SYNTHESIS AND CHARACTERIZATION OF MIL-101(Cr) AND ZnO@MIL-101(Cr) FOR PHOTOCATALYTIC DEGRADATION OF PHENANTHRENE

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by

USMAN ABUBAKAR ADAMU

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To all my other family members, thank you so much for your love, prayers, support and encouragement. Also, I am grateful to the many wonderful people who have grown to become my well-wishers throughout my PhD journey. As we all know there is always a woman behind the success of a man and for me it's my better half. My love, thanks to my dearest wife Jamila Adamu Ardo for her love, patient, taking care, support, and prayers. I would never been able to achieve this success without you. You sacrificed your time with patience and stood firm to give me encouragement in every difficult moment. Last but not least it's time to appreciate my daughters Fateema

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LIST OF ABBREVIATIONS

AA	Ascorbic acid
AAS	Atomic Absorption Spectroscopy
AB92	Acid Blue 92
AOP	Advanced Oxidation Process
B.P.	Boiling Point
BET	Brunauer-Emmet-Teller
BJH	Barret-Joyner-Halenda
BP	Banana Peel
CB	Conduction Vand
DMF	Dimethylformamide
DR80	Direct red 80
DSSC	Dye sensitised cells
EDTA	Ethylenediamminetetraacetic acid
EIS	Electrochemical Impedance Spectroscopy
FCC	Face centred cubic
FTIR	Fourier Transform Infrared spectroscopy
FWHM	Full width at half maximum
GO	Graphene oxide
HF	Hydrogen fluoride
HKUST	Hongkong University of Science and Technology
HMW	High Molecular weight
HOMO	Highest Occupied Molecular Orbitals
IPA	Isopropanol
IUPAC	International Union of Pure and Applied Chemistry
LED	Light emitting diode
LLDP	Linear Low-density polyethylene

LMW	Low molecular weight
LNR	Liquid natural rubber
LUMO	Lowest unoccupied molecular orbital
M.P.	melting point
MB	Methyl blue
MG	Methyl green
MIL	Material Institute Lavoisier
MO	Methyl orange
MOFs	Metal-organic frameworks
NAD	Nitrogen adsorption desorption
NPs	Nanoparticles
NR	Natural rubber
NR-PVP	Natural rubber-polyvinylpyrrolidone
NTs	Nanotubes
PAHs	Polycyclic Aromatic Hydrocarbons
PCPs	Personal Care Products
PDMS	Polymethylsiloxane
PHE	Phenanthrene
PL	Photoluminiscence
Ppm	Part per million
RHA-PANI	Rice husk ash-polyaniline
RhB	Rhodamine blue
ROS	Reactive oxygen species
SBU	Secondary building units
SEM-EDX	Scanning electron microscopy-energy dispersive x-ray
SPR	Surface Plasmon Resonance
SRB	Sulforhodamine B

SSNTs	Stainless steel nanotubes
TC	Tetracycline
TGA	Thermogravimetry Analysis
UiO	University of Oslo
USEPA	United State Environmental Protection Agency
UV	Ultraviolet
UV/Vis	Ultraviolet/ visible
UV-VIS DRS	Ultraviolet/ visible diffuse reflectance spectroscopy
VB	Valence Band
WHO	World Health Organization
XPS	X-ray Photoelectron Spectroscopy

LIST OF APPENDICES

SINTESIS DAN PENCIRIAN MIL-101(Cr) DAN ZnO@MIL-101(Cr) UNTUK PENGURAIAN FOTOKATALITIK PHENANTHRENE

ABSTRAK

Dalam kajian ini, kaedah hidroterma suhu rendah digunakan untuk menyediakan kerangka logam organik MIL-101(Cr) yang sangat berliang dan jelas. Satu siri MOF berasaskan kromium (MIL-101) disintesis pada suhu yang berbeza: 150, 160, 170, 180, 200, dan 220 ºC. MOF yang disintesis dicirikan menggunakan pelbagai teknik. Keberkesanan fotopemangkin yang disintesis ini dinilai untuk penguraian fotopemangkinan phenanthrene (PHE) di bawah pendedahan cahaya UV. Kemerosotan 98% PHE dicapai dalam masa 150 minit penyinaran cahaya UV menggunakan MIL-101@160 di bawah keadaan optimum tertentu, termasuk kepekatan PHE 2 ppm, pH 7, dan dos pemangkin sebanyak 30 mg. Kecekapan penguraian yang lebih baik oleh MIL-101@160 boleh dikaitkan dengan luas permukaan yang tinggi dan kestabilan terma. ZnO disintesis melalui kaedah biosintesis dan kemudiannya digunakan untuk menghasilkan nanokomposit ZnO@MIL-101(Cr), pada suhu 160 ºC dan 220 ºC. Nanokomposit ini dicirikan menggunakan analisis spektroskopi inframerah transformasi fourier, pembelauan sinar-X, mengimbas mikroskop, specktroscopi fotoelektron sinar-X, sinaran ultralembayung-nampak dan photoluminescence. Keberkesanan pemangkin ZnO@MIL-101(Cr) dinilai untuk penguraian PHE, di bawah sinaran UV dan cahaya nampak. Kesan parameter yang berbeza seperti, pH larutan, kekuatan sumber pemangkin cahaya, kebolehgunaan semula pemangkin, dan kesan suhu pada degradasi PHE telah dinilai. Fotopemangkin yang disintesis mempamerkan kinetik pseudo-peringkat pertama, dengan pemangkin yang paling cekap iaitu ZnO@MIL-101(Cr)@220 mencapai kadar penguraian 98%

selepas 150 minit pendedahan cahaya nampak. Tambahan pula, nanokomposit ZnO@MIL-101(Cr)@220 telah diimobilasasi pada getah asli-polivinil pirrolidon (NR-PVP) menggunakan kaedah taburan. Filem komposit ini, dinotasi sebagai 1% ZnO@MIL-101 / NR-PVP, 3% ZnO@MIL-101 / NR-PVP, dan 5% ZnO@MIL-101 / NR-PVP, disediakan dengan jumlah nanokomposit ZnO@MIL-101 yang berbeza. Analisis struktur dan morfologi menunjukkan bahawa taburan nanokomposit sama rata dan diintegrasi ke dalam matriks NR-PVP. Prestasi pemangkin filem ini disiasat untuk penguraian PHE di bawah cahaya nampak. Hal ini adalah bertujuan untuk mengkaji pengaruh berat pemangkin, pH larutan, kepekatan PHE, suhu, dan kebolehgunaan semula filem-filem untuk penguraian PHE. Dalam semua kes, mangkin yang disintesis mengikuti kinetik pseudo-peringkat pertama, dengan pemangkin filem yang paling berkesan adalah 98% kecekapan selepas 150 minit pendedahan cahaya nampak. Selain itu, pemangkin filem yang disediakan mudah diasingkan dan dapat digunakan semula sebanyak lapan kitaran.

SYNTHESIS AND CHARACTERIZATION OF MIL-101(Cr) AND ZnO@ MIL-101(Cr) FOR PHOTOCATALYTIC DEGRADATION OF PHENANTHRENE

ABSTRACT

In this study, a low-temperature hydrothermal method was employed to prepare highly porous and well-defined MIL-101(Cr) metal-organic frameworks. A series of chromium-based MOFs (MIL-101) was synthesized at different temperatures: 150, 160, 170, 180, 200, and 220 ºC. The synthesized MOFs were characterized using various techniques. The effectiveness of these synthesized photocatalysts was assessed for the photocatalytic degradation of phenanthrene (PHE) under UV light exposure. Remarkably, 98% degradation of PHE was obtained within 150 minutes of UV light irradiation with MIL-101@160 under specific optimized conditions, which included a PHE concentration of 2 ppm, pH 7, and a catalyst dosage of 30 mg. The enhanced degradation efficiency of MIL-101@160 could be attributed to its high specific surface area and thermal stability. ZnO was synthesized through a biosynthesis method and subsequently utilized to fabricate ZnO@MIL-101(Cr) nanocomposites, with preparation carried out at temperatures of 160 ºC and 220 ºC, respectively. These catalysts were characterized using fourier tranform infrared, X-ray diffraction, Scanning Electron Microscopy, X-ray Photoelectron Spectroscopy, ultraviolet-visible diffuse reflectance spectroscopy, and photoluminescence analyses, The effectiveness of the ZnO@MIL-101(Cr) nanocomposite in photocatalysis was evaluated for the degradation of PHE, utilizing both UV and visible light irradiation. The effect of different parameters such as solution pH, catalyst loading, the source of light, catalyst reusability, and the effect of temperature on PHE degradation were evaluated. The prepared photocatalysts were found to follow a pseudo-first-order kinetics, with the most efficient catalyst ZnO@MIL-101(Cr)@220 achieving a remarkable 98% degradation after 150 minutes of visible light exposure. Furthermore, the ZnO@MIL-101(Cr) nanocomposites were immobilized on natural rubber-polyvinyl pyrrolidone (NR-PVP) using the strewn method. These composite films, designated as 1% ZnO@MIL-101/NR-PVP, 3% ZnO@MIL-101/NR-PVP, and 5% ZnO@MIL-101/NR-PVP, were prepared with varying amounts of the ZnO@MIL-101 nanocomposite. The morphological and structural analyses demonstrated that the catalysts were evenly dispersed and integrated into the NR-PVP matrix. The photocatalytic performance of these film photocatalysts were investigated in the degradation of PHE in visible light. The focus was on examining the influence of solution pH, pollutant concentration, catalyst loading, temperature, and the reusability of the films on PHE degradation. In all cases, the synthesized photocatalysts followed pseudo-first-order kinetics, with the most effective film photocatalyst having 98% efficiency after 150 minutes of visible light exposure. Moreover, these prepared film photocatalysts were conveniently separated and employed again for as many as eight cycles.

CHAPTER 1
INTRODUCTION

1.1 Background

The demand on "clean" water supplies has increased due to the rapid growth of industry and the human population. The strains on natural resources are growing as the world strives to meet the increased demand for clean water, which is being made worse by unpredictable climate change. Water is the most important natural resource, but freshwater habitat quality is declining. Since clean water is necessary for human development and well-being, protecting water quality and safety has become crucial for governments and water regulatory authorities in order to prevent health issues. According to the World Health Organization's 2017 estimate 844 million people are in danger of drinking polluted water (WHO, 2023). Water supplies are being continuously contaminated with harmful substances. It is an immediate and critical concern in a world that is confronting increasing pollution and limited energy resources. Water pollution depletes the planet's approximately meager 1% supply of freshwater resources. By 2025, two-thirds of the world's population will lack access to pure water, according to the United Nations (UN, 2020).

Human activity pollutes and releases waste into rivers, lakes, and groundwater, which all end up in the oceans. As a result, the water quality is altered, rendering it harmful to the environment, aquatic life, and human consumption. Herbicides, pesticides, textile dyes, and inorganic compounds are only a few examples of water contaminants such as heavy metals, mercury, cadmium, lead etc. (Ahmad et al., 2022; Tzanakakis et al., 2020). Moreover, widespread use of new contaminants, such as endocrine disrupting substances (EDS), personal care products (PCPs), and pharmaceutical active substances with mutagenic, genotoxic, and carcinogenic properties, is becoming more common in water resources (Samal et al., 2022; Vinu et al., 2010). These compounds are of increasing concern. It is a threat to human and aquatic life and are being considered by government regulatory agencies around the world. Most of these contaminants are reported to have toxic effects on humans even at very low concentrations. (Patel et al., 2019; Samal et al., 2022).The improper disposal of these contaminants in developing countries is attributed to the unreliability of conventional methods of treatment.

Rapid economic growth, industrial development, and urban expansion, coupled with inadequate investment in fundamental water supply and purification infrastructure, have resulted in water contamination, heightened prevalence of infectious and parasitic illnesses, and greater vulnerability to industrial pollutants, heavy metals, and algal toxins (Chen et al., 2020; Ferronato & Torretta, 2019). Polycyclic aromatic hydrocarbons (PAHs) are a group of organic compounds made up of fused-benzene rings. PAH have been identified as one of the major by-products released from petroleum and petrochemical industries (Balmer et al., 2019). They constitute the vast majority of the components of petroleum products, which are typically released into the water bodies by both anthropogenic and natural processes. The extraction of coal, the manufacture of coke, the pyrolysis of oil shale, the production of petrochemicals, the processing of textiles and leather, and other processes are some of the sources from which PAHs enter the environment (Ghosh & Mukherji, 2021; Shi et al., 2021;). PAHs consist of mainly carbon and hydrogen atoms only which are bonded in a benzene ring in a linear or angular arrangements. Out of the many known PAHs, sixteen have been identified as the high priority pollutants. These 16 PAHs including phenanthrene (PHE) are of environmental concern due to their potential toxicity to people and other creatures, as well as their abundance and persistence in the environment. Many PAHs are either recognized or are likely carcinogens (Bratovčić, 2019).

Accompanied by the expansion of industries, rapid urban growth, and swift economic progress, water pollution has emerged as a significant environmental concern in Nigeria. Many urban centers and rural areas have experienced substantial economic advancement, resulting in increased waste generation. The inadequate waste management infrastructure, particularly the presence of unlined dumpsites, poses a serious threat to the environment due to the seepage of harmful leachates ,(Aralu et al., 2023). These leachates contain a mixture of organic and inorganic pollutants, posing a threat to ecosystems if not adequately treated before release. PAH pollution in the environment stems from various sources, including leachates from domestic and agricultural waste and the discharge of untreated industrial effluents. PAHs, which are widespread organic compounds, are produced during combustion processes involving biomass, fossil fuels, waste materials, and industrial operations. PAHs are present in the environment at low concentrations because of their poor biodegradability and challenges in elimination (Adeniji et al., 2017; Wang et al., 2018) Moreover, these compounds have biological effects, including impacts on blood-related parameters and developmental toxicity. PAH contamination of groundwater and surface water can occur through leaching from landfills, oil spills, and the combustion of fossil fuels, drawing worldwide concern. Residents living near waste sites may be exposed to PAHs through contamination of borehole water by leachates (Iwegbue et al., 2019).

In recent times, researchers have developed photocatalytic nanomaterials and nanocomposites aimed at eradicating environmental contaminants (Deshmukh et al., 2021). These materials facilitate oxidation and reduction reactions during the photocatalytic process, utilizing light and semiconductors. They demonstrate exceptional stability and offer a non-toxic, economical, and straightforward operation with minimal risk of secondary pollution. Devanesan et al. (2023) reported the novel photocatalyst g–C_3N_4–Ag nanocomposite by thermal heating for photocatalytic degradation of PHE. The prepared g–C_3N_4–Ag composite proved to be a strong photocatalyst in the removal of phenanthrene from simulated water under sunlight and UV light. Although these materials proved to be good potential photocatalyst, However, Because of the lower exploitation of visible light, rapid recoupling of light-generated electron-hole pairs, and low surface area, the photocatalytic efficiency of g-C_3N_4 is insufficient and harder to employ practically (Dai et al., 2022). Hence, the need to further synthesize. MOFs-based photocatalyst for enhanced visible light harvesting and rapid recombination of electron-hole pairs.

The United States Environmental Protection Agency (USEPA) has strict laws in place to get rid of these potentially dangerous substances.

Metal-organic frameworks (MOFs) and ZnO nanoparticles have been introduced to address wastewater issues for the aforementioned contaminants. Both MOFs and ZnO nanoparticles may serve as a viable tertiary treatment. Although there has been a lot of global research on photocatalysts (Ji et al., 2021), less work has been focused on MOFs, especially MIL-101(Cr) and ZnO for degradation of PHE.

1.2 Problem Statement

MIL-101(Cr) is commonly synthesized using hydrofluoric acid (HF). This acid serves as a mineralizing agent and improves the crystallization process of MIL-101(Cr) in the hydrothermal reaction. However, HF is highly corrosive and can be poisonous, demanding even greater caution in its handling compared to other mineral acids. Due to its low dissociation constant, HF penetrates tissue more swiftly than conventional mineral acids, potentially leading to poisoning incidents. Hence, it is imperative to find an alternative way for the synthesis of MIL-101(Cr) while preserving the properties of MIL-101(Cr), such as their exceptionally large specific surface area and porosity. Subsequently, MOFs have emerged as prevalent catalysts for the degradation of organic pollutants in aqueous environments. However, it is important to broaden their range of responsiveness of MIL-101(Cr) to visible light. and address the intricate issue of photogenerated charge carriers. The introduction of ZnO nanoparticles into MIL-101(Cr) can improve dispersion as well as reduce aggregation of the ZnO NP. Thus, it indirectly reduces the rapid electron-hole pairs recombination of the nanocomposites. Furthermore, it can result in the reduction of the bandgap compared to the original MOFs, achieved through the creation of a heterostructure Younis et al., (2020). This can promote adsorption in the visible region. As such the synergistic effect of ZnO NP and MIL-101(Cr) can effectively degrade PHE using visible light.

To date, several studies on the catalytic application of MIL-101(Cr) in the degradation of organic pollutants have been reported. However, to the best of knowledge, no report has been made on the acid-free synthesis as well as the incorporation of ZnO into MIL-101(Cr) and its application in the photocatalytic degradation of PHE. Therefore, in the present work MIL-101(Cr) and ZnO@MIL-101(Cr) are synthesized using acid-free technique and their roles as suitable photocatalyst in the degradation PHE in aqueous solutions were systematically carried out and reported for the first time. The PHE was determined using UV spectrophotometry.

1.3 Research Objectives

The specific objectives for this study are:

1. To investigate the relationship between the properties of MIL-101(Cr) prepared using various synthesis parameters towards photodegradation of PHE under UV light.
2. To investigate the role of bio-inspired ZnO nanoparticles in the modification of MIL-101(Cr) properties for visible light degradation of PHE.
3. To study the potential of strewn ZnO@MIL-101/NR-PVP composite films towards the photodegradation of PHE under visible light irradiation.

1.4 Scope of Research

The focus of this research is on the synthesis and characterization of MIL-101(Cr), ZnO@ MIL-101(Cr) and ZnO@MIL-101(Cr) immobilized on NR-PVP films for the photocatalytic degradation of PHE. Thus, the scope is limited to the acid-free synthesis of MIL-101(Cr) and biosynthesis of ZnO from banana peel. The MIL-101(Cr) photocatalysts were prepared using the acid-free hydrothermal method, in which metal salt solution was mixed with terephthalic acid. Characterization of the prepared photocatalysts was carried out by using different techniques. The chemical states, structural features, morphology, electronic state and functional groups of the photocatalysts were analysed using XRD, Nitrogen adsorption desorption, Scanning Electron Microscopy with Energy Dispersive X-ray Spectrometry (SEM/EDX), X-ray Photoelectron Spectroscopy (XPS) and Fourier Transform Infrared (FTIR) Spectroscopy. The photocatalytic degradation of PHE was carried out under different parameters (effect of catalytic dosage, effect of pH, effect of irradiation time, and effect of temperature) in order to obtain degraded PHE products.

1.5 Thesis Organization

This thesis consists of seven chapters. Chapter 1 highlights the background of the research, problem description and objectives of the research. The scope of the study and thesis organisation were also described.

Chapter 2 outlines an in-depth assessment of the relevant literature review to this work. The occurrences and sources of PAHs into the environment, advanced oxidation process, heterogeneous semiconductor photocatalysis were highlighted. The different methods for the preparation MIL-101(Cr) MOF were described. Furthermore, different methods of modification of MOFs for enhanced photocatalytic activity were also described. Chapter 3 describes the materials and methods used in the study. Different characterization techniques for the prepared materials were also discussed. The chapter also describes the detailed procedure for the photocatalytic degradation of PHE. Chapter 4 discusses the detailed characterizations of MIL-101(Cr) series and their photocatalytic degradation of PHE. Chapter 5 discussed the detailed characterizations of green ZnO, ZnO@MIL-101(Cr) and their photocatalytic degradation of PHE.

Chapter 6 discusses on the characterizations of NR-PVP/ZnO@MIL-101(Cr) films and their photocatalytic degradation of PHE. Chapter 7 summarises the overall research findings and proposed future recommendations.

CHAPTER 2
LITERATURE REVIEW

2.1 Occurrences and Sources of PAHs

Environmental pollution is currently regarded as one of the important areas of research due to the harmful effects of the pollutants in human and the environment. These pollutants include heavy metals, oxides of nitrogen and sulphur, pharmaceuticals, persistent organic pollutants (POP), and PAHs. The US Environmental Protection Agency (USEPA) has categorized some PAHs as primarily regulated pollutants. Furthermore, The International Agency for Research on Cancer found that PAHs are probably carcinogens and a threat to environments and human health (Lamichhane et al., 2016). PAHs contains two or more fused benzene rings which are very hazardous and are characterized by low solubility, high melting and boiling points, low vapour pressure as is shown in Table 2.1. Due to their high levels of toxicity, carcinogenic and mutagenic effect on human, some the PAHs are classified as priority contaminants (Gutierrez-Urbano et al., 2021). PAHs are generally formed as a result of natural phenomenon (through incomplete combustion of coal, crude oil, e.tc.) as well as anthropogenic processes associated with emissions from power plants, coal mining and crude oil spills as shown in Figure 2.1. Some PAHs are believed to originate from biogenic sources which include those formed by algae, plants and microorganisms as well as those formed during the slow alteration of organic matter (Mojiri et al., 2019).

The increasing demand for clean water is driven by rapid population expansion, urbanization, and heightened requirements from agriculture, industry, and energy sectors. This demand surge has surpassed population growth, leading to severe water scarcity affecting half of the world's population for at least one month annually.

Projections indicate that water scarcity will escalate further due to global warming caused by climate change.

According to Pona et al. (2021), the issue of water pollution in Nigeria persists as a major worry. Numerous factors contribute to this problem, encompassing industrial operations, runoff from agriculture, improper disposal of waste, incidents of oil spills, and insufficient facilities for treating wastewater. Here are some key aspects concerning the state of water pollution in Nigeria:

Oil Spills: Nigeria has faced numerous incidents of oil spills in the Niger Delta region, mainly stemming from oil exploration and production activities. These spills have severe consequences on water quality, marine life, and the livelihoods of communities reliant on fishing and agriculture.

Industrial Pollution: Water pollution from industrial sources results from the release of untreated or poorly treated waste into water bodies. Industries such as manufacturing, mining, and chemical processing often discharge harmful substances into rivers and streams, contributing to pollution.

Agricultural Runoff: Water pollution from agriculture arises from the runoff of fertilizers and pesticides into nearby water sources. This runoff carries pollutants like nitrogen, phosphorus, and pesticides, which can degrade water quality and harm aquatic ecosystems.

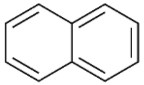
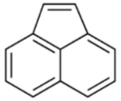
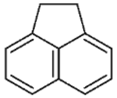
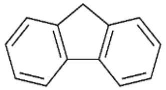
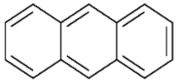
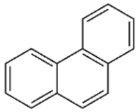
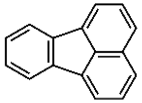
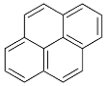
Waste Disposal: Improper disposal of waste, including solid waste and untreated sewage, significantly adds to water pollution in Nigeria. Many communities lack adequate waste management systems, leading to the contamination of surface and groundwater.

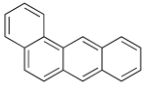
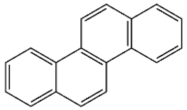
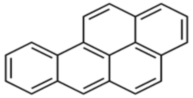
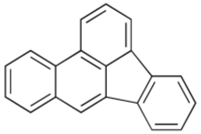
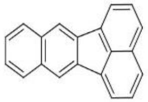
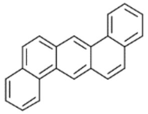
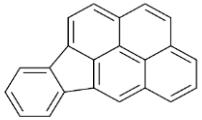
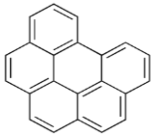
Urbanization: Rapid urban growth in Nigeria puts increased strain on water resources and infrastructure. Inadequate sanitation facilities and the discharge of untreated sewage exacerbate water pollution in urban areas.

Health Impacts: Water pollution poses serious health risks to Nigerian communities, including the spread of waterborne diseases like cholera, typhoid fever, and diarrhea. Exposure to contaminated water sources can also result in long-term health issues from exposure to toxins.

Efforts to combat water pollution in Nigeria involve enforcing environmental regulations, investing in wastewater treatment infrastructure, educating communities on proper waste management, and promoting sustainable agricultural practices. However, challenges such as insufficient funding, weak enforcement, and limited access to clean water and sanitation services impede progress in tackling water pollution (Alum & Okoye, 2020)

Table 2.1 Characteristics of the 16 PAHs priority pollutants.

PAH	Structure	Molecular Formula	Weight (g/mol)	Solubility in water	Melting Point	Boiling Point	Partition coefficient
Naphthalene		$C_{10}H_8$	128.17	3.1	80.26	218	3.37
Acepnathylene		$C_{12}H_{10}$	152.20	16.1	92-95	265-275	4.0
Acenapthene		$C_{12}H_{10}$	154.21	3.8	95	96	3.92
Fluorene		$C_{13}H_{10}$	166.22	1.9	116-117	295	4.18
Anthracene		$C_{14}H_{10}$	178.23	0.0045	218	340-342	4.54
Phenanthrene		$C_{14}H_{10}$	178.23	1.1	100	340	4.57
Fluoranthene		$C_{16}H_{10}$	202.26	0.26	110.8	375	4.58
Pyrene		$C_{16}H_{10}$	202	0.135	150-156	360-404	4.45

Benzo(a) anthracene		$C_{18}H_{12}$	228	0.0094	157-167	435	5.76
Chrysene		$C_{18}H_{12}$	228	0.002	252-256	441-448	4.81
Benzo(a) pyrene		$C_{20}H_{12}$	252	0.0016	177-179	493-496	6.13
Benzo (b) Fluoranthene		$C_{20}H_{12}$	252	0.0008	167-168	481	6.11
Benzo (k) Fluoranthene		$C_{20}H_{12}$	252	0.0015	195-217	471-480	5.78
Dibenzo (a,h) anthracene		$C_{22}H_{14}$	278	0.00249	266-270	524	6.75
Indeno (1,2,3-cd) pyrene		$C_{22}H_{12}$	276	0.00019	162–163	530	6.70
Benzo (g,h,i) perylene		$C_{22}H_{12}$	276	0.00026	275-278	525	6.63

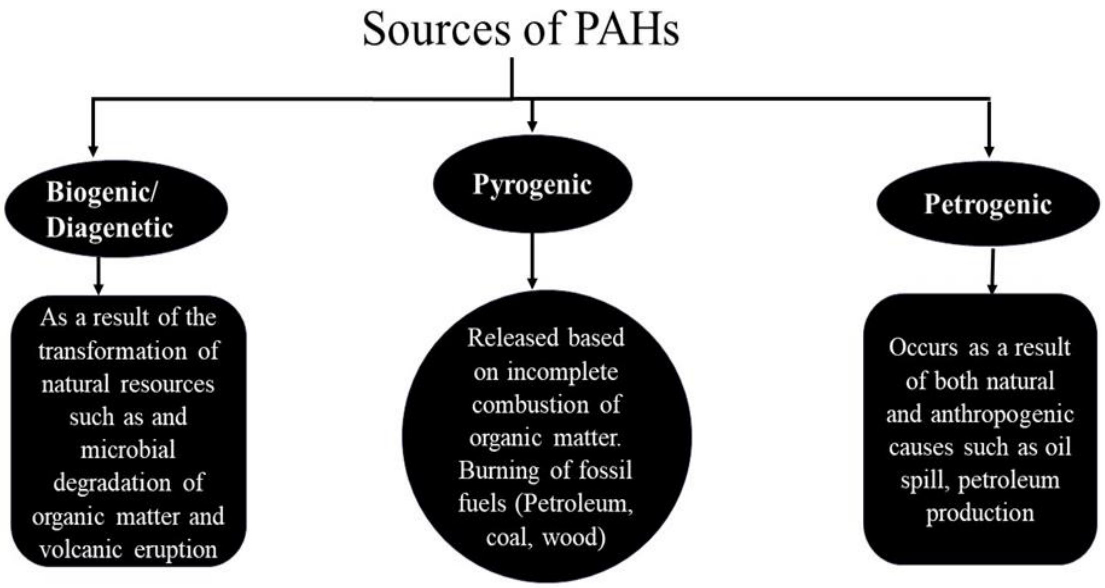


Figure 2.1 Different sources of PAHs

Figure 2.2 shows the schematic diagram through which PAHs gets into the environment from different sources (Akinpelu et al., 2019). PAHs are present in all elements of the environment, including the air, soil, water, and living organisms. They arise from both natural and human activities and can enter the environment through multiple pathways. Volcanic eruptions and forest fires are the primary natural origins of PAHs, releasing them into the atmosphere (Faboya et al., 2020; Patel et al., 2020). The anthropogenic sources of PAHs comprise vehicular emissions, agricultural burnings, power stations, coke facilities, steel mills, foundries, and various industrial outlets. Additionally, PAHs can arise from human activities such as accidental petroleum product leaks, the disposal of sewage sludge, and the management of tarry or creosote waste materials (Abdel-Shafy & Mansour, 2016). There are two categories of human-made PAH sources namely petrogenic and pyrogenic. Petrogenic sources involve the release of PAHs from both crude and processed petroleum, typically due to events like oil spills, inadvertent discharges from regular tanker activities, urban and municipal runoff, and similar occurrences in aquatic environments, whereas pyrogenic PAH are those se arising from the incomplete combustion of fossil fuels and organic matter (Balmer et al., 2019). The release of crude oil is a significant contributor to the presence of PAHs in natural water bodies (Akinpelu et al., 2019). It was estimated that, every year about 5-30 million tons of crude oil spills into the ocean due to either accident or activities of oil tankers (Xie et al., 2017). These origins are linked to the production of PAHs with high molecular weights (Gutierrez-Urbano et al., 2021; Overton et al., 2022). The physicochemical properties and structural feature of 16 priority PAHs are presented in Table 2.1. The structural variation and the arrangement of the aromatic rings are responsible for the properties of PAH compounds. Pure PAHs are usually solid, colourless, and insoluble in water but readily dissolved in organic solvents and less volatile at room temperature. They are generally nonpolar and uncharged organic compounds (Singh et al., 2022).

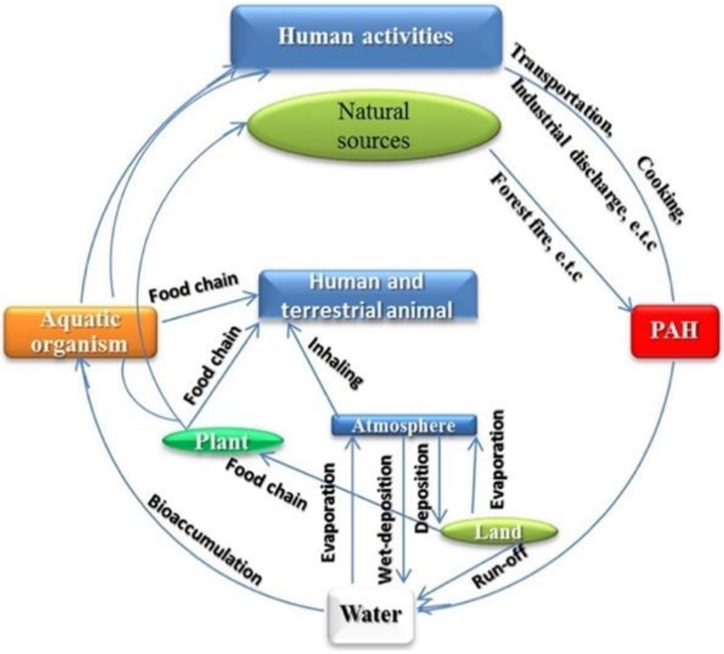


Figure 2.2 Illustrating the environmental cycle of PAHs (Akinpelu et al., 2019).

In addition to the production of petroleum and petrochemicals, the coal processing plant for power generation has also been recognized as another way of PAHs is generated and transported into water bodies (Ihsanullah et al., 2015). Coal is a combination of organic and inorganic components used in a variety of processes, including the production of electricity and the synthesis of chemicals (such as gasoline, ammonia, and urea). The primary components of coal-based facilities are PAHs (Jiao et al., 2017).

2.2 Properties and structure of PAHs

PAHs are organic compounds with two or more fused aromatic rings that are regarded as environmental pollutants due to their intrinsic chemical stability, carcinogenicity and endocrine disruption (Hwang et al., 2007). PAHs are generally classified into two groups as low molecular weight (LMW) and high molecular weight (HMW). Those with less than four aromatic rings are referred to as LMW PAHs, whereas those with four or more aromatic rings are the HMW PAHs that are characterized with very stable, toxic, highly lipophilic and hydrophobic, which allowed them to accumulate in biota (Eldos et al., 2022). The high sorption capacity of PAHs causes them to stay in the environment for a longer period of time. They are adsorbed in the fatty organs of people and other animals because they are lipophilic. The partition coefficient (Log Pow) in water -octanol range from 3.37 to 6.75 (Patel et al., 2020). PAHs with Log Pow greater than 4.5 have higher bioaccumulation rate as is shown in Table 2.1. They also have high melting and boiling points.

2.3 PAHs in water bodies

Many research investigations from around the world have revealed differences in the distribution of PAHs in environmental elements, with water compartments having the highest concentrations (Eldos et al., 2022; Wang et al., 2017). PAHs are extremely hydrophobic and are resistant to undergoing natural degradation. Thus when present in water, they exert harmful effects to aquatic organisms and humans (Gong et al., 2017; Kafilzadeh, 2015). Table 2.2 presents the distributions of PAHs detected in environmental waters across the world. With concentrations varying from mg/L to ng/L, these pollutants have been found in surface waters of the ocean, rivers, and rivers. The European Union’s drinking water standard, which forces the total concentration of PAHs should not exceed 100 ng/L whereas the maximum permissible limit set by WHO for total PAHs in drinking water is 0.2 μg/L. the maximum permissible limit of 10 μg/L recommended by WHO for safety groundwater. (Aralu et al., 2023; Onydinma et al., 2021).

To efficiently eliminate these toxic pollutants from the environment's waters, it's crucial to explore alternative remediation technologies capable of addressing the limitations of conventional treatment methods.

Table 2.2 PAHs reported in various environmental waters in some countries.

Country	Source	No of PAHs detected	Level of detection	Reference
USA	Coastal zones	16	199 ng/g	(Sakizadeh, 2020)
France-Belgium	Fresh water systems	16	3100 – 4940 ng/L	(Rabodonirina et al., 2015)
Italy	Tiber river and estuary	16	10.3 – 951.6 ng/L	(Montuori et al., 2016)
Colombia	Cauca river	16	3.70 – 4476.5 ng/L	(Sarria-Villa et al., 2016)
Turkey	Drinking water	16	1.04 – 5.85 ng/L	(Aygun & Bagcevan, 2019)
Spain	Mediterranean Sea	16	100-112 ng/g	(López-Berenguer et al., 2023)
Nigeria	Ovia river	16	2.33 – 25.83 µg/L	(Tongo et al., 2017)
Nigeria	Oburun lake	16	409 – 18800 ng/L	(Boehm et al., 2018)
Nigeria	Awka	16	5.8 - 13.94 µg/L	(Chiedozie Chukwuemeka Aralu et al., 2023)
South Africa	Vhembe river	16	13.17 – 26.38 mg/L	(Edokpayi et al., 2016)
South Africa	Buffalo river	16	14.91 – 206 mg/L	(Adeniji et al., 2019)
China	Drinking water	16	3.89 – 231.39 ng/L	(Zhang et al., 2019)
China	East China Sea	16	24 - 43 ng/L	(Qian Wang et al., 2019)
China	Subsidence Water Bodies in Huainan Coal Mining Area, China Xinyue	16	212 to 283 ngL^{-1}	(Deng et al., 2023)
Malaysia	Riverine and coastal areas in Peninsular Malaysia	16	57.7-19300 ng/g	(Vaezzadeh et al., 2021)
Malaysia	Southern Terengganu coast	16	2.59-155 ng/g	(Pang et al., 2022)

India	Damodar River	16	36 µg/L	(Ambade et al., 2021)
Iran	Anzali wetland	16	89.19 µg/kg	(Cheshmvahm et al., 2023)

2.4 Exposure and Toxicity of PAHs on human

Several studies on the exposure and toxicity of PAHs to living organisms have (Patel et al., 2020; Sun et al., 2021) recently received a lot of attention. Consumption of contaminated food and water, as well as inhalation of polluted air have been the major ways of exposure to PAHs (Qadeer et al., 2019). Communities residing near coastal regions, where contaminated water is discharged into rivers and oceans, as well as in proximity to sites involved in crude oil exploration and refining, experience a heightened level of exposure (Nwaichi & Ntorgbo, 2016). Coal plants produce substances such as phenols, PAHs and aromatics containing nitrogen groups (Patel et al., 2020). As a result, individuals residing in proximity to these regions face an increased likelihood of being exposed to contaminated water, posing a greater potential risk. The degree of toxicity associated with PAHs in humans depends on the extent of bioaccumulation. Prolonged exposure typically leads to severe toxic effects, including carcinogenic and mutagenic properties (De la Rosa et al., 2019). An increase in the levels of exposure can heighten the likelihood of cancer development in multiple organs, including the breasts, lungs, bladder, prostate, stomach, kidneys, and skin. Additionally, it may lead to reproductive complication (Patel et al., 2020).

In cases of high exposure, there is an elevated risk of developing cancer in different organs such as the breast, prostate, kidney, lung, bladder, stomach as well as reproductive failure (Dai et al., 2020). A study conducted by Cioroiu et al., (2013) in Romania investigated lung cancer in 13 patients with prolonged exposure to PAHs. Among the PAHs analyzed are: Acenaphthene, Anthracene, Benz(a)anthracene, and Fluorene, were the major components detected in concentrations ranging from 0.33 to 31.94 ng/g of wet tissue. Although the specific mechanistic relevance of each component was not provided, the study associated the increased risk of lung cancer with exposure to these toxic PAHs (Cioroiu et al., 2013). Hamidi et al., (2016), reported the bioavailability of PAHs in meat can serve as a valuable method for assessing the potential risk of cancer in humans. The study also emphasized the importance of reducing the accumulation of food contaminants, particularly in meat products, given their significant contribution to the global diet. Ye and his coworkers reported an increased likelihood of reproductive failure associated with elevated levels of PAHs in the bloodstream. The study identified 157 Chinese women who experienced premature hormone failure and imbalances in reproductive hormones due to their high exposure to PAHs. The research revealed a significant correlation between seven specific PAHs (Acenaphthene,Naphthalene,Anthracene, Crysene, Benzo[a]pyrene, benzo]b]fluoranthene, and, benzo[k]fluoranthene and hormones related to premature ovarian failure (Ye et al., 2020).

2.5 Phenanthrene

Phenanthrene (PHE) is among the 16-listed priority PAHs by USEPA (1982). It is one of the most abundant PAHs present in food and environment. Yu et al. (2019) reported the bioaccumulation of polycyclic aromatic hydrocarbons (PAHs) in wild marine fish from the coastal waters of the northern south China sea. The total concentration of the PAHs ($\sum$16PAHs) ranged from 199 to 606 ng/g d.w., indicating moderate contamination. PAHs in fish species found in the Pearl River Delta (PRD) were significantly higher than those from the Yachen (YC) gas fields ($p < 0.05$). Planktivorous fish exhibited significantly higher concentrations of PAHs than carnivorous and omnivorous fish ($p < 0.05$). The PAHs were dominated by three-ring compounds. Source identification analyses indicated that the PAH pollution originated from petroleum inputs. Phenanthrene was found to be the most prevalent of the PAHs in tap water (Yu et al., 2019). According to Zhang et al., (2019) PHE constitutes the highest proportion of all the PAHs found in tap water, making up roughly one-third of the sixteen priority PAHs designated by the USEPA.

Phenanthrene, categorized as a Low Molecular Weight Polycyclic Aromatic Hydrocarbon (LMW-PAH), shares isomerism with anthracene in its chemical structure and manifests as a crystalline substance with a white or yellow hue. It serves as a significant component in derivatives of coal and fossil fuels, as highlighted. As a tricyclic PAH, phenanthrene is a primary byproduct resulting from the combustion of organic materials. Its application extends to various industrial processes, serving as an intermediate in the synthesis of phenanthrenequinone used in pesticides, plastics manufacturing, and the production of diphenic acid (Okedere & Elehinafe, 2022). Additionally, it plays a role in resin production for dyes. Phenanthrene finds utility in the synthesis of bile acids, cholesterol, and steroids. These inherent physical properties contribute to its widespread industrial applicability. From an environmental perspective, phenanthrene does not pose a direct health risk to humans, in contrast to High Molecular Weight Polycyclic Aromatic Hydrocarbons (HMW-PAHs). However, it exhibits toxicity towards fish and algae. Consequently, it is listed as one of the 16 priority pollutants among PAHs by the United States Environmental Protection Agency (USEPA). As a result, these materials hold significant potential for practical applications in the field of wastewater treatment. Although PHE has a LMW, it resembles the HMW PAH benzo[a]pyrene (Samanta et al., 1999). In order to assess the toxicity of both high- and low-molecular-weight PAHs, the research is very useful. Hence, the study proves valuable in evaluating the toxicity of PAHs, whether they are high or low in molecular weight.

2.6 Advanced Oxidation Processes (AOPs)

Advanced oxidation processes (AOPs) are considered as highly effective techniques for the treatment of organic pollutants in water. It offers considerable potential as viable alternatives to conventional water treatment methods. They are characterized by their broad applicability, rapid reaction rates, and the ability to achieve complete conversion of pollutants into harmless end products, rather than just going through phase changes (Khan et al., 2020). These processes operate on the basis of the non-selective reactivity of hydroxyl radicals (HO•), which possess a high oxidation potential, with organic pollutants at faster reaction rates. Thus, AOPs demonstrate the ability to oxidize a different range of organic pollutants (Fu et al., 2021; Rayaroth et al., 2022; Yuan et al., 2020). Apart from HO•, other reactive oxygen species (ROS) such as $SO_4^{\bullet-}$, $O_2^{\bullet-}$, and $HO_2^{\bullet}$ also exhibit pollutant-degrading capabilities (Dong et al., 2022; Rayaroth et al., 2022). Figure 2.3 illustrates the various types of AOPs, and the specific ROS involved in each type. The application of AOPs for the elimination of pollutants provides numerous advantages such as:

1) Fast reaction speeds and simultaneous breakdown of multiple contaminants: AOPs exhibit fast reaction rates due to the highly oxidizing and non-selective nature of $OH^{\cdot}$ radical. This allows for the efficient degradation of various pollutants.
2) Complete mineralization of pollutants: AOPs facilitate the complete breakdown of pollutants into water, carbon dioxide, and inorganic ions. This ensures thorough and comprehensive pollutant removal.
3) Generation of different radical species: AOPs employ different techniques are employed to generate $OH^{\cdot}$ and other radical species, tailored to meet the specific requirements for degrading different types of organic contaminants. This

flexibility enables effective customization of the AOPs for targeted pollutant degradation (Dong et al., 2022; Rayaroth et al., 2022).

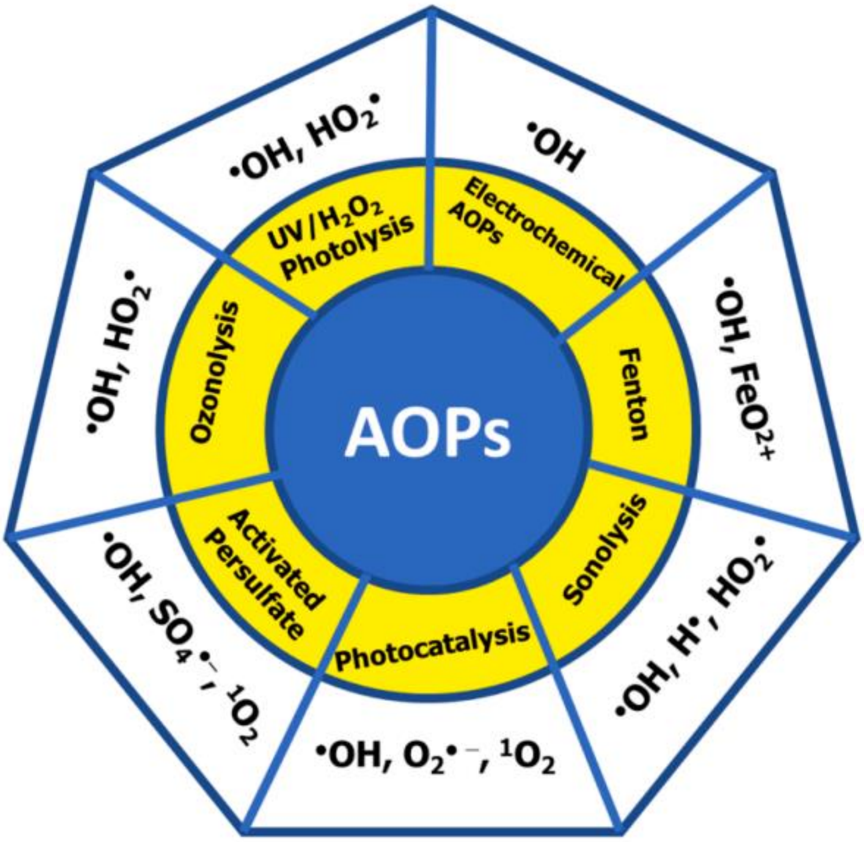


Figure 2.3 Different types of AOPs and the specific ROS involved (Rayaroth et al., 2022).

One major drawback of AOPs in wastewater treatment is that scavenger species are commonly found in wastewater. Scavenger species consist of organic molecules such as carbohydrates, proteins, and humic acid, and inorganic ions including carbonates, nitrate, and dissolved sulfides. They undergo reactions with $OH^{\cdot}$, resulting in fewer $OH^{\cdot}$ available for pollutant degradation (Ma et al., 2021).

AOPs can be conducted either as homogeneous or heterogeneous processes, which are determined by the phase of the reaction. In homogeneous AOPs, the reaction occurs within a single phase, while in heterogeneous, the interaction between the catalyst and the substrate occurs in separate phases. Homogeneous AOPs include processes such as ozone-based reactions, wet oxidation with H_2O_2 as an oxidizing agent, and Fenton-based processes. In homogeneous AOPs, the chemical process depends entirely on the interaction between the introduced oxidant and the pollutant.

In contrast, heterogeneous AOPs rely not only on the interplay between the oxidant and pollutant but also on the adsorption of the pollutant and the release of byproducts at the active site of the catalyst. Typical classes of heterogeneous AOPs are: (i) employing photocatalysts that are heterogeneous under light exposure, (ii) utilizing a heterogeneous catalyst in catalytic wet peroxide oxidation, and (iii) engaging in catalytic ozonation and employing Fenton-like processes (Ribeiro et al., 2015).

2.6.1 Heterogeneous Semiconductor Photocatalysis

Heterogeneous semiconductor photocatalysts are solid substances possessing semiconductor characteristics that expedite chemical reactions upon light exposure, notably within the visible or ultraviolet range. They are widely used in environmental remediation processes like water purification and air detoxification, where they can degrade pollutants like organic dyes, pesticides, and volatile organic compounds (VOCs).

2.6.1(a) Historical Background

Photocatalysis can be defined as the acceleration of a photogenerated electrons from catalyst in which the catalyst is not consumed in the reaction (Belousov & Suleimanov, 2021). The term “photocatalysis” appeared first in different scientific articles in 1911, after Alexander Eibner investigated the effect of the illumination of ZnO on the bleaching of Prussian blue (Belousov & Suleimanov, 2021). This