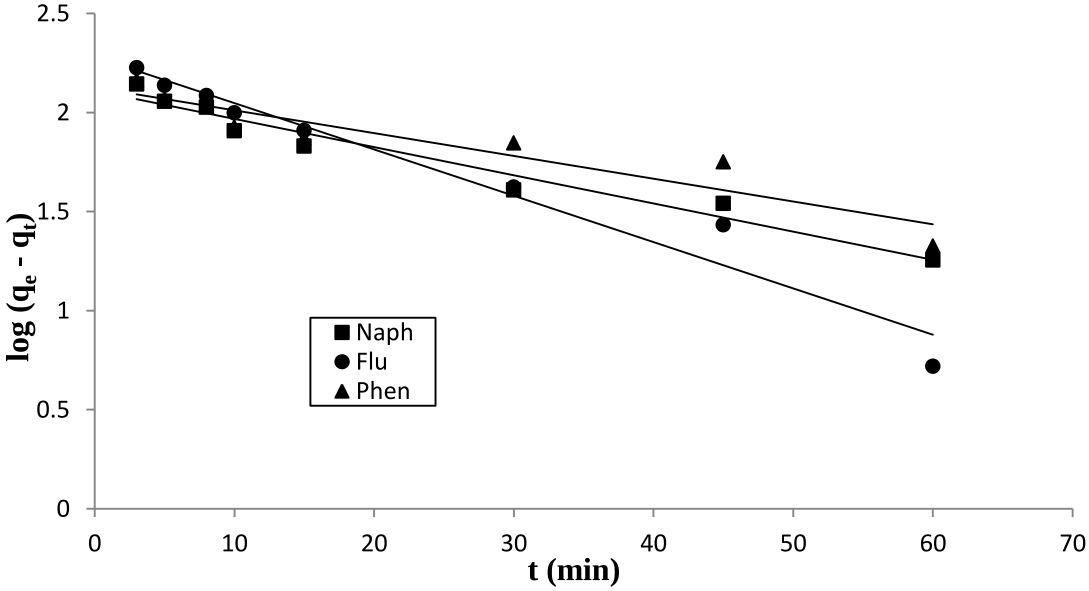

Fig. 5.19: Pseudo first order adsorption plots for adsorption of PAHs on BPAC

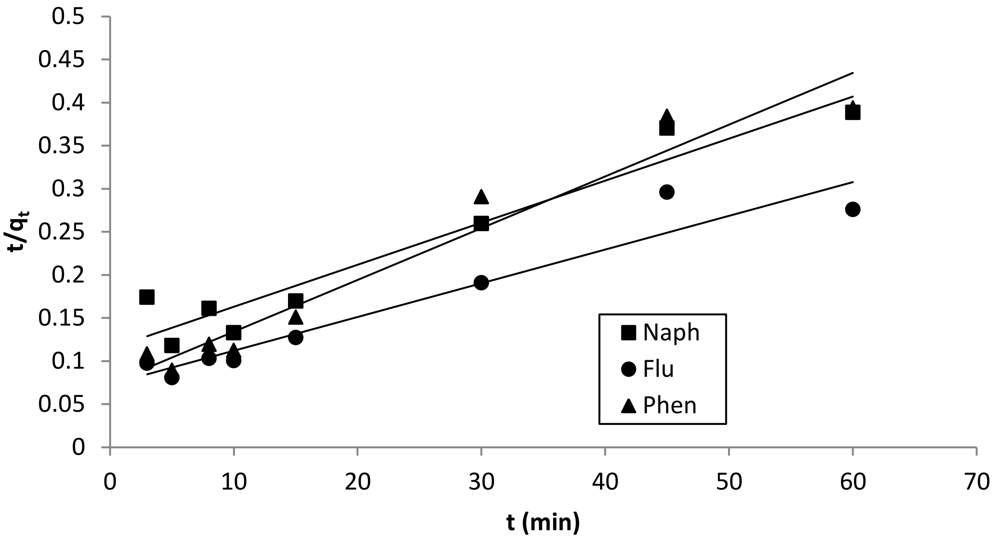

Fig. 5.20: Pseudo second order adsorption plots for adsorption of PAHs on BPAC

5.2.8 Intra-particle diffusion model

The transfer of adsorbate from solution to the adsorbent surface may occur in different steps involving any combination of rate controlling mechanism- (i) transport of the adsorbate to the external surface of the adsorbent (film diffusion), (ii) transport of adsorbate within the pores of the adsorbent (particle diffusion) (iii) physical or chemical adsorption on the internal or external adsorbent surface. The step (iii) is extremely rapid and not assumed to be rate determining step. The overall process may occur with one or more steps. To investigate the mechanism of PAH adsorption, the experimental data was subjected to intra-particle diffusion model.

According to Weber and Morris [109] if the rate limiting factor is intra-particle diffusion, the adsorption of the adsorbate is proportional to the square root of time. Intra-particle diffusion model is presented by Eq. (3) given below:

$$q_t = k_i\, t^{0.5} + C \qquad (3)$$

where qt is the amount of PAH adsorbed per gram of the adsorbent at time t, K_i is the rate constant for intra-particle diffusion and C is the measure of boundary thickness. The plots drawn between amount of PAH adsorbed and square root of time were straight lines which do not pass through the origin (Fig. 5.21). The intra-particle diffusion rate constants along with correlation coefficients are given in Table 5.4. The high values of the correlation coefficient suggest that the adsorption of PAHs occur due to intra-particle diffusion. However, the straight lines observed do not pass through the origin, indicating that the adsorption is not solely controlled by intra-particle diffusion, but some other mass transfer mechanisms, occur simultaneously.

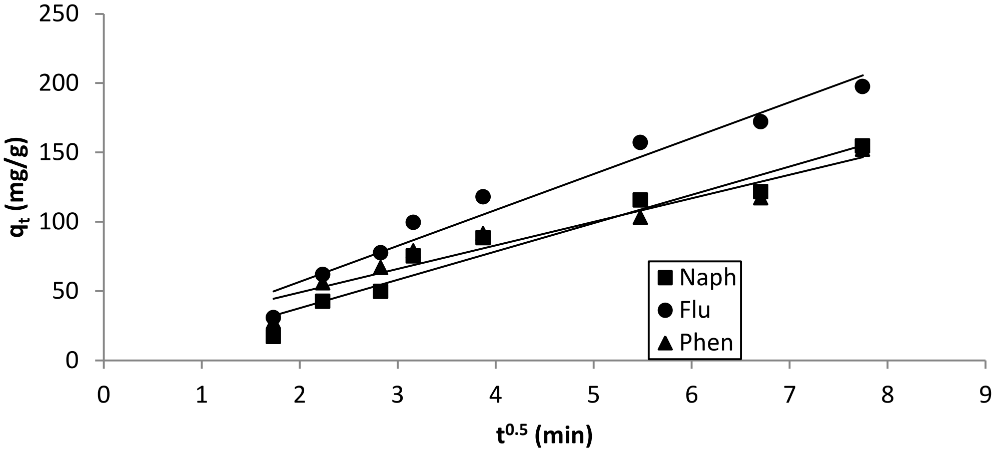

Fig. 5.21: Intra-particle diffusion plots for adsorption of PAHs on BPAC

Table 5.4: Kinetic parameters for pseudo-first order, pseudo-second order and intra-particle diffusion model

	Pseudo-first order model		**Pseudo-second order model**		**Intra-particle diffusion model**	
PAH	**K_1**	**R^2**	**K_2**	**R^2**	**K_i**	**R^2**
Naphthalene	0.0327	0.9686	2.10×10^{-4}	0.8308	20.46	0.9461
Fluorene	0.0244	0.9585	2.28×10^{-4}	0.8871	25.92	0.9616
Phenanthrene	0.0264	0.9797	4.87×10^{-4}	0.8513	23.99	0.9313

5.2.9 Thermodynamic parameters

The spontaneity and the nature of an adsorption process is depicted by various thermodynamic parameters. The thermodynamic parameters, Gibb's free energy change, ΔG°, enthalpy change, ΔH° and entropy change, ΔS°, were evaluated from Langmuir adsorption isotherms using the following equations (4) and (5):

$$\Delta G° = -RT \ln K_a \tag{4}$$

and

$$\Delta G° = \Delta H° - T\Delta S° \tag{5}$$

where R is universal gas constant (8.314 JK^{-1} mol^{-1}), T is absolute temperature in Kelvin and K_a is equilibrium constant obtained from Langmuir adsorption isotherms. Gibb's free energy, ΔG°, was evaluated using equilibrium constants at varying temperatures. A plot between ΔG° and temperature, T, gave a straight line with a slope value corresponding to ΔS° and intercept to ΔH°. The values of thermodynamic parameters, ΔG°, ΔH° and ΔS° are presented in Table 5.5.

Table 5.5: Thermodynamic parameters for the adsorption of PAHs on BPAC

	-ΔG°(KJ mol^{-1})				**ΔH°**	**ΔS°**
	20°C	**30°C**	**40°C**	**50°C**		
Naphthalene	5.107	6.440	8.167	9.733	40.702	0.1561
Fluorene	6.184	7.419	8.434	10.072	31.024	0.1268
Phenanthrene	8.041	9.577	11.590	13.146	42.782	0.1733

The negative values of ΔG° indicate the spontaneity of the studied adsorption processes. ΔG° values decrease with the increase in temperature indicating the adsorption of PAHs to be favorable at higher temperatures. The endothermic nature of the adsorption process is depicted by the positive value of enthalpy change, ΔH°. The positive value of the entropy change, ΔS°, indicates increase in randomness at the interface (solid/liquid) during adsorption of PAHs and suggests good affinity of the PAHs towards the banana peel activated carbon.

5.2.10 Desorption Studies

Desorption studies were carried out in batch mode. In the first step adsorption was carried out under optimum conditions to load the BPAC with the respective PAH. In the second step the loaded BPAC was agitated with NaOH and ethanol mixture (50%) of varying compositions for different time (5-30 min) [110]. The results are depicted in Fig. 5.22, 5.23 and 5.24 which indicate that 1.0 M NaOH in 50 % ethanol is most effective for quantitative desorption of naphthalene (97%), fluorene (95%) and phenanthrene (95%).

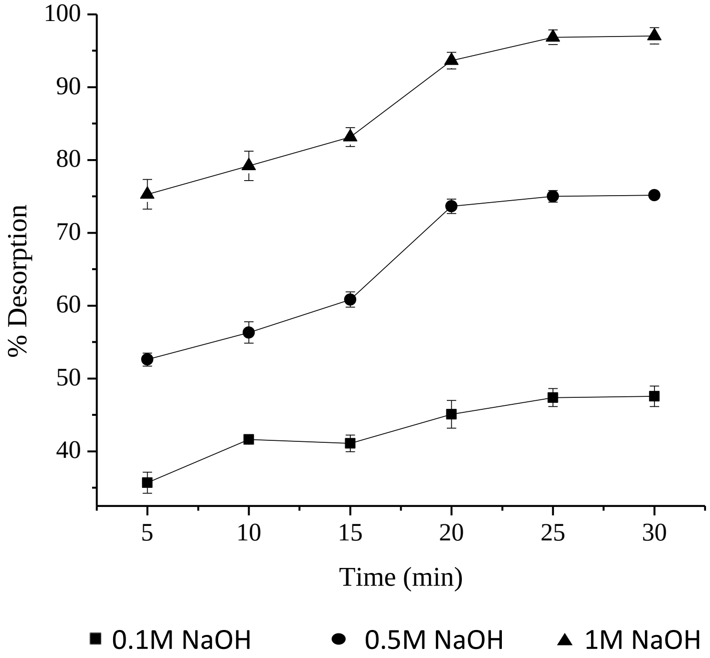

Fig. 5.22: Desorption of naphthalene from BPAC with different NaOH concentrations

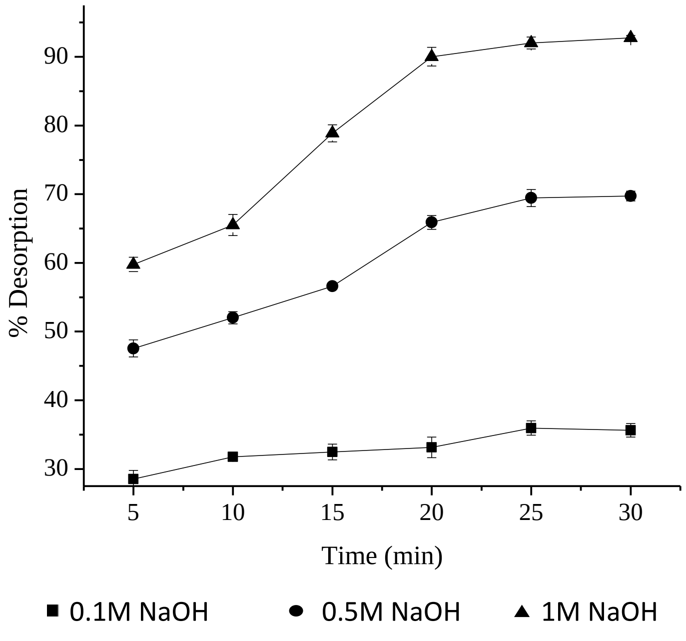

Fig. 5.23: Desorption of fluorene from BPAC with different NaOH concentrations

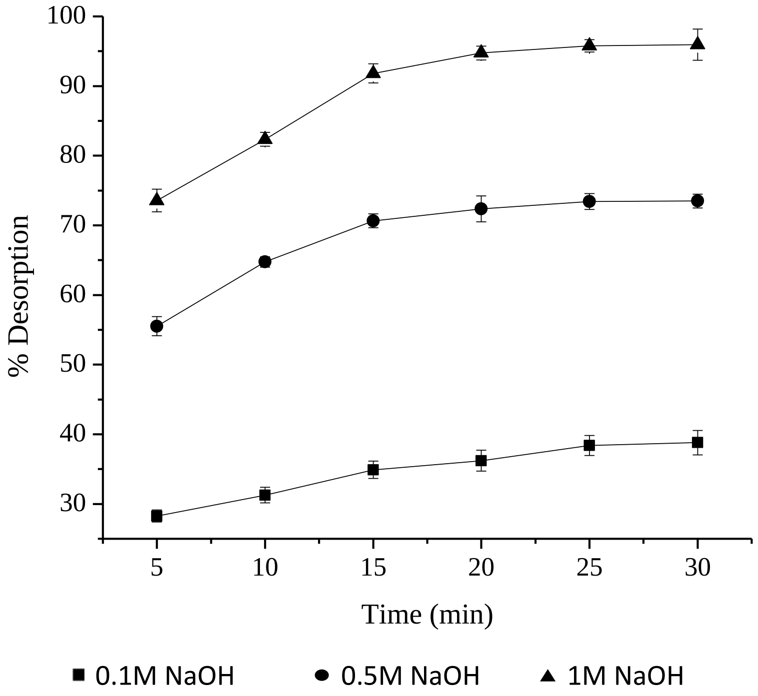

Fig. 5.24: Desorption of phenanthrene from BPAC with different NaOH concentrations

The content of this chapter have been published in the form of a research paper in the journal "**Desalination and Water Treatment**".

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INTRODUCTION

In today's world, environmental pollution due to solid and liquid waste is one of the biggest threats for the living population. The twentieth century has seen an unprecedented large scale growth in industrialisation and urbanisation. As a result, basic needs and priorities have changed and one typical example is transportation. It is not improper to say that automobiles have become an important means of transportation and a part and parcel of our day to day life. On an average, the life time of a vehicular tire is 20,000 miles. Therefore, a huge number of vehicular tires are discarded every year. According to literature, 190 million old vehicular tires are discarded per year in United States [1]. In Canada, 26 million used vehicular tires are generated every year and in UK, 1 million generated per day [2]. In India, 112 millions of vehicular tires are discarded each year [3]. Vehicular tires do not decompose easily due to the presence of stabilizers, additives and cross-linked structure. Therefore, these are generally disposed by incineration and landfilling. The world's biggest tire graveyard is in Kuwait city, which is so huge that it is visible even from space (Fig. 6.1).

(Picture taken from internet (daily mail reporter): http://www.dailymail.co.uk/news/article-2337351)

Fig. 6.1: A picture showing tire graveyard in Kuwait City

Accumulation of huge number of vehicular tires presents a serious environmental problem and scientists are intending towards the recycling and reuse of discarded tires. The short term solution of the problem is stockpiling, landfilling or illegal dumping. The stockpiled vehicular tires provide suitable space for breeding of mosquitos, cockroaches and rats. Dumping of the waste tires may cause accidental fires releasing a huge amount of toxic fumes. At Jahra dumpsite in Kuwait, where more than 5 million vehicular waste tires were stored, an accidental and massive fire brokedown causing serious environmental damage [4]. Due to the large volumes and void spaces (75%), vehicular tires are not suitable for landfilling. As the landfilling space is becoming scarcer, the tire disposal is also becoming expensive [4]. Jang et al. [5] reported the use of waste tires as highway crash barriers. The scrap tires are binded with steel cable and enclosed with fiber glass to absorb or reduce the impact of crash from the vehicles moving with high speeds. But, this application has not been used on a large scale due to more appropriate absorption characteristics of the sand filled crash barriers. In 1910, natural rubber was a valuable commodity and more than 50% of the rubber products were recycled. By 1960, the recyclable content was dropped to 20% and by 1990, it was dropped to only 2%. The main reasons for the decline in recycling were the production of steel-belted tires and use of synthetic rubber on a large scale [6]. Vehicular tire consists of a mixture of natural rubber, styrene butadiene rubber (SBR), polybutadiene rubber and other additives like carbon black, zinc oxide and sulphur [7]. The most commonly used rubber is SBR which consists of 25 wt % of styrene. Murillo et al. [8] reported that nearly 40% of the waste tire is comprised of carbon black. A highly acceptable use of waste tires can be as raw material for the preparation of activated carbon. Conversion of waste vehicular tire into activated carbon will lead to dual benefit (i) utilization of the unusable vehicular tires (ii) production of high quality activated carbon. The activated carbon can be used for several applications such as water purification (adsorption of toxic aromatic compounds, dyes, chlorine, treatment of municipal and drinking water), preparation of batteries, fuel cells and cigarette filters [9].

World is facing freshwater crisis due to the reduction in freshwater resources. The industrial as well as domestic wastes have polluted both the surface and the ground water to a larger extent. Wastewater treatment and its reuse are the major issues of present time related to environmental protection. Scientists are focussing for inexpensive and environmental friendly technologies in this regard. The emphasis of the present work is on the development of high quality activated carbon from vehicular waste tires which are available in abundance and have no economic importance. The developed vehicular tire activated carbon can be used as low cost alternative to the commercial activated carbons for the removal of various pollutants from aqueous systems. In the last decade, several researchers have examined the adsorption of various pollutants on activated carbon prepared from waste tires.

Adsorption of mercury on carbonaceous adsorbent prepared from rubber tire waste was conducted by Manchon-Vizuete et al. [10]. The rubber tire was heated at 400 or 900 °C and/or chemically treated with H_2SO_4, HNO_3 or their mixture. The adsorption capacity for mercury was higher for heated adsorbents than the treated ones. Tanthapanichakoon et al. [11] investigated the adsorption and desorption of phenol and reactive dyes from aqueous media using activated carbon derived from waste tires. The results reveal that the adsorption of reactive dye was significantly higher on prepared carbon than commercial carbon, but for phenol the adsorption was comparable on the two carbons. Furthermore, the regeneration efficiency of the prepared activated carbon was more than the commercial activated carbon. Alam et al. [12] evaluated the thermodynamic characteristics of adsorption of 2,4-dichloro-phenoxy-acetic acid (2,4-D) and atrazine using granules of rubber tire. Adsorption of 2,4-D on tire granules was endothermic in nature, whereas, adsorption of atrazine was exothermic in nature. Gibb’s free energy was found to be negative for both the adsorbates, indicating stability of the system.

Adsorption of Cd (II) from aqueous medium using discarded rubber tire in the presence of ultrasound was examined by Entezari and associates [13]. The experimental data fitted with Langmuir and first order kinetic model. Intra-particle and film diffusion coefficients were 1.8 and 2.7 times low in absence of ultrasound than in presence. Alexandre-Franco et al. [14] studied the adsorption of lead on adsorbents prepared from rubber tire by thermal and chemical treatment. The effect of pH was studied at pH 2.0, 5.7 and12.6 and it was observed that adsorption of lead was negligible at pH 2 and increased with the increase in pH.

The adsorption of copper ions from aqueous solution on untreated and chemically and physically treated tire rubber was reported by Al-Asheh and Banat [15]. The adsorption capacity was in the order: physically treated > chemically treated > untreated. The adsorption of Cu (II) enhanced with the increase in pH of the solution. The adsorption process was described by Langmuir and Freundlich adsorption isotherms. Calisir et al. [16] reported the adsorption of Cu(II) from aqueous media using recycled tire rubber. The effect of contact time, initial metal ion concentration and pH on the adsorption of Cu(II) was examined. The adsorption of Cu(II) was pH dependent and optimum adsorption was obtained at pH 6. The data were subjected to Freundlich and Langmuir models and Langmuir model fitted well with the equilibrium data. Mui et al. [17] explored activated carbon obtained from rubber tire waste for the removal of dye from industrial effluents. The effect of holding time, acid treatment and temperature were studied on the porosity of developed activated carbon. The prepared activated carbon was employed for the adsorption of acid blue 25, acid yellow 117 and methylene blue. The equilibrium data were fitted to different isotherm models and the data best fitted with Redlich-Peterson model. The same group of researchers [18] investigated char preparations using waste rubber tires. The results suggested that temperature above 773 K did not have any significant improvement in the surface area, but resulted in low yield. The adsorption of Acid Yellow 117 was studied which fitted well with Redlich-Peterson model. Removal of cadmium from aqueous solution using carbonaceous adsorbents derived from tire rubber was reported by Alexandre-Franco and co-workers [19]. The adsorbents were prepared by treating tire rubber thermally and chemically. The results indicated that thermal and thermal-chemical treatments were more effective than chemical treatment for the adsorption of metal ions from aqueous solutions. The adsorption data fitted well with pseudo-second order model.

Gupta et al. [20] investigated the adsorption of azo dye acid blue 113 on activated carbon prepared from rubber tire and commercial activated carbon. The effect of contact time, adsorbate concentration, adsorbent dose, pH and temperature were examined. The data fitted well with Langmuir and Freundlich adsorption models and various thermodynamic parameters were evaluated. The adsorption process followed first order kinetics. The dye was recovered using 0.1 M NaOH solution. The studies were extended for the removal of the pesticides (methoxychlor, methyl parathion and atrazine) from industrial wastewater [21]. Effect of various experimental parameters was examined. The adsorption followed pseudo first order kinetics. Thermodynamic parameters were evaluated, which confirmed that the adsorption process was spontaneous, random and exothermic. Gupta et al. [22] also investigated the adsorption of lead and nickel from aqueous solutions on activated carbon prepared from waste rubber tire. The results revealed that the uptake of lead was greater than nickel, based on the electronegativity and ionic radii of the adsorbate. Equilibrium data were fitted with the Langmuir adsorption model and kinetic data were described by pseudo-second-order model. Thermodynamics data showed the feasibility and endothermic nature of the adsorption process. Regeneration of activated carbon (98%) was achieved with 0.1 M HNO_3. They prepared activated carbon from waste rubber tire by physical heating and microwave assisted chemical treatment [23]. Two types of activated carbons were used for the adsorption of phenols from water. It was observed that due to higher solubility phenol adsorbs to a lesser extent on both the kinds of activated carbon. In both the cases, adsorption was exothermic and occurs through pore diffusion mechanism.

The possibility to use the activated recycled tire rubber for the clean up of oil spill was explored by Aisien and Aisien [24]. It was observed that the efficiency of oil removal increased on activation. A decrease in adsorption capacity of activated rubber was observed with the increase in temperature. Lian et al. [25] synthesized activated carbons from waste polymers such as tire rubber, polyvinylchloride and polyetheleneterephthalate through KOH activation. The synthesized activated carbons were employed for the adsorption of dyes. The effects of ionic strength, pH of the solution and concentration of surfactants on the adsorption of dyes have been investigated. The Langmuir adsorption capacities for the dyes were much higher than with commercial activated carbon. Adsorption of methyl orange was lower than that of methylene blue.

Spectroscopic and computational studies were conducted by Al-Saadi et al. [26] for the adsorption of Cd(II) from aqueous media on activated carbon prepared from rubber tire. FTIR studies confirmed oxygen containing groups on the surface of the activated carbon. The theoretical calculations based on density functional theory indicated that the binding energy of adsorption process was in the range 190-212 kcal/mol and Cd(II) ions approach more conveniently towards oxygen atoms of carboxylic group as compared to the carbonyl and alcoholic groups. The adsorption of chromium from aqueous solutions using activated carbon prepared from waste rubber tires was examined [27]. The effect of various experimental parameters was examined and the adsorption of chromium was high in the pH range 4-6. Saleh et al. [28] investigated the removal of Pb(II) ions from aqueous solutions using activated carbon derived from rubber tire. The adsorption was higher in the pH range 4-7. Computational studies were carried out and binding energies of lead ions with carboxylic, carbonyl and hydroxyl groups were calculated using density functional theory (DFT). Binding energies were high and in the range 310-340 kcal mol^{-1}, indicating towards chemisorption process.

Brahim et al. [29] studied the adsorption of cationic azo dye and methylene blue, on activated carbon developed from cryogenic grinding of waste tires. The effect of pH was investigated in the range 2-11 and adsorption was found to be optimum at pH 11. The equilibrium data were subjected to Langmuir, Freundlich and Dubinin-Radudhkevich isotherms and the data fitted best to Langmuir adsorption isotherm.

Literature survey reveals that activated carbons derived from waste tires have been investigated for various pollutants such as dyes, phenols, pesticides and metal ions. But no reports are available on the use of activated carbon derived from vehicular tire for adsorption of polycyclic aromatic hydrocarbons. Inspite of several other remediation methods available for the removal of PAHs, adsorption is a versatile and easily applicable technique for the removal of pollutants from aqueous systems. Therefore, it was planned to synthesize activated carbon from vehicular tire for the removal of three PAHs, namely, naphthalene, fluorene and phenanthrene based on their solubility and availability in water and wastewater systems. The adsorption data was subjected to Freundlich and Langmuir isotherms. The effect of various parameters such as contact time, adsorbent dose, pH and temperature on the adsorption was evaluated. Different thermodynamic parameters were calculated to ascertain the nature and spontaneity of the adsorption. The present work will not only provide an efficient method for the removal of hazardous pollutants, from various water and wastewater systems, but also a solution to disposal problem of waste vehicular tires.

6.1 EXPERIMENTAL

The details of synthesis and characterization of vehicular tire activated carbon (VTAC) and adsorption studies are discussed in chapter II.

6.2 RESULT AND DISCUSSION

6.2.1 Characteristics of adsorbent

XRD spectrum of the adsorbent VTAC is shown in Fig. 6.2. Broad peaks around 24° and 42° indicate the amorphous nature of the activated carbon [30]. BET surface area of the adsorbent VTAC was 643.86 m^2/g. FE-SEM images depicting morphology of the adsorbent, before and after adsorption of PAHs are shown in Fig. 6.3, 6.4, 6.5 and 6.6. The surface of VTAC before and after adsorption of PAHs is dissimilar. The dissimilarity after adsorption may be due to the adsorption of PAHs in the pores of the adsorbent.

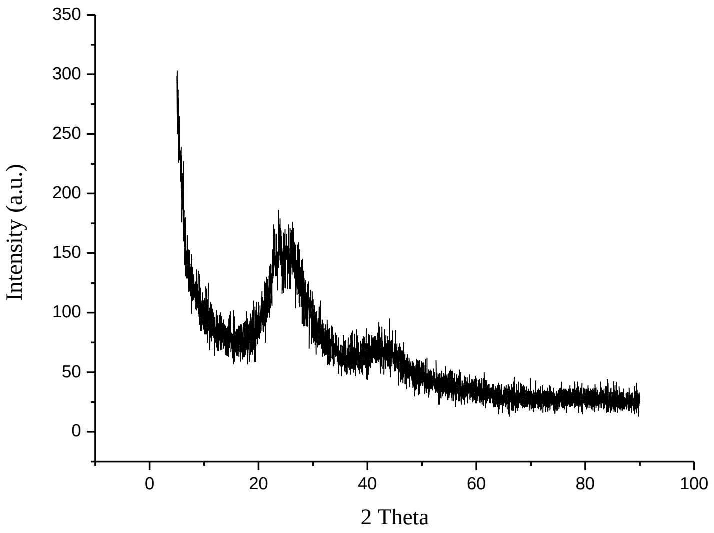

Fig. 6.2: XRD spectrum of vehicular tire activated carbon

FT-IR spectra of VTAC before and after adsorption of PAHs are shown in Fig. 6.7. In FT-IR spectrum of the adsorbent major bands appear at 3416, 1707, 1621, 1394, 1294 and 1210 cm^{-1}. The peak at 3416 cm^{-1} is due to –OH group stretching and at 1707 cm^{-1} is due to C=O group stretching vibration. The band at 1621 cm^{-1} is due to C=C stretching vibration. The bands at 1394 cm^{-1} is due to S=O stretching or O-H bending vibration. The bands at 1294 cm^{-1} and 1210 cm^{-1} are due to O-H bending vibration and C=S stretching vibration, respectively. The FT-IR spectra clearly indicate that the major groups on the VTAC are –OH and C=O groups. The appearance of new peaks and shifting of the peaks after adsorption are due to the adsorption of PAHs on the surface of the adsorbent. The peaks due to S=O, –OH, and C=S groups are shifted after adsorption of all the three PAHs. Additional peaks appearing after adsorption around 1500 cm^{-1} are due to aromatic stretch. Several new peaks in the region 900-700 cm^{-1} are due to out of plane bending vibration of aromatic C-H which confirms the adsorption of aromatic compounds on VTAC in all the cases. The additional peaks at 2916, 1440 and 1303 cm^{-1} in case of fluorene adsorption are due to stretching and bending C-H vibration of methylene group and stretching of C-C single bond, respectively. The assignments of IR peaks after adsorption of PAHs on VTAC are given in Table 6.1.

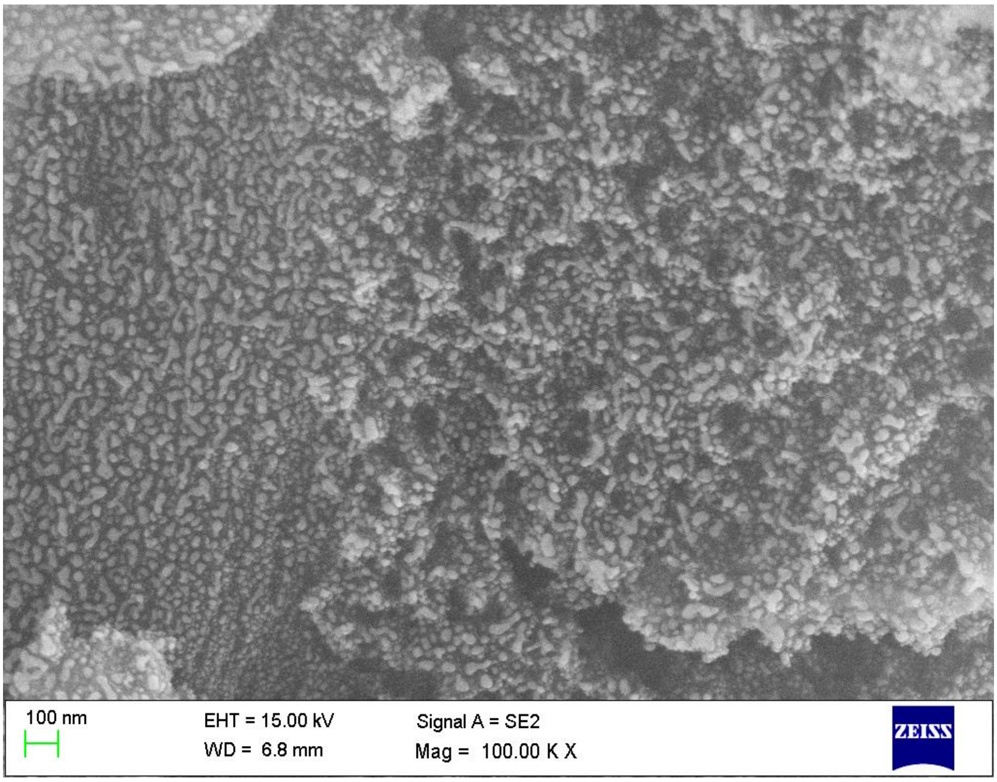

Fig. 6.3: FE-SEM image of activated carbon before adsorption of PAH

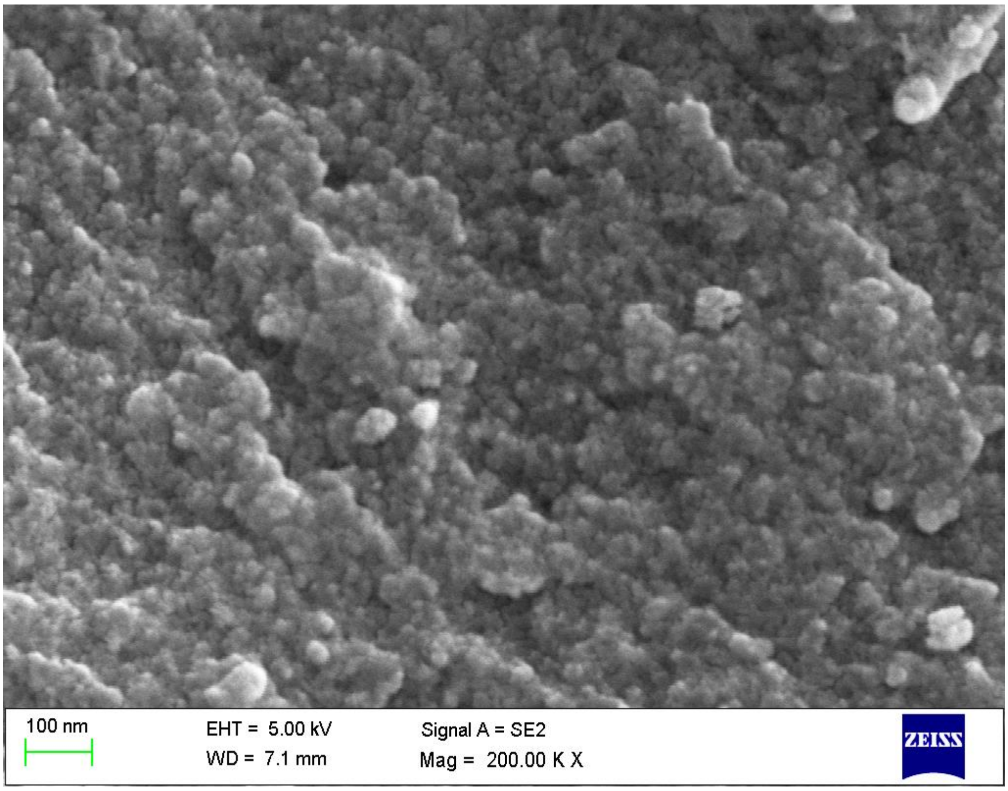

Fig. 6.4: FE-SEM image of activated carbon after adsorption of naphthalene

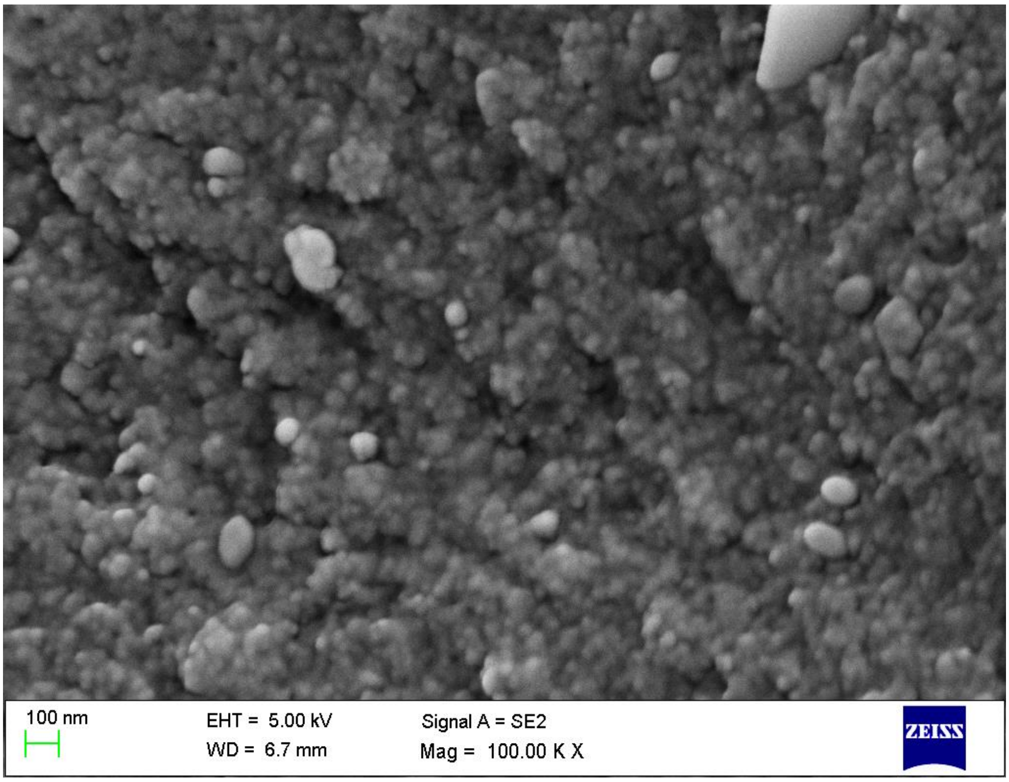

Fig. 6.5: FE-SEM image of activated carbon after adsorption of fluorene

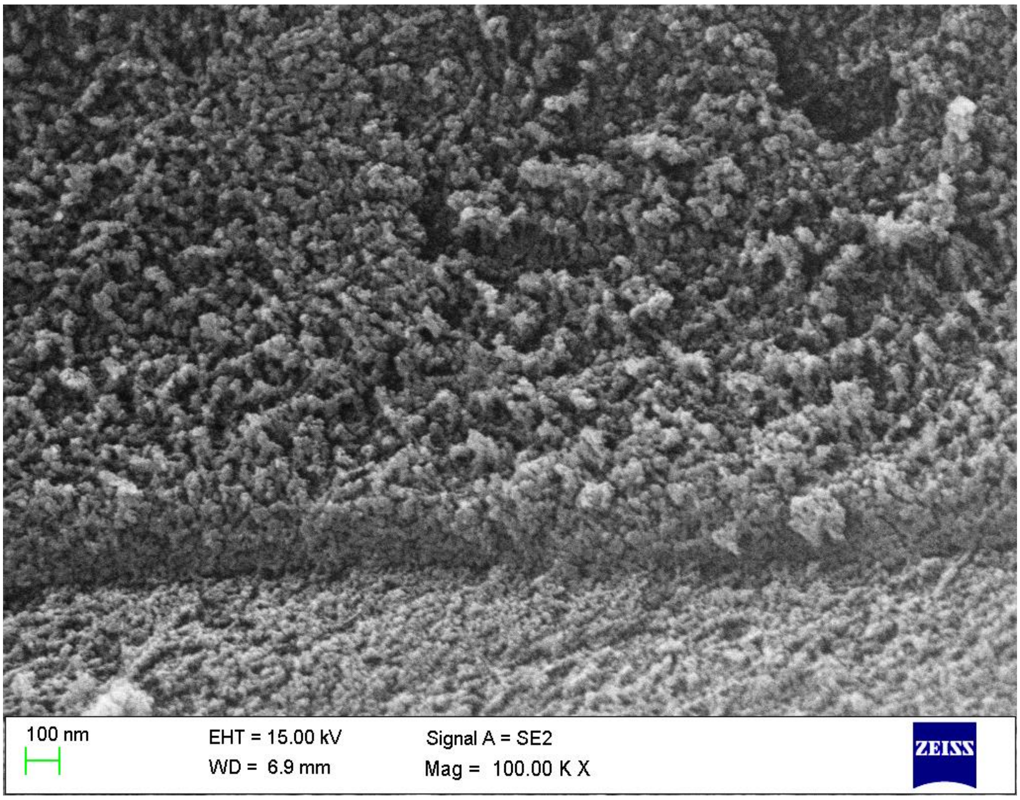

Fig. 6.6: FE-SEM image of activated carbon after adsorption of phenanthrene

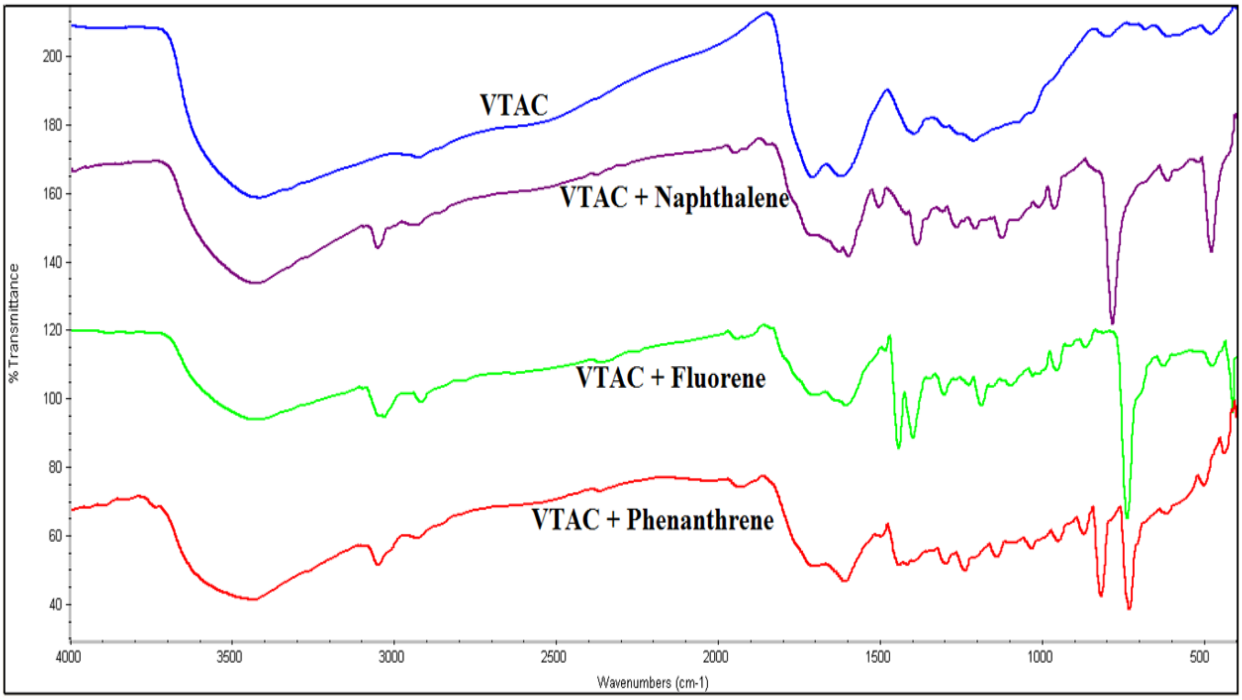

Fig. 6.7: FT-IR spectra of PAH-VTAC system

Table 6.1 IR frequencies of VTAC and VTAC + PAH

VTAC (cm^{-1})	**VTAC + Naph** (cm^{-1})	**VTAC + Flu** (cm^{-1})	**VTAC + Phen** (cm^{-1})	**Assignments**
3416	3434	3423	3436	υ (O-H)
	3050	3049	3049	υ (Aromatic C-H)
		2916		υ (C-H)
1707	1709	1706	1706	υ (C=O)
1621	1630	1600	1607	υ (C=C-C)
	1497	1483	1497	υ (C=C-C)
		1440		δ (C-H)
1394	1386	1397	1401	υ (S=O)/δ(O-H)
		1303		υ (C-C)
1294	1261	1297	1296	β (O-H)
1210	1205	1224	1237	υ (C=S)
	873	865	870	γ (C-H)
		812	816	γ (C-H)
	780	735	728	γ (C-H)

υ = stretching; δ = bending; β = in plane bending; γ = out of plane bending

6.2.2 Effect of contact time

The effect of contact time on adsorption of PAHs on VTAC was analysed for 150 min, at periodic intervals of 15 min. The adsorption of PAH on VTAC increases upto 105 min and remains constant thereafter (Fig. 6.8). For all the subsequent studies a contact time of 120 min was observed. Initially, the percentage adsorption increases with time because of the availability of the active sites on the surface of the adsorbent. As soon as the active sites on the surface are occupied the adsorption process attains equilibrium.

The results further reveal that the adsorption of the three PAHs is in the order: naphthalene < phenanthrene < fluorene. Authors obtained similar results for the adsorption of PAHs on banana peel activated carbon [31]. Lower adsorption of naphthalene is attributed to its most hydrophilic nature among the studied PAHs (log K_{ow} values: Naph – 3.30 , Flu – 4.18, Phen – 4.57) and higher adsorption of fluorene than phenanthrene to smaller diameter of fluorene than phenanthrene (Flu – 1.14 nm, Phen – 1.17 nm, [32]). Results thus suggested that the adsorption is influenced by various factors such as solubility, hydrophilic nature, molecular size, nature of activated carbon and chemical properties of the adsorbent [33]. Yakout et al. [34] also reported lower adsorption of naphthalene than phenanthrene.

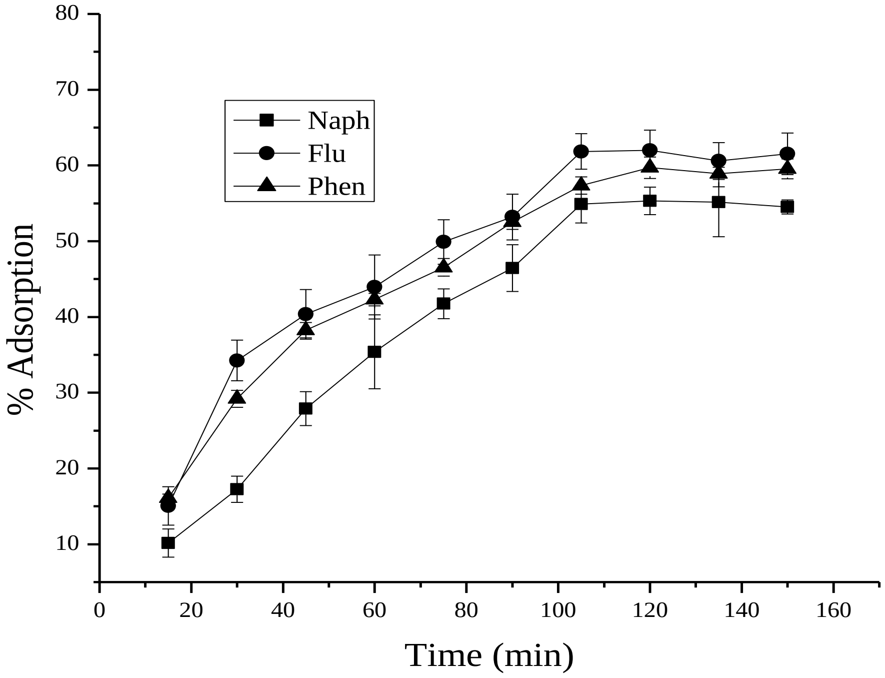

Fig. 6.8: Effect of contact time on adsorption of PAHs on VTAC

[PAH] = 20 mg L^{-1}; pH = 7; adsorbent = 5 mg; temperature = 25±2°C

6.2.3 Effect of adsorbent dose

To study the effect of adsorbent dose on the adsorption of PAHs, the amount of adsorbent was varied in the range 2-20 mg for 30 mL aqueous phase at pH 7.0 containing 20 mg L^{-1} of PAH. A shaking time of 120 min was observed. The adsorption of PAHs increases linearly with the amount of the adsorbent and is quantitative at 16 mg of the adsorbent for all the three PAHs (Fig. 6.9). The initial increase in adsorption with increasing amount of adsorbent is due to an increase in the number of available active sites for adsorption.

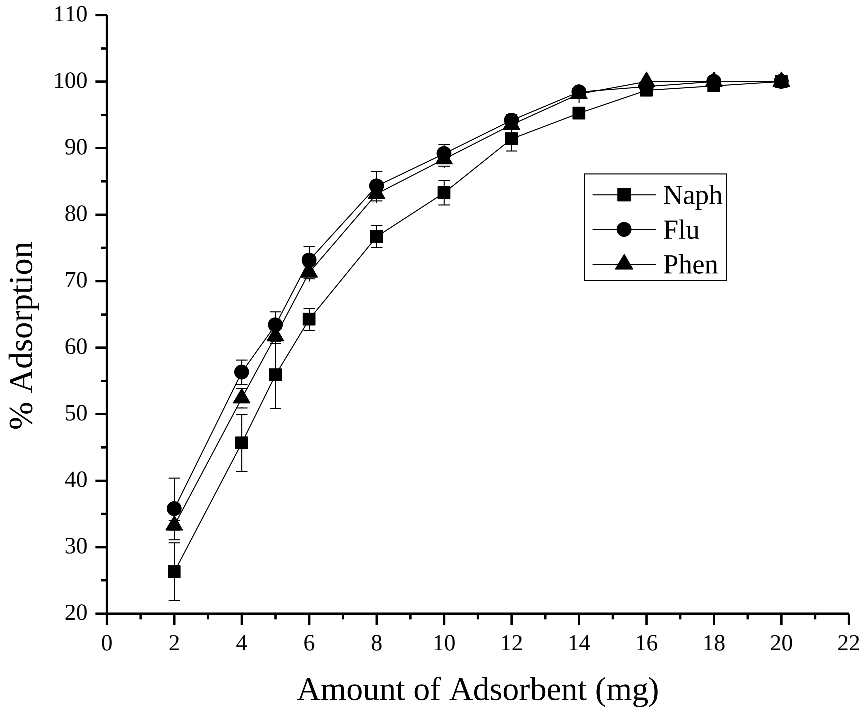

Fig. 6.9: Effect of adsorbent dose on PAHs adsorption on VTAC
[PAH] = 20 mg L^{-1}; pH = 7; shaking time = 120 min; temperature = 25±2°C

6.2.4 Effect of pH

The influence of solution pH on the adsorption of PAHs on VTAC was studied with 30 mL of 20 mgL^{-1} PAH solution in the pH range 2 – 12. The results obtained at different pH are shown in Fig. 6.10. At low pH, the adsorption of PAHs on VTAC is high, whereas it decreases with the increasing pH of the solution. This is probably due to the presence of positive charge on the surface of adsorbent at low pH, which results in higher interaction between positive adsorbent surface and π-electron cloud of adsorbate rings. As the pH increases the positive charge on the adsorbent surface decreases which results in less interaction between adsorbent surface and adsorbate.

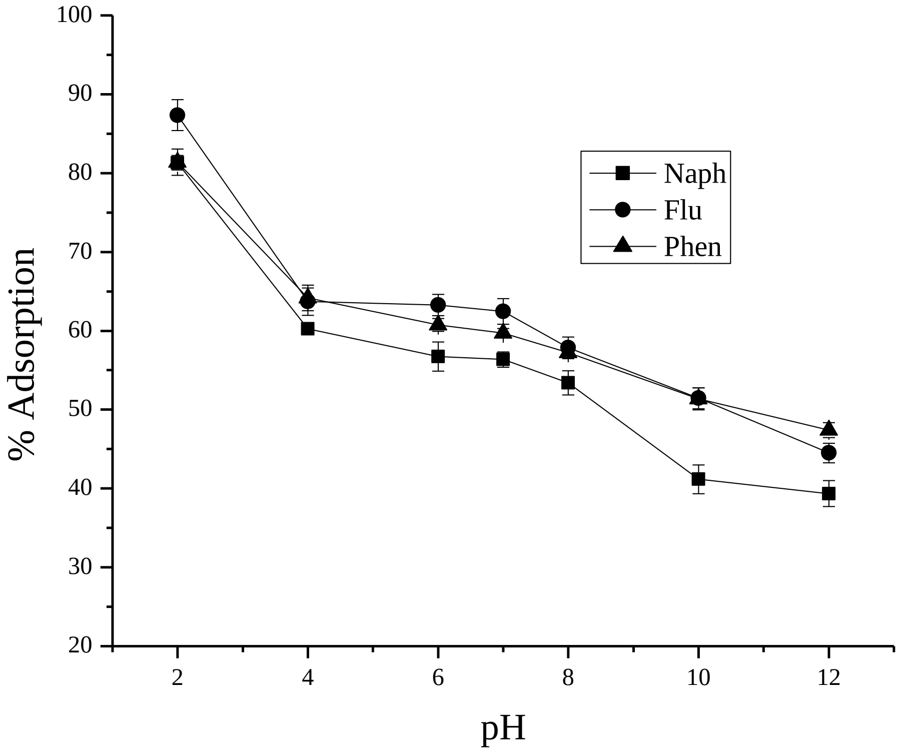

Fig. 6.10: Effect of pH on adsorption of PAHs on VTAC
[PAH] = 20 mg L^{-1}; shaking time = 120 min; adsorbent = 5 mg; temperature = 25±2°C

6.2.5 Effect of Temperature

The effect of temperature on the adsorption of PAHs onto VTAC was studied under optimised conditions at 20°C, 30°C, 40°C and 50°C (Fig. 6.11, 6.12 and 6.13). The plots show a decrease in adsorption with increasing temperature indicating thereby an endothermic adsorption process. Similar trend was observed for the adsorption of p-xylene [35] and Congo Red [36] on activated carbons obtained from coconut shell and coir pith, respectively.

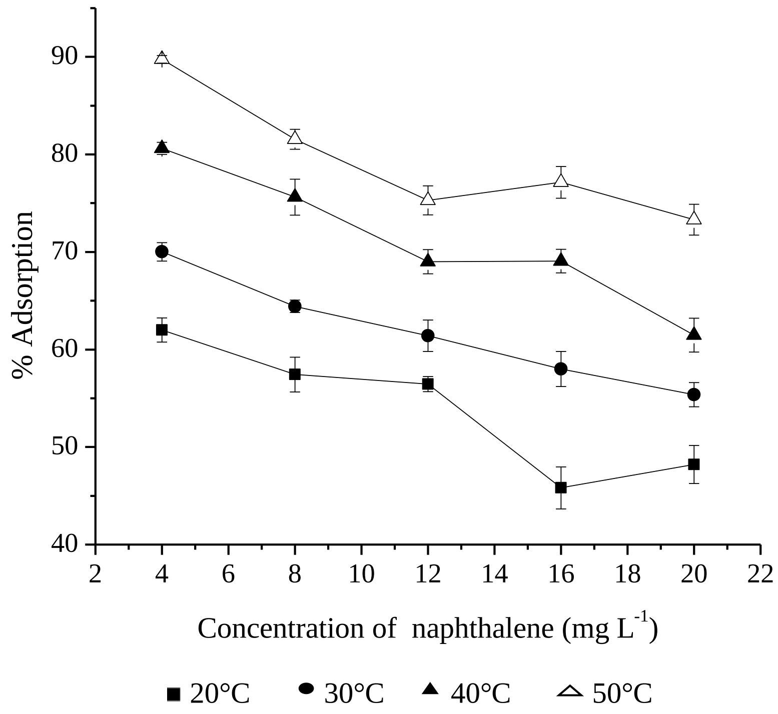

Fig. 6.11: Effect of temperature on adsorption of naphthalene on VTAC

[PAH] = 20 mg L^{-1}; Shaking time = 120 min; pH = 7; adsorbent = 5 mg

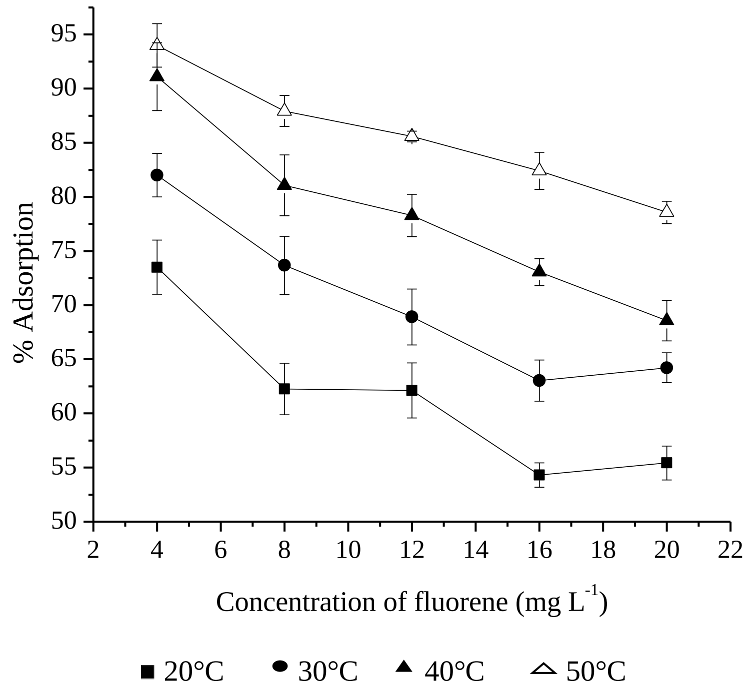

Fig. 6.12: Effect of temperature on adsorption of fluorene on VTAC

[PAH] = 20 mg L^{-1}; Shaking time = 120 min; pH = 7; adsorbent = 5 mg

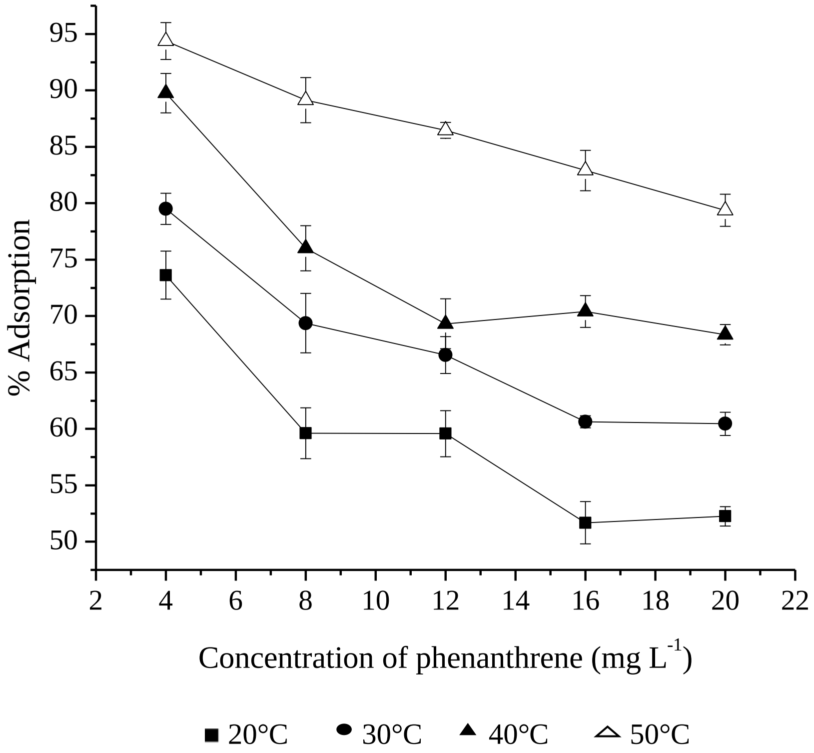

Fig. 6.13: Effect of temperature on adsorption of phenanthrene on VTAC
[PAH] = 20 mg L^{-1}; Shaking time = 120 min; pH = 7; adsorbent = 5 mg

6.2.6 Modelling of adsorption isotherms

Langmuir adsorption isotherm plots were drawn between 1/qe and 1/Ce (Fig. 6.14, 6.15 and 6.16). The slope and intercept of the straight lines observed were used to calculate Langmuir adsorption constants Q° and b. Similarly, Freundlich adsorption isotherm plots between log qe and log Ce were straight line and the constants n and K_f were evaluated using slope and intercept values (Fig. 6.17, 6.18 and 6.19). The Langmuir and Freundlich constants along with R^2 values for adsorption of PAHs on VTAC at different temperatures are presented in Table 6.2. The R^2 values clearly indicate that the data fitted better to Freundlich isotherm.

The R_L values calculated according to the above equation were in the range 0.0396 to 0.6578 for all PAHs which suggest the adsorption to be favourable (R_L> 1 Unfavorable, R_L= 1 Linear, 0 <R_L< 1 Favorable, R_L=0 Irreversible) [37].

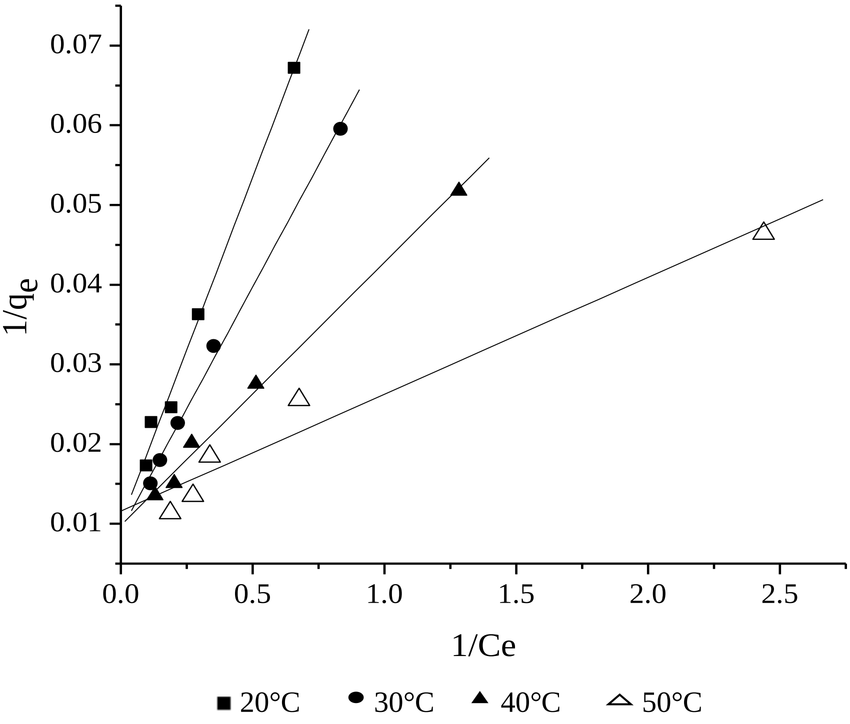

Fig. 6.14: Langmuir adsorption isotherms for naphthalene-VTAC system at different temperatures

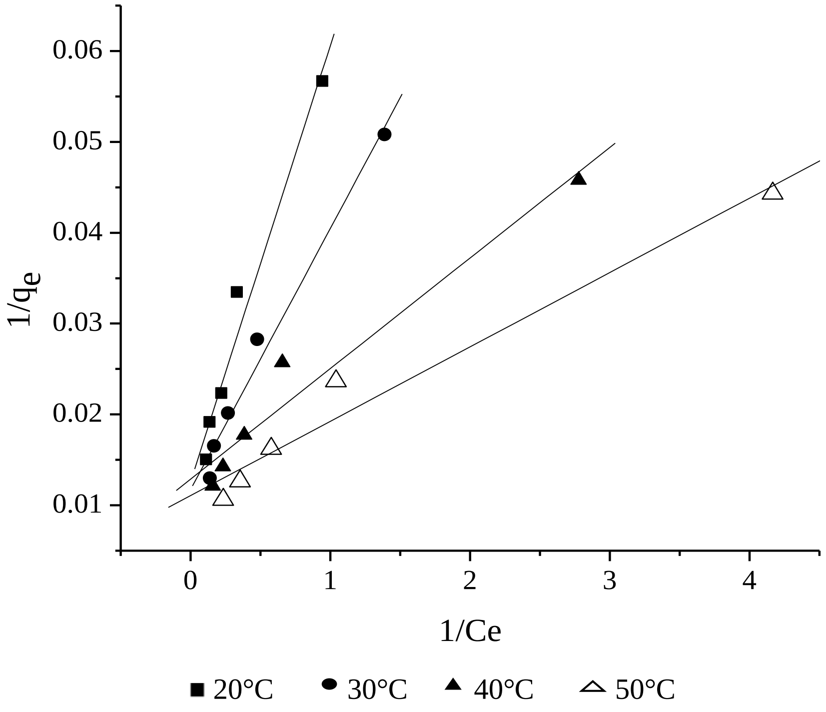

Fig. 6.15 Langmuir adsorption isotherms for fluorene-VTAC system at different temperatures

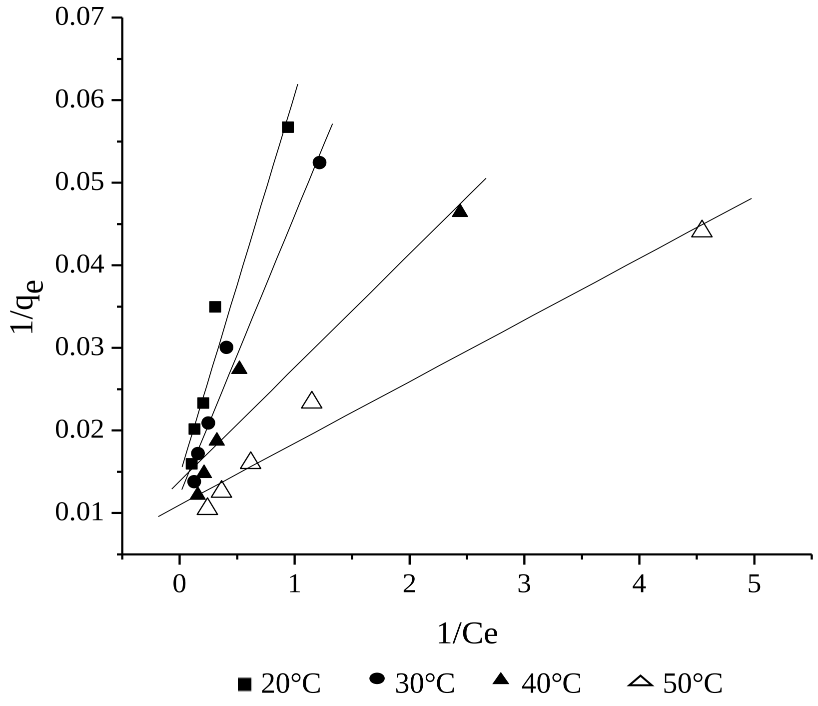

Fig. 6.16: Langmuir adsorption isotherms for phenanthrene-VTAC system at different temperatures

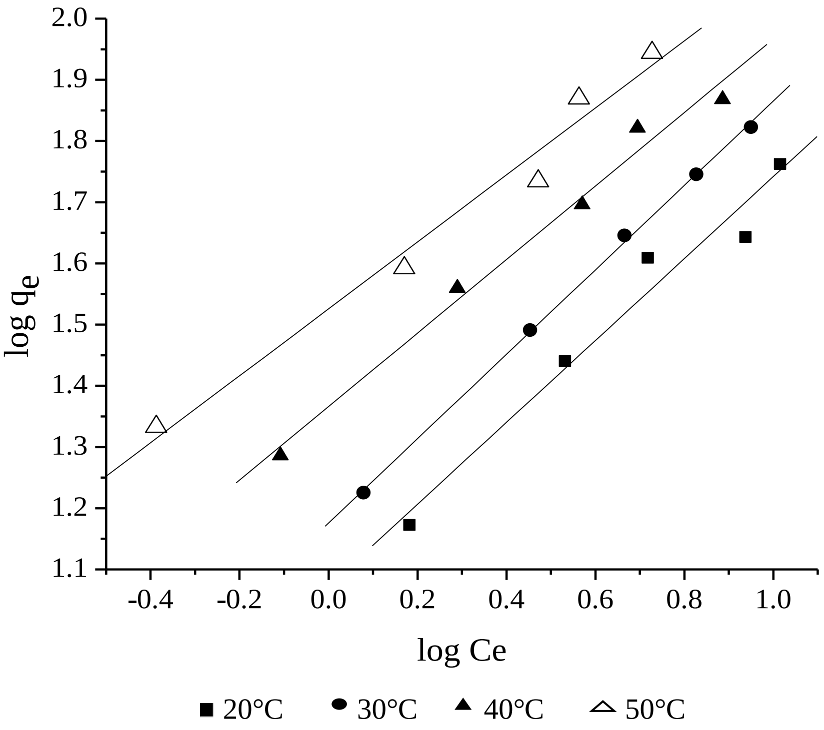

Fig. 6.17: Freundlich adsorption isotherms for naphthalene-VTAC system at different temperatures

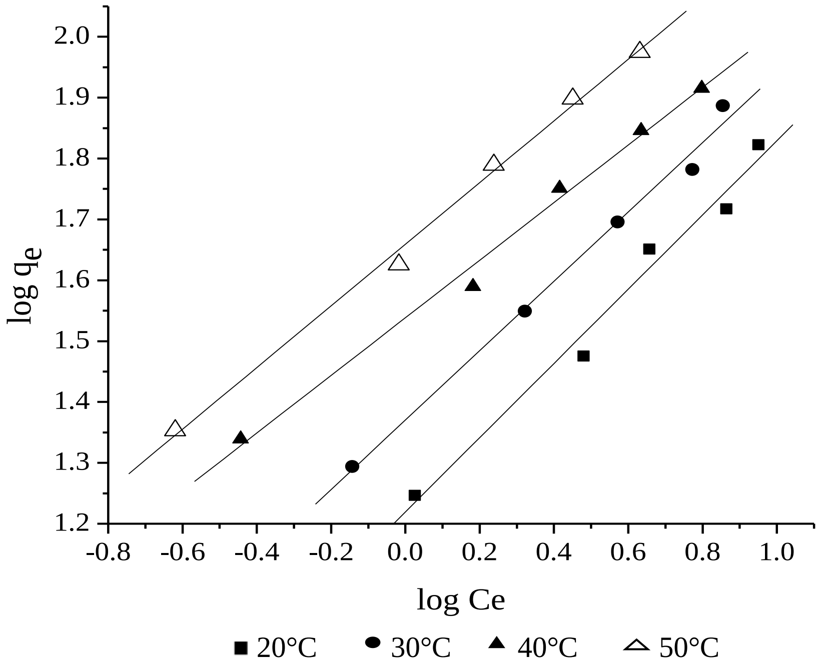

Fig. 6.18: Freundlich adsorption isotherms for fluorene-VTAC system at different temperatures

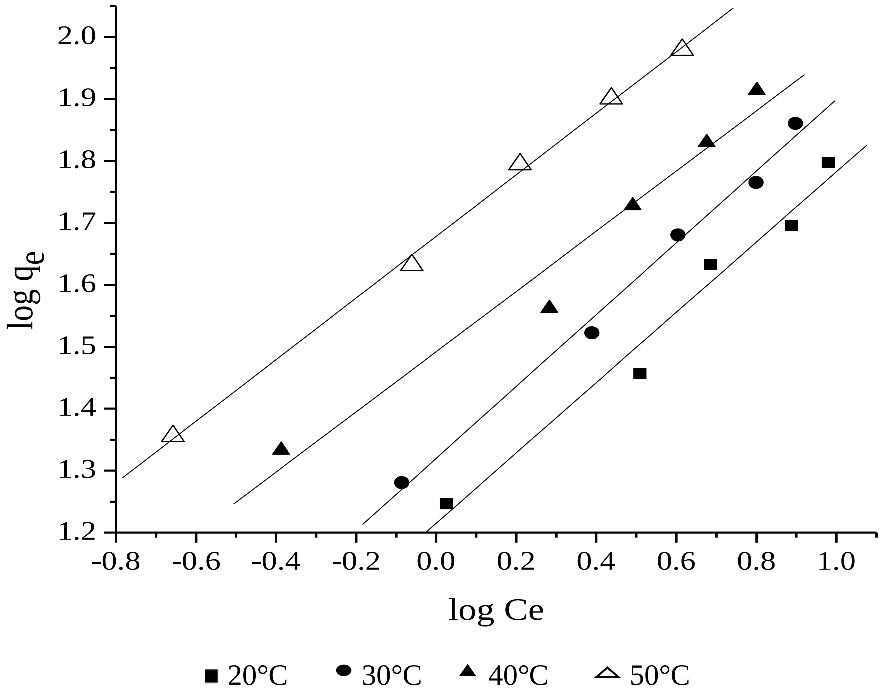

Fig. 6.19: Freundlich adsorption isotherms for phenanthrene-VTAC system at different temperatures

Table 6.2: Langmuir and Freundlich constants and R^2 values for PAHs adsorption on VTAC at different temperatures

	Naphthalene				**Fluorene**				**Phenanthrene**			
Langmuir Parameters												
	20°C	**30°C**	**40°C**	**50°C**	**20°C**	**30°C**	**40°C**	**50°C**	**20°C**	**30°C**	**40°C**	**50°C**
Q^o(mg/g)	86.20	99.01	114.94	138.88	79.36	85.47	101.01	113.63	68.49	81.30	93.45	109.89
b(L/mg)	0.13	0.16	0.26	0.48	0.2625	0.35	0.69	1.07	0.31	0.36	0.77	1.21
R^2	0.9417	0.9369	0.9547	0.9574	0.9684	0.9815	0.9554	0.9668	0.952	0.9743	0.921	0.9704
Freundlich Parameters												
n	1.45	1.49	1.66	1.82	1.63	1.75	1.97	2.11	1.76	2.04	2.14	2.28
K_f	11.81	14.98	23.23	33.55	16.57	23.45	34.53	45.62	16.79	24.54	35.41	47.65
R^2	0.966	0.999	0.9856	0.9780	0.9812	0.9918	0.9922	0.9963	0.9758	0.9929	0.9691	0.998

6.2.7 Kinetics of adsorption

The rate constants for the adsorption of PAHs on VTAC were studied using Lagergren pseudo-first order [38] and pseudo-second order model by Ho and McKay [39]. For pseudo-first order model following expression has been used.

$$\log (q_e - q_t) = \log q_e - (K_1/2.303)\, t \qquad (1)$$

where q_e and q_t denote amount of PAH adsorbed per gram of adsorbent at equilibrium and at time t and K_1 is rate constant. Plots were drawn between log (q_e - q_t) and t for the adsorption of all the three PAHs (Fig. 6.20). The plots obtained are straight lines with R^2 values >0.97.

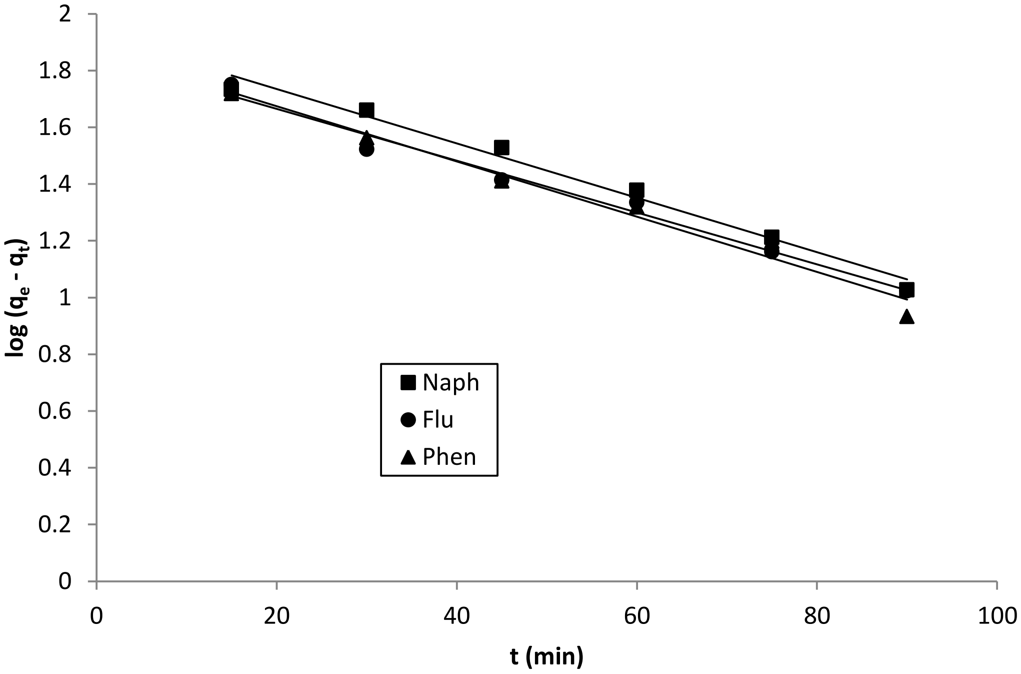

Fig. 6.20: Pseudo first order plots for adsorption of PAHs on VTAC

The pseudo-second order model is given by the following equation-

$$t/q_t = (1/K_2 q_e^2) + (1/q_e)t \qquad (2)$$

where q_e and q_t denote amount of PAH adsorbed per gram of adsorbent at equilibrium and at time t and K_2 is rate constant for pseudo-second order model. The pseudo-second order plots between t/qt and t are straight lines (Fig. 6.21) with R^2 values <0.90. The rate constants K_1

and K_2 evaluated from the pseudo first order and pseudo-second order plots along with R^2 values for each PAH are given in Table 6.3. High values of correlation coefficients suggest better applicability of pseudo-first order kinetic model for PAH adsorption on VTAC.

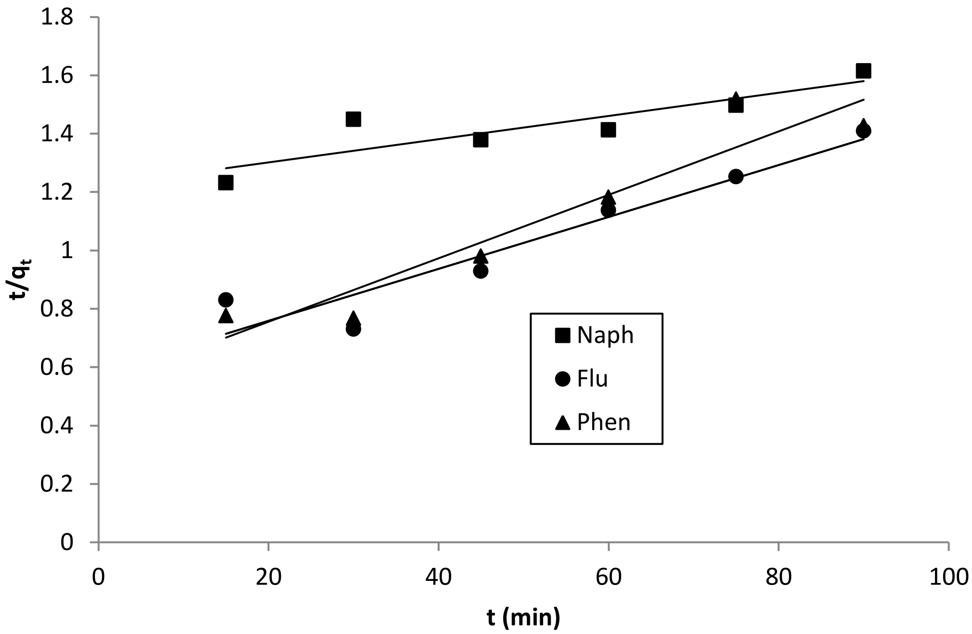

Fig. 6.21: Pseudo second order plots for adsorption of PAHs on VTAC

6.2.8 Intra-particle diffusion model

Adsorption data was subjected to intra-particle diffusion model which is expressed by the following equation:

$$q_t = k_i t^{0.5} + C \quad (3)$$

where qt is the amount of PAH adsorbed per gram of the adsorbent at time t, K_i is the rate constant for intra-particle diffusion and C is the measure of boundary thickness. The plots drawn between amount of PAH adsorbed and square root of time are straight lines which do not pass through the origin (Fig. 6.22). The intra-particle particle rate constants along with correlation coefficients are given in Table 3. The high values of the correlation coefficient suggest that the adsorption of PAHs occur due to intra-particle diffusion. However, the straight lines observed do not pass through the origin, indicating that the adsorption is not solely controlled by intra-particle diffusion, but some other mass transfer mechanisms, occur simultaneously.

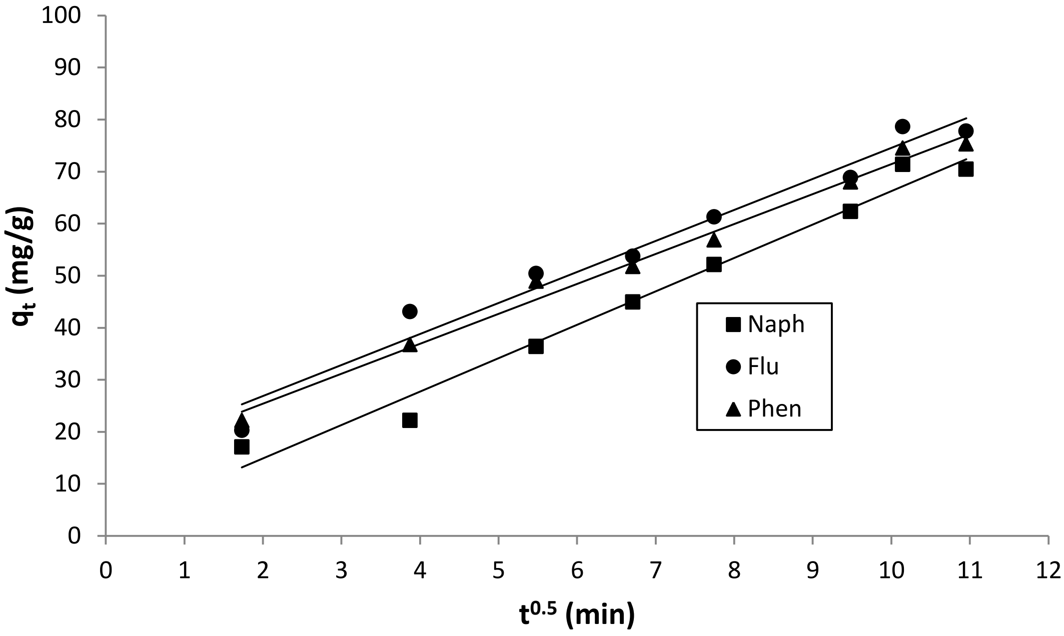

Fig. 6.22: Intra-particle diffusion plots for adsorption of PAHs on VTAC

Table 6.3: Kinetics parameters for pseudo-first order, pseudo-second order and intra-particle diffusion model

	Pseudo-first order model		**Pseudo-second order model**		**Intra-particle diffusion model**	
PAH	**K_1**	**R^2**	**K_2**	**R^2**	**K_i**	**R^2**
Naphthalene	0.0221	0.9837	1.32×10^{-5}	0.8695	8.079	0.9822
Fluorene	0.0209	0.9820	1.36×10^{-4}	0.9084	7.236	0.9635
Phenanthrene	0.0214	0.9768	2.21×10^{-4}	0.8987	7.541	0.9887

6.2.9 Thermodynamic parameters

Thermodynamic studies provide essential information towards the spontaneity and nature of an adsorption process. Thermodynamic parameters, Gibb's free energy change, (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°), for the adsorption of PAHs on VTAC were evaluated from Langmuir isotherms using the following equations:

$$\Delta G° = -RT \ln K_a \quad (4)$$

and

$$\Delta G° = \Delta H° - T\Delta S° \quad (5)$$

where R is the universal gas constant (8.314 JK^{-1} mol^{-1}), T is the absolute temperature in Kelvin and K_a is the equilibrium constant obtained from Langmuir adsorption isotherms. The values of Gibb's free energy change, for the adsorption process were calculated using Langmuir equilibrium constants at varying temperatures (Table 4). The plot of Gibb's free energy change, against temperature, T, was found to be linear. The values of the entropy change and enthalpy change were evaluated from the slope and intercept, respectively (Table 6.4). Negative values of ΔG° suggest the adsorption process to be spontaneous. A decrease in ΔG° values with the increase in temperature indicate that the adsorption of PAHs on VTAC is favourable at high temperatures. Positive values of the enthalpy change and the entropy change suggest the endothermic nature of the adsorption process and good affinity of PAHs towards the prepared activated carbon.

Table 6.4: Thermodynamic parameters for the adsorption of PAHs on VTAC

-ΔG°(KJ mol^{-1})					**ΔH°**	**ΔS°**
	20°C	**30°C**	**40°C**	**50°C**		
Naphthalene	6.922	7.692	9.160	11.116	34.550	0.1405
Fluorene	9.197	10.284	12.367	13.921	38.616	0.1625
Phenanthrene	9.824	10.510	12.825	14.437	37.855	0.1615

6.2.10 Desorption studies

Regeneration of the used activated carbon is an important step in adsorption studies. Desorption studies were carried out in batch mode. First of all, adsorption of three PAHs was achieved individually on 20 mg VTAC from 30 mL of 20 mg L^{-1} PAH solution under optimised conditions. For desorption studies, the adsorbent loaded with adsorbed PAH was agitated with 30 mL of 50 % ethanolic solution of NaOH (0.1 M, 0.5 M and 1M) for 30 min and the solution was analysed periodically after 5 min to determine the concentration of desorbed PAH. It is clear from the results (Table 6.5) that desorption is enhanced by increasing the concentration of NaOH in the solution. Maximum desorption of naphthalene, fluorene and phenanthrene from VTAC is achieved with 1.0 M NaOH (50% ethanolic solution).

Table 6.5: Effect of time on the desorption of PAHs with varying NaOH concentrations

	Desorption (%)								
	Naphthalene			**Fluorene**			**Phenanthrene**		
NaOH **Time**	**0.1 M**	**0.5 M**	**1 M**	**0.1 M**	**0.5 M**	**1 M**	**0.1 M**	**0.5 M**	**1 M**
5 min	35.45	57.40	69.32	30.65	55.40	62.12	27.92	50.97	65.20
10 min	44.95	66.40	77.35	38.42	60.57	73.01	37.40	59.02	71.02
15 min	53.60	73.52	89.20	51.15	67.80	82.20	47.75	68.47	80.12
20 min	62.45	79.75	94.50	57.77	76.55	93.07	54.07	71.32	90.35
25 min	62.87	84.42	97.27	57.42	77.27	94.10	54.17	71.50	91.60
30 min	63.10	84.87	96.87	57.60	76.40	93.52	54.35	71.42	91.57

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Conclusions

Revolutionary increase in the basic needs of human beings and their fulfilment through the development of novel techniques or equipments has resulted in rigorous pollution all over the world. Large scale industrialisation and urbanisation, mainly in the developing countries, imposes potential impact on the quality of environment. A large number of pollution incidents and cases of severe illness of human beings due to various pollutants have attracted the attention of scientists and toxicologists towards monitoring and remediation of environmental pollutants. Among them, polycyclic aromatic hydrocarbons are globally distributed and persistent environmental contaminants. The extent and seriousness of the potential hazards due to these pollutants has already been defined by various environmental agencies such as USEPA and EC by categorising them as priority pollutants. It is well known that the urban areas are more prone to these contaminants than the rural areas. Therefore, the present study focuses on the assessment of PAH pollution in soil at various sites of the urban city, Delhi and remediation of PAH contamination from different environmental matrices.

Present study is an endeavour to assess the PAH pollution in Delhi. Ten sites with some localised activities were selected. The results of the present study reveal that the soil quality of the various sites of Delhi is getting deteriorated as a result of PAH pollution due to industrial, vehicular, domestic and other anthropogenic activities around the area. The individual PAH concentrations and total PAH concentrations at different sites were compared with Dutch and polish standards. The individual PAH concentrations were several times higher than the Dutch standards and ∑PAHs values corresponded to polluted category i.e. class III with respect to polish standards of PAHs. Results further indicated that PAH concentrations are higher in post-winter season than in pre-winter season. This may be attributed to higher PAH emission in post-winter season due to increased use of heaters, wood and other substances for heating, emission of higher amounts of PAHs through the burning of fuels and slow photochemical degradation. Role of TOC in controlling PAH concentrations in urban soil was found to be insignificant. The isomer pair ratios suggest that the sources of PAHs are mainly pyrogenic in nature in both the seasons. The results of Principal Component Analysis suggest that in both the seasons, sources of B[a]P are different from the sources of other PAHs and the major source of benzo[a]pyrene is vehicular emission. The percentage contributions of different PAH sources were evaluated using PCA-MLR and it was concluded that the vehicular contribution is more in post-winter season. Based on TEQ values sites near inter state bus terminal, sarai kale khan and income tax office have highest carcinogenic potential.

It is evident from the present monitoring studies that PAH contamination is present in different regions of Delhi. The results of PAH monitoring study in Delhi will act as a database for formulating the guidelines for pollution in urban cities and introduction of any legislation, if required. The results also reflect on PAH pollution in urban cities of developing countries where industrialization and urbanization is taking place at a fast pace and the legislations are inadequately implemented.

The photodegradation studies carried out on benzo[a]pyrene and pyrene indicated that the photodegradation of the two PAHs is fastest with goethite among the studied iron oxides. The rate of photodegradation of PAHs in soil increases with the increase in catalyst dose and oxalic acid concentration and decreases with the increase in wavelength of the irradiated light. The rate of degradation of PAHs is faster in acidic and alkaline soils than neutral soils. The photocatalytic degradation of PAHs follows first order rate kinetics in all the cases.

The studies on the identification of metabolites of benzo[a]pyrene and pyrene reveal that the photodegradation of the PAHs occurs through oxidative mechanism. The metabolic pathways seem to be complex and different metabolites were observed in the soils of different pH. During photodegradation of benzo[a]pyrene, metabolite benzo[a]pyrene-[4,5]-dione (m/z 283) was observed in neutral and acidic soil due to full oxidation of benzo[a]pyrene, while in case of basic soil metabolite 4,5-dihydroxybenzo[a]pyrene (m/z 285) was observed due to partial oxidation of benzo[a]pyrene. The metabolite 9-hydoxybenzo[a]pyrene-7,8-dione (m/z 299) was observed in neutral soil only and in acidic and alkaline soils, it was further oxidised to benzo[a]pyrene-4,5-ketol-7,8-dione-9,10-epoxide (m/z 331). Metabolite 5-hydroxybenzo[a]pyrene (m/z 269) was persistent after 120 h in both basic and acidic soils, but was not observed in neutral soil after 120 h. In acidic soil appearance of a metabolite peak at m/z 203 after 120 h indicates the conversion of carcinogen benzo[a]pyrene to smaller PAH, pyrene.

In case of pyrene, metabolites corresponding to naphthalene and its derivatives are persistent after 120 h in basic and neutral soil, but in acidic soil, hydrogenated phenanthrene is persistent after 120 h. The degradation pathways thus indicate that the mutagen pyrene is degraded efficiently in presence of goethite into smaller non-carcinogenic/non-mutagenic hydrocarbons (naphthalene, phenanthrene and their derivatives) after 120 h. Photodegradation studies further reveal that the metabolites of benzo[a]pyrene and pyrene, reported to be toxic, such as diones, diols and epoxides, disappear after 120 h in all the three soils. Thus, the study provides an efficient method for the remediation of PAH contaminated soil surfaces and also provide a data bank for toxicological studies. This study has certain limitations but will definitely serve as a benchmark to predict the fate of PAHs in soils of varying pH. The author is conscious of the fact that metabolites of benzo[a]pyrene and pyrene proposed in different soils, need to be confirmed by some advanced characterization techniques. But there are some constraints for an environmental chemistry laboratory to conduct advanced characterizations, which cannot be always overcome.

The remediation of PAH contaminated water has been achieved using activated carbons prepared from two different waste materials, banana peels (BPAC) and vehicular tires (VTAC). Low molecular weight PAHs, namely, naphthalene, fluorene and phenanthrene on activated carbons will serve as representatives for the adsorption of other PAHs and pollutants. The quantitative adsorption of the studied PAHs is achieved with 10 and 26 mg of BPAC and VTAC, respectively in relatively small contact time. With both the synthesized activated carbons, the adsorption of PAHs follow the order: naphthalene < phenanthrene < fluorene. Low adsorption of naphthalene is attributed to its most hydrophobic character among the studied PAHs. On the other hand, lower adsorption of phenanthrene than fluorene suggests that the adsorption of PAHs is not solely dependent on hydrophobic character, but also on other factors like molecular size, solubility, chemical properties of adsorbate and nature of adsorbent.

The adsorption of PAHs is pH dependent and decreases with the increase in pH for both the adsorbents. The temperature studies indicated the adsorption of PAHs to be endothermic, which is further confirmed by the thermodynamic parameters. The adsorption data is feasible with both Langmuir and Freundlich models and better fitted to Freundlich model. Kinetics of adsorption process is best described by pseudo-first order model and mechanism of adsorption process has been described by intra-particle diffusion model. The adsorbents can be readily regenerated using 50% ethanolic NaOH solution which is cheap and easily available. The surface area and adsorption capacity of BPAC is higher than the VTAC. The results of the study suggest that BPAC and VTAC are cheap and efficient adsorbents developed from such waste materials which are generated in large quantities on daily basis.

The study thus provides a solution to the waste disposal problem. It is important to mention that author is aware of the fact that open burning of tire is not advisable and is banned by the environment protection agencies. Therefore, it is necessary to produce activated carbon in high temperature purpose built furnaces for the abatement of pollution, which is not banned, rather supported by the environment agencies such as EPA (EPA 183/10, 2001).

The present study has been helpful in gauging the level of PAHs pollution in the soils of Delhi at various sites and assessment of the overall situation. The data can be useful for various government and non-government organisations for identifying the areas for improvement and for designing environment related policies. The present study mainly focuses on pollution through thermal power plants, vehicular traffic and crematorium in Delhi, but the data may reflect on the status of pollution in other urban areas of India. It will not be improper to say that a similar condition of the urban environment may prevail in some other developing nations.

On the basis of the results of the present study, some suggestions are proposed by the author to control the pollution levels in the soil surfaces and aqueous bodies. The environment protection agencies should implement strict laws and keep an eye on industries and their treatment plant for the implementation of laws. The thermal power plants and other pollution causing industries should be placed outside the cities. The soil quality of the urban cities should be regularly monitored for the levels of the pollutants. The identified areas of pollution such as sites in the vicinity of heavy traffic areas, cremation grounds, bus stops and power plants should be remediated periodically using suitable techniques. Proper monitoring and upgradation of existing treatment plants and installation of new treatment plants, wherever necessary, is strictly recommended. The common treatment plants should be installed and connected to various small scale industries to ensure that no liquid or solid waste reaches any environmental segment without proper treatment. New, cheap and more efficient activated carbons should be tested and incorporated in the treatment plants.

Because of time constraints the data presented in the thesis is based on limited sampling and conclusions serve only as an indicator of the state of pollution.

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