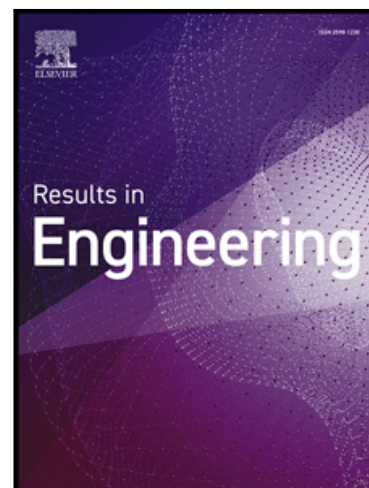


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Biochar-Based Adsorption of Polycyclic Aromatic Hydrocarbons in Contaminated Soils: Advances, Mechanisms, and Bibliometric Analysis

Tumelo M Mogashane , Moshalagae A Motlatle ,  
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**HIGHLIGHTS**

Key highlights of our review include:

- Reviews recent advances in using biochar for PAH-contaminated soil remediation.
- Explores adsorption mechanisms including  $\pi$ - $\pi$  interactions, hydrogen bonding, and pore filling.
- Discusses the role of biochar properties and modification techniques in enhancing adsorption.
- Summarizes key findings from experimental and field-scale studies.
- Includes a bibliometric analysis highlighting research trends from 2000 to 2024.

## **Biochar-Based Adsorption of Polycyclic Aromatic Hydrocarbons in Contaminated Soils: Advances, Mechanisms, and Bibliometric Analysis**

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### **Abstract**

Polycyclic aromatic hydrocarbons (PAHs) are persistent organic pollutants that pose significant environmental and health risks due to their toxicity, mutagenicity, and resistance to degradation. Concern over PAHs contamination of soil is on the rise, especially in regions impacted by petrochemical accidents, industrial operations, and the burning of fossil fuels. Adsorption with biochar has become one of the most promising, economical, and environmentally friendly remediation techniques for removing PAHs from polluted soils. This review provides a comprehensive analysis of biochar as an adsorbent for PAHs, focusing on its physicochemical properties, production methods, and adsorption mechanisms. The impact of critical elements on PAH adsorption efficiency is examined, including biochar surface area, functional groups, pyrolysis temperatures, and environmental factors. To improve adsorption efficiency, recent developments in biochar modification techniques, such as functionalisation and the creation of composite materials are also emphasised. The review also examines biochars field-scale applications, contrasts it with other adsorbents, and highlights issues with long-term stability, large-scale deployment, and regulatory concerns. By addressing current knowledge gaps and future research directions, this study aims to support the development of improved biochar-based remediation strategies for PAH-contaminated soils. A bibliometric analysis was conducted to assess research trends on the use of biochar for the adsorption of PAHs in polluted soil. The results revealed a limited number of studies in this area, highlighting the need for further research and innovation.

**Keywords:** PAHs; Biochar; Adsorption mechanisms; Bioremediation; Bibliometric analysis

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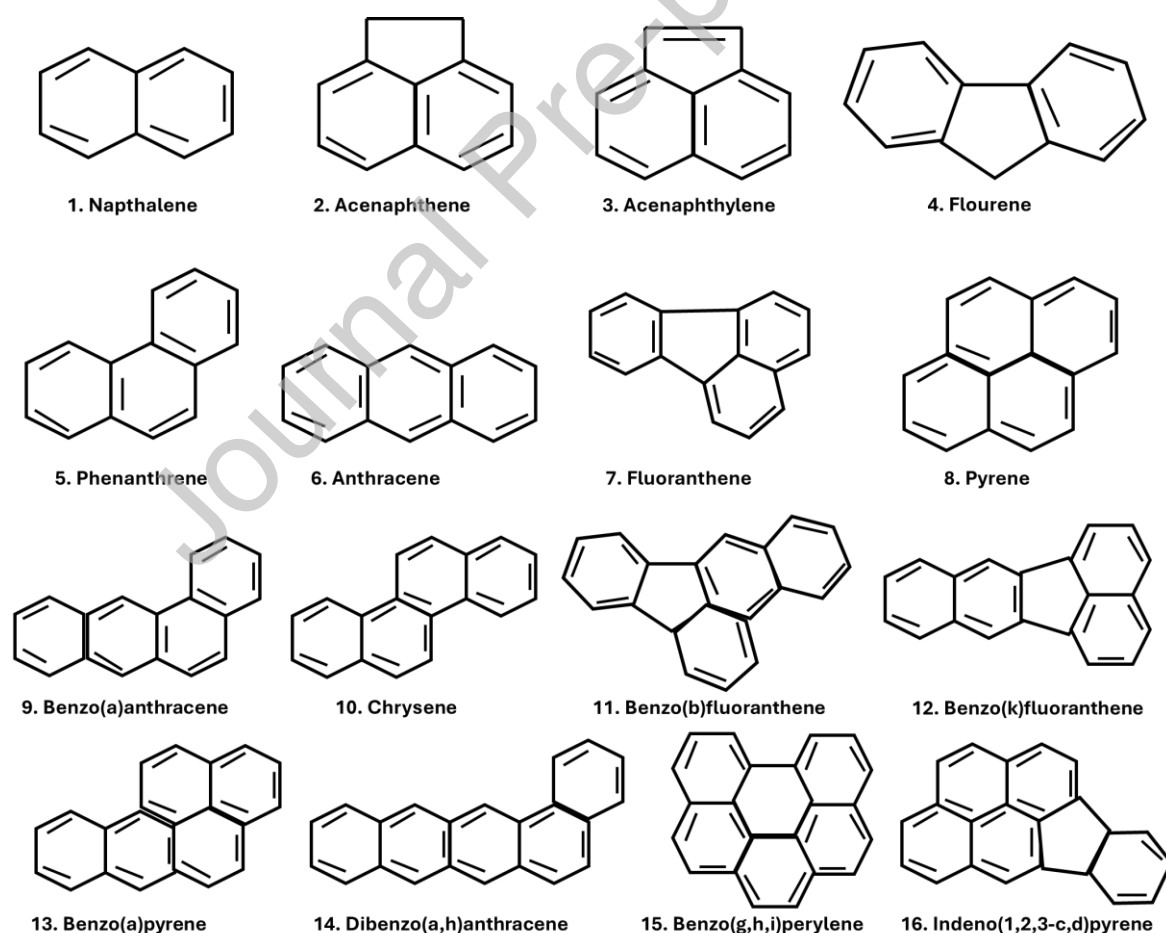
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## 1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) contamination in soil has emerged as a major environmental issue due to their persistent nature and widespread presence in terrestrial ecosystems [1, 2]. PAHs are a class of hazardous organic chemicals that are mostly produced by incomplete burning of fossil fuels, burning of biomass, and industrial processes such as waste incineration and petrochemical processing [3, 4]. PAHs tend to accumulate in soils due to their hydrophobic qualities and high molecular stability, which can pose long-term ecological and health risks [5, 6]. Their accumulation in soil affects not only terrestrial ecosystems but also threatens groundwater and food security through bioaccumulation in crops [7, 8]. Because of the chemicals poor bioavailability and strong attraction for organic matter, standard treatment procedures are frequently ineffective and expensive when it comes to remediating PAH-contaminated soils [9, 10, 11].

Recent studies show that PAH pollution in soils continues to be a significant environmental issue since concentrations often exceed advised limits, particularly around industrial areas, transit routes, and mining sites [12, 13, 14]. Due to their high hydrophobicity and poor biodegradability, these substances accumulate in soil organic matter and pose serious threats to human health and terrestrial ecosystems through cutaneous exposure and food chain transfer [15, 14]. The persistence of PAHs in surface and subsurface soils is made worse in many developing regions by a lack of monitoring and a lack of suitable remedial infrastructure [9]. Therefore, for soil restoration and environmental preservation, it is now essential to comprehend the existing level of PAH pollution and create sustainable remediation techniques, including biochar-based adsorption [16].

The environmental and health impacts of PAHs are well documented, with several high-molecular-weight PAHs classified as probable or known carcinogens by the United States Environmental Protection Agency (USEPA) and the International Agency for Research on Cancer (IARC) [17, 18]. Respiratory problems, skin irritation, and developmental toxicity are among the negative health impacts associated with exposure to PAHs through contaminated soil, water, or air [2]. **Figure 1** shows the 16 priority PAHs listed by the USEPA. These substances are divided into low-molecular-weight PAHs (2–3 aromatic rings) and high-molecular-weight PAHs (4–6 rings) according to their molecular structure, emphasizing variations in volatility, hydrophobicity, and environmental behaviour. Furthermore, because PAHs alter microbial populations and lower soil fertility, they represent a major risk to soil health [19, 20]. Effective and long-lasting remediation techniques that may effectively remove PAHs while reducing their negative effects on the environment are desperately needed, given their persistence and toxicological hazards [1, 21, 22].



**Figure 1.** The 16 PAHs designated as priority pollutants by the USEPA.

Adsorption-based remediation has drawn a lot of interest as an economical and sustainable method of removing PAHs from polluted soils [7, 23, 24]. Rapid pollutant removal, low secondary pollution, and high efficiency even for resistant compounds are some benefits of adsorption over more conventional techniques like chemical oxidation and bioremediation [17, 25]. Traditional methods for remediating PAH-contaminated soils, such as chemical oxidation, soil washing, and microbial degradation, often present limitations in terms of efficiency, cost, and potential secondary pollution [26, 27]. While chemical oxidation can result in partial breakdown of PAHs and the production of hazardous by-products, soil washing necessitates the use of significant amounts of surfactants and may cause secondary contamination [28]. Although bioremediation shows promise, it is frequently slow and heavily reliant on site-specific variables such as ambient conditions, microbial activity, and nutrient availability [29]. Therefore, there is an urgent need for more economical, ecologically friendly, and effective methods of cleaning up soils contaminated by PAHs [28, 30].

Biochar, a carbon-rich material made by pyrolysing biomass, has emerged as a promising alternative to existing adsorbents due to its many functional groups that enhance PAH adsorption, wide surface area, and porous structure [31, 32]. This allows PAHs to be immobilised and lowers their bioavailability in soils. Furthermore, by providing a home for microorganisms that break down PAHs, biochar might increase microbial activity and encourage PAH breakdown [33, 34]. Furthermore, the synthesis of biochar makes use of forestry and agricultural waste, which makes it a financially and environmentally sound method of remediating soil [35]. Biochar offers a sustainable and cost-effective substitute for the removal of PAHs from contaminated soils due to its high surface area, porous structure, and functionalised chemistry, all of which enhance PAH adsorption and immobilisation [36, 37]. However, its efficacy fluctuates according to the type of feedstock, pyrolysis settings, and environmental factors, resulting in uneven performance [21, 38]. Potential disadvantages include the possibility of pollutants leaking out of subpar biochar and the paucity of long-term stability research. While more refinement is required for large-scale applications, biochar is still a viable option for PAH remediation despite these obstacles [39, 40]. Although biochar is frequently used to remediate PAHs, it may also be a source of PAHs because incomplete pyrolysis of biomass can produce and retain these chemicals in the matrix of biochar [41]. Therefore, to reduce PAH generation and guarantee the safe use of biochar in soil remediation, it is crucial to optimize pyrolysis conditions and post-treatment procedures [42].

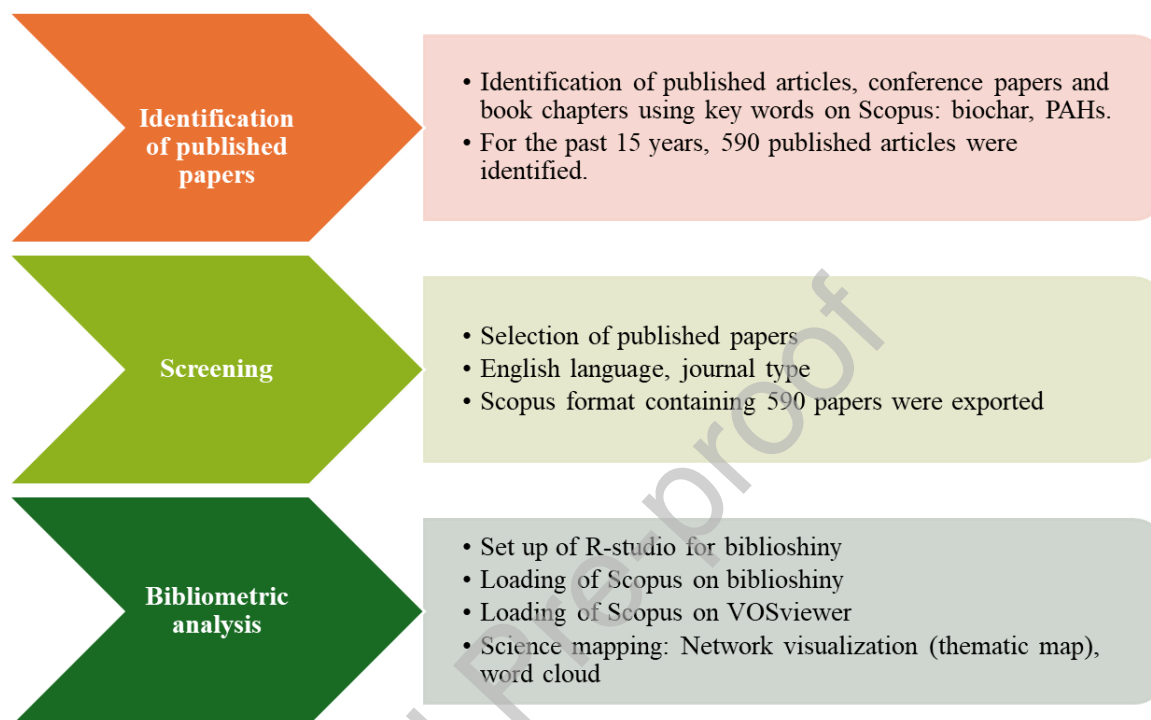
This review provides an in-depth analysis of biochar as an adsorbent for PAH-contaminated soil remediation. It examines important elements that affect PAH adsorption, such as the physicochemical characteristics, conditions under which biochar is produced, and methods of modification to improve effectiveness. Recent developments in biochar engineering, like surface functionalisation and composite materials, which increase adsorption efficiency, are given particular emphasis. Additionally, a comparison of biochar with traditional adsorbents such as clay minerals and activated carbon is provided to gauge its efficacy and suitability for practical applications. This work comprehensively relates biochar physicochemical parameters, modification techniques, and adsorption efficacy using quantitative comparisons, in contrast to earlier reviews that mainly outline adsorption mechanisms or specific modification procedures. A bibliometric analysis of research trends on biochar-based PAH remediation is also included to provide insights into the evolution of this field [43, 44]. To improve the knowledge and use of biochar for PAH-contaminated soil remediation and aid in the creation of more sustainable and efficient environmental management techniques, this study will summarise existing research and suggest future lines of inquiry.

## **2. Bibliometric analysis**

### **2.1. Data collection and methodology**

Bibliometric analysis involves the systematic evaluation of published literature to identify research trends, key contributors, and knowledge gaps in each field [45]. Bibliometric information on PAH adsorption with biochar was collected for this review from reputable academic source like Scopus database. The Scopus database was chosen due to its reliability, compatibility with bibliometric tools, and indexing scope. To visualise the development of research in this field, bibliometrix (R-studio, version 4.4.2) software tools like bibliometrix (Biblioshiny) and VOSviewer (version 1.6.20) were used for authorship distribution, to identify trends, research hotspots, pinpoint knowledge gaps systematically, and co-occurrence mapping of keywords. The Preferred Reporting Items for Systematic Reviews and Meta-Analyses (PRISMA) criteria were used to set the search parameters, locate relevant academic papers, and systematically extract bibliographic information from the published literature spanning the years 2010 to 2025. Using time filters to evaluate trends over the previous 15 years, the search method used specific keywords such as biochar and PAHs. The search before refinement yielded 590 documents from Scopus. After refining the search by limiting the publication years and only including articles, book chapters, conference papers, 589 documents were obtained

from Scopus. An article was eligible for inclusion in the bibliometric study if it addresses the remediation of soils contaminated with PAHs using biochar. **Figure 2** presents methodological framework demonstrating the PRISMA-based search and selection procedure for finding and screening pertinent scholarly works on biochar-based adsorption of PAHs in contaminated soils.



**Figure 2:** Methodological framework illustrating the PRISMA-based search and selection process used to locate and screen relevant academic publications for the bibliometric analysis of this study.

## 2.2. Publication trends and research growth

The number of publications on PAH adsorption using biochar has increased significantly in recent years, reflecting the growing interest in sustainable soil remediation strategies as shown in **Figure 3** [1, 46]. The general characteristics of biochar and its potential for pollutant adsorption were the main emphasis of early study (before to 2013) [47]. In contrast, mechanistic investigations, biochar modification methods, and field-scale applications have been in focus of more recent research (2015–2025) [48]. Global environmental regulations that support biochar-based solutions and sustainable remediation technologies are in line with the publication's exponential expansion.



**Figure 3:** The annual scientific distribution on adsorption of PAHs using biochar.

### 2.3. Co-occurrence and research themes

Keyword analysis revealed dominant themes in the field, including Charcoal, adsorption, Chemistry, kinetics and water pollutants. Future paths for innovation are suggested by emerging research that focusses on field-scale performance, engineered biochar composites, and biochar interactions with soil microorganisms [45]. According to the bibliometric analysis, Hunan University, Nankai University, Northeast Agricultural University, Institute of Soil Science, Shandong University, Zhejiang University and the Changsha University of Science and Technology are the top research institutions that have produced many high-impact publications in the field of biochar-based adsorption of PAHs. The growing emphasis on sustainability, wastewater treatment, and circular economy strategies in biochar-based remediation is further highlighted by the co-occurrence mapping of terms [43].

### 2.4. Research Gaps and future directions identified from bibliometric analysis

Despite the increasing number of studies, bibliometric insights reveal critical gaps in long-term field applications, biochar stability in complex soil matrices, and regulatory considerations for large-scale deployment [44, 45]. Standardised approaches for biochar characterisation, real-world case studies, and Life Cycle Assessments (LCAs) to gauge economic and environmental viability should be the focus of future study [10]. Furthermore, to convert laboratory-scale results into workable remediation methods, more cooperation between academics, business, and legislators is required. The network visualization in **Figure 4** indicates that each node in the network denotes distinct keywords, while the lines reflect the channels of association



Yellow cluster	Pyrene, naphthalene, chrysene, fluorene, carbonization
----------------	--

### 3. Sources and environmental fate of PAHs in soil

#### 3.1. Natural and anthropogenic sources of PAHs

Natural and man-made sources both contribute to the release of PAHs into the environment [49, 50]. Natural causes of PAH production include forest fires and volcanic eruptions, where organic matter is burned at high temperatures [51, 52]. However, human activity is the primary cause of the great majority of PAH contamination, with industrial processes, the burning of fossil fuels, and urban runoff being the main sources. Large volumes of PAHs are released into the atmosphere by industrial processes such as coal gasification, coke manufacture, and petroleum refining [2, 53]. These PAHs eventually find their way into soil and water bodies [5, 54]. Similarly, PAHs are produced by burning fossil fuels in power plants, automobiles, and home heating systems, and they build-up in roadside and urban soils [18, 55]. Soil contamination is exacerbated by urban runoff because PAHs from asphalt, tire wear, vehicle emissions, and industrial discharge are carried into neighbouring areas during rainy seasons [56]. PAHs are a serious environmental problem because to their persistence and extensive distribution in soil, especially in regions with high levels of industrialisation and urbanisation [57].

#### 3.2. Transport, persistence, and degradation mechanisms in soil

Once PAHs enter the soil, their environmental fate is determined by various transport and degradation mechanisms, including sorption, volatilization, microbial degradation, and leaching [9, 58]. Because PAHs have strong affinity for clay minerals and organic matter, which cause them to accumulate in soil matrices, sorption is crucial to PAH retention [59]. Hydrophobic interactions and  $\pi$ - $\pi$  stacking further increase their longevity, which reduces their availability for breakdown [29]. Low-molecular-weight PAHs with greater vapour pressures are more likely to undergo volatilisation, the process by which they move from the solid or liquid phase into the atmosphere [60, 61]. High molecular weight PAHs, on the other hand, tend to stay attached to soil particles, which limits their capacity to volatilise [62]. One important natural attenuation process for PAHs is microbial degradation, in which certain bacteria and fungi break down these substances [63]. The physicochemical characteristics of PAHs, such as their molecular weight, vapour pressure, water solubility, hydrophobicity (log

Kow), and environmental persistence (soil half-life), are all detailed in **Table 2**. These characteristics have a major impact on their bioavailability, mobility, and possible biochar-based remediation techniques [10].

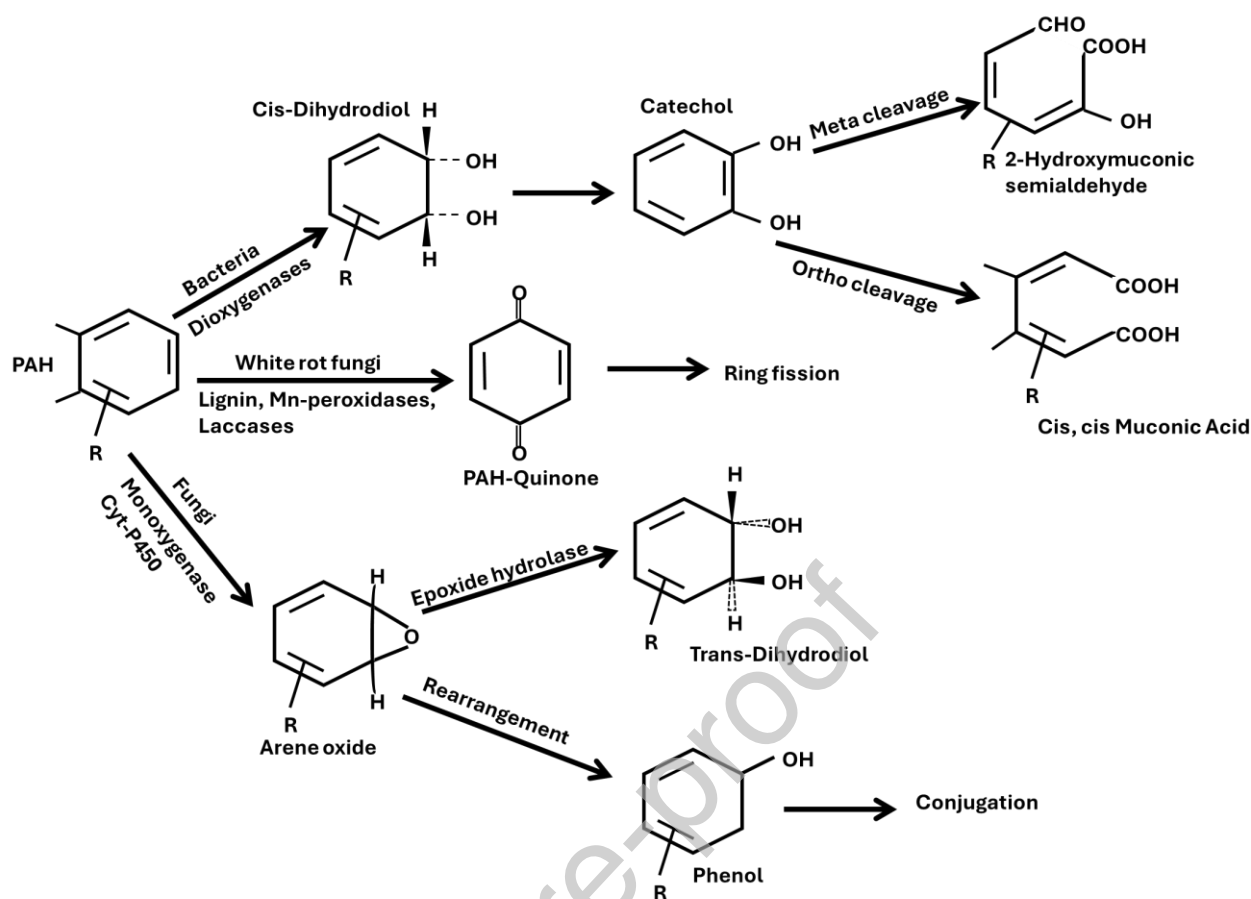
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**Table 2:** Key physicochemical properties of the 16 priority PAHs classified by the USEPA [6].

PAH Compound	Molecular Weight (g/mol)	Primary Sources	Vapor Pressure (Pa at 25 °C)	Water Solubility (mg/L at 25 °C)	Hydrophobicity (Log Kow)	Half-Life in Soil (Days)
Naphthalene	128.17	Fossil fuel combustion, cigarette smoke, industrial discharge	$11.5 \times 10^{-1}$	31.7	3.37	30–300
Acenaphthylene	152.19	Wood combustion, vehicular emissions	$1.71 \times 10^{-1}$	16.1	4.00	60–140
Acenaphthene	154.21	Industrial waste, coal tar	$8.30 \times 10^{-2}$	3.93	3.92	40–120
Fluorene	166.22	Gasoline and diesel exhaust, municipal waste incineration	$1.94 \times 10^{-2}$	1.98	4.18	50–200
Phenanthrene	178.23	Coke oven emissions, petroleum refining	$8.23 \times 10^{-4}$	1.18	4.57	50–200
Anthracene	178.23	Incomplete combustion of organic matter	$1.33 \times 10^{-5}$	0.045	4.54	50–200
Fluoranthene	202.26	Diesel emissions, wood burning	$8.01 \times 10^{-6}$	0.26	5.22	100–400
Pyrene	202.26	Asphalt production, industrial combustion	$6.72 \times 10^{-6}$	0.14	5.18	100–400
Benz[a]anthracene	228.29	Found in soot, vehicle exhaust, grilled foods	$9.40 \times 10^{-7}$	0.011	5.91	200–500
Chrysene	228.29	Coal tar, diesel exhaust, wood smoke	$8.70 \times 10^{-7}$	0.006	5.91	200–500

Benzo[b]fluoranthene	252.31	Fossil fuel combustion, waste incineration	$5.20 \times 10^{-8}$	0.0015	6.12	200–700
Benzo[k]fluoranthene	252.31	Gasoline combustion, industrial emissions	$1.10 \times 10^{-8}$	0.0008	6.11	200–700
Benzo[a]pyrene	252.31	Cigarette smoke, wood burning, grilled meat	$5.70 \times 10^{-9}$	0.0038	6.13	200–700
Indeno[1,2,3-cd]pyrene	276.32	Diesel emissions, hazardous waste sites	$6.20 \times 10^{-10}$	0.00019	6.58	300–1000
Dibenz[a,h]anthracene	278.35	Industrial waste, coal burning	$2.00 \times 10^{-10}$	0.0005	6.75	300–1000
Benzo[g,h,i]perylene	276.32	Exhaust emissions, oil spills	$6.00 \times 10^{-11}$	0.00026	6.65	300–1000

Degradation rates, however, differ according to the structure of PAHs, the environment, and the makeup of the microbial community [64]. Due to their poor solubility in water, leaching the downward movement of PAHs through soil layers is often restricted; nevertheless, it can happen when surfactants or co-contaminants are present, which increase mobility [65, 66]. The biodegradation pathways of PAHs by bacteria and fungi are depicted in **Figure 5**, emphasizing the successive enzymatic transformations that contribute to their disintegration. Bacterial dioxygenases first add oxygen to the aromatic rings to create cis-dihydrodiols [67]. These are then transformed into catechols and further broken down into intermediates of the tricarboxylic acid (TCA) cycle through ortho- or meta-cleavage pathways. By using laccases, lignin peroxidases, and manganese peroxidases, fungi especially white-rot species extracellularly break down PAHs to produce quinones and simpler organic acids. When combined, these microbial mechanisms are essential to the bioremediation and natural attenuation of soils contaminated with PAHs [67].

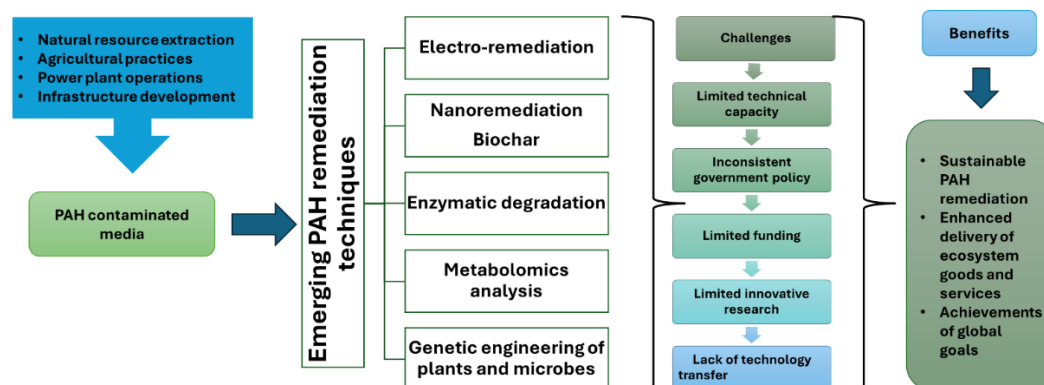


**Figure 5:** Bacterial and fungal biodegradation pathways of PAHs.

### 3.3. Challenges in PAH Remediation

PAH-contaminated soils are difficult to remediate, mostly because of their low bioavailability, hydrophobicity, and resistance [26]. Because PAHs are frequently firmly bonded to the surfaces of minerals and soil organic matter, they are less amenable to chemical or microbial breakdown [10, 68]. The efficacy of aqueous-based remediation methods is decreased by their hydrophobic characteristics, which also make it more difficult for them to dissolve in water [69, 70]. Additionally, because of their intricate structures and low vulnerability to microbial degradation, high-molecular-weight PAHs, those with five or more aromatic rings are especially resistant [71, 72]. Long-term contamination is the result of this persistence, necessitating creative remediation techniques such as adsorption with biochar to improve PAH removal from soil [32, 73]. To overcome these obstacles, effective, economical, and sustainable treatment solutions that can increase PAH bioavailability while reducing secondary environmental effects must be developed [74]. The conceptual model of PAH developing remediation strategies, possible green remediation techniques, and obstacles that need to be

addressed to engender benefits are depicted in **Figure 6**, illustrating the interconnections between contamination sources, environmental compartments, and remediation pathways.



**Figure 6:** Emerging PAH remediation strategies, green remediation potentials, and key challenges to realizing their benefits.

Biochar is a viable method for treating contaminated soil since it offers several benefits for PAH remediation [27, 75]. Biochar can be altered to improve its sorption effectiveness, providing a sustainable and affordable alternative to traditional remediation techniques [76]. Its position as an environmentally friendly remediation method is further supported by its capacity to promote soil health by increasing microbial activity and nutrient retention [1]. Additionally, biochar can be made from a variety of biomass sources, supporting the circular economy and waste valorisation [31]. However, several obstacles prevent biochar from being widely used in PAH remediation [77].

Despite the presence of International Biochar Initiative (IBI) and European Biochar Certificate (EBC) standards, standardizing biochar is still difficult because its effectiveness still varies greatly depending on the type of feedstock, the conditions of pyrolysis, and the characteristics of the soil [78, 79]. Concerns arise from desorption and possible secondary pollution since PAHs can return to the environment in specific circumstances [80]. Another obstacle is whether large-scale application is economically feasible given the high costs of production and customisation [43]. It will be crucial to address these issues by conducting field-scale research, cost-benefit evaluations, and additional research on biochar modification to maximise its application in PAH-contaminated settings [7].

Depending on the biochar feedstock and production circumstances, case studies have demonstrated that the effectiveness of PAH removal varies significantly [81, 82]. For example, research employing biochars made from rice husks has found that these biochars had better

adsorption capabilities for PAHs [82]. The study also indicated that the combination of rice husk biochar and alfalfa is a potential method for remediation of soils that are co-contaminated with PAHs [82]. Furthermore, issues like decreased adsorption effectiveness under variable climatic conditions, possible secondary pollution, and regeneration concerns are shown by field applications [83]. Studies employing biochars made from rice husks or sewage sludge has found that these materials have relatively lower adsorption capabilities for high-molecular-weight PAHs because of their smaller surface area and lesser aromaticity when compared to biochars made from wood or manure [82, 84, 85]. These findings highlight the necessity of enhancing modification methods, choosing feedstocks wisely, and carrying out long-term field tests to get over the enduring obstacles in PAH remediation with biochar-based systems [86].

#### 4. Synthesis and characterization of biochar

The process of pyrolysis, which is the thermal breakdown of organic material with little to no oxygen present, is used to synthesise biochar [87]. The pyrolysis temperature, heating rate, and residence time have a significant impact on the physicochemical properties of the resulting biochar, including its surface area, porosity, functional groups, and elemental content [23, 88]. A range of feedstocks, including wood, agricultural waste, and animal dung, could be used to synthesize biochar, and each one gives the finished product distinct qualities [32]. While high-temperature pyrolysis ( $>700\text{ }^{\circ}\text{C}$ ) produces highly carbonised, hydrophobic biochar with greater surface area and microporosity, increasing its adsorption capacity for PAHs, low-temperature pyrolysis ( $300\text{--}500\text{ }^{\circ}\text{C}$ ) typically produces biochar with higher volatile matter and surface functional groups [89, 90]. **Figure 7** shows schematic for the synthesis of biochar samples, starting from MWCNTs through pre-treatment, controlled pyrolysis under limited oxygen conditions, and subsequent cooling.

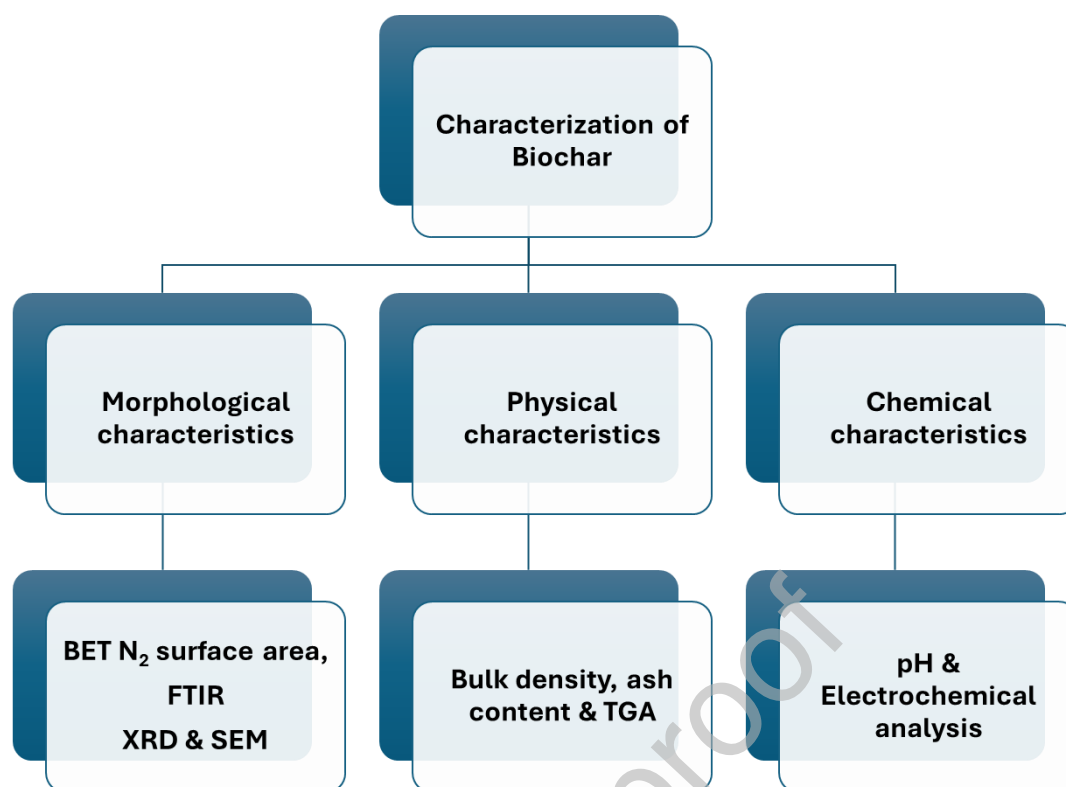


**Figure 7:** Schematic for the synthesis of biochar samples.

A study by Roy et al. [89] examined the synthesis and characterisation of exfoliated biochar using four different agricultural feedstocks. Slow pyrolysis in a nitrogenous atmosphere has been used to create highly porous charcoal structures from low-cost biomasses such as rice straw, bamboo, sugarcane waste, and corn cob. Carbon, Scanning Electron Microscopy (SEM), Brunauer-Emmett-Teller (BET), and Fourier Transform Infrared Spectroscopy (FTIR), Hydrogen, and Nitrogen (CHN) are standard surface and elemental characterisation techniques that were used to compare the properties of each biochar sample after a surface engineering technique was used to increase the surface-to-volume ratio. It was found that every biochar sample was highly aromatised and carbonised. Compared to their original form (30.92-74.46 %), exfoliated structures have higher elemental carbon contents (34.14-77.32 %). Exfoliated biochars were consistently more efficient than their original form, as confirmed by their comparative characterization results presented in the study [89].

Recent advancements in the synthesis and characterization of biochar have introduced new techniques that enhance its performance for PAH adsorption [45, 91]. New techniques that have been demonstrated to greatly increase surface area, porosity, and the quantity of functional groups essential for PAH binding include co-pyrolysis with metal oxides, hydrothermal carbonization, and activation utilizing green chemical agents [92]. More in-depth knowledge of the structural and chemical changes that biochar undergoes during alteration is now possible because of sophisticated characterisation techniques like X-ray Photoelectron Spectroscopy (XPS), FTIR, Raman spectroscopy, and BET surface analysis. Recent discoveries show that magnetic functionalization and heteroatom doping (such as N, S, or P inclusion) enhance adsorption efficiency while also making recovery and reuse simpler [93, 94]. These advancements signal a move toward more application-specific, engineered biochars with specialized qualities for the efficient and long-term cleanup of soils contaminated by PAHs [95].

Characterization of biochar is essential to evaluate its suitability for PAH adsorption in contaminated soils [96, 97]. To ascertain its structural, textural, and chemical characteristics, a variety of analytical methods are employed [91]. SEM and BET surface area analysis are frequently used to evaluate surface morphology and porosity [98]. To find surface functional groups that affect how biochar interacts with PAHs through hydrogen bonding and  $\pi$ - $\pi$  interactions, FTIR is used [46]. X-ray Diffraction (XRD) offers information about the mineral composition and crystalline structure, whereas Thermogravimetric Analysis (TGA) evaluates the stability of biochar [31, 92, 99]. A study by García-Prats et al. [100] examined the characteristics of biochars from various sources and their use in the anaerobic digestion of a source-selected organic component of municipal solid waste at several doses and in batch circumstances. SEM imaging, BET, GC, ICP, and FTIR were among the methods used to characterise the three biochars (BC1, BC2, and BC3) in their investigation. It was discovered that the production technique and the feedstock both influenced BC's characteristics [100]. Furthermore, surface charge is determined by zeta potential analysis, which might affect adsorption performance in various soil settings. Through the optimisation of biochar synthesis conditions and a comprehensive characterisation of its characteristics, scientists can create customised biochars that have improved PAH adsorption efficiency [89]. Chemical activation, metal oxide impregnation, and polar group functionalisation are among modification methods that increase biochars affinity for hydrophobic organic contaminants. These developments aid in the creation of effective, long-lasting, and reasonably priced remediation methods for PAH-contaminated soil. Modified biochar typically costs more than pristine biochar because it requires extra chemical or physical activation processes. However, its superior adsorption efficiency and regeneration potential frequently make the higher cost of remediating PAH-contaminated soils justified [83]. The several characterisation methods utilised to examine the structural, chemical, and physical characteristics of biochar are shown in **Figure 8**, emphasising the material's aptitude for adsorption applications.



**Figure 8:** Characterization of Biochar for PAH Remediation.

## 5. Biochar as an adsorbent for PAHs

### 5.1. Properties of biochar

Biochar's potential uses in pollutant adsorption, carbon sequestration, and soil remediation are well known [101]. The distinct composition, structure, and surface properties of biochar are primarily responsible for its efficacy in eliminating pollutants like PAHs [83]. Although the feedstock and production conditions affect the composition of biochar, it typically comprises of minerals, carbonised organic matter, and leftover volatile chemicals [102, 103]. With its highly porous matrix of micro, meso, and macropores, biochar offers a substantial surface area for adsorption [31, 32]. Furthermore, its surface has a variety of functional groups that improve interactions with hydrophobic organic contaminants like PAHs, including hydroxyl (-OH), carboxyl (-COOH), and aromatic  $\pi$ -electron systems [104]. For PAH-contaminated soils, biochar is a promising adsorbent due to its high stability, chemical heterogeneity, and adjustable surface characteristics [105]. Biochar may contain residual PAHs during pyrolysis, and if these PAHs are not adequately regulated, they may leak into the soil under specific circumstances, such as low production temperatures or high soil moisture [63, 79]. Therefore, when using biochar for soil remediation, quality control procedures including adhering to IBI PAH limitations are required [79]. The basic characteristics of biochar that determine its

effectiveness as an adsorbent for PAHs are highlighted in **Table 3**, with a focus on how each feature affects how the material interacts with pollutants in soil environments.

**Table 3:** Key properties of biochar relevant to the adsorption of PAHs in contaminated soil [31, 106].

Property	Description	Influence on PAH Adsorption
Surface Area	Determined by feedstock type and pyrolysis conditions; typically ranges from 100 to 1000 m <sup>2</sup> /g	Higher surface area increases adsorption capacity by providing more binding sites
Porosity	Micro-, meso-, and macropores contribute to overall structure	Affects diffusion and accessibility of PAH molecules
Pore Size Distribution	Ratio of micropores to macropores varies with production conditions	Micropores enhance adsorption of low-molecular-weight PAHs; macropores aid in high-molecular-weight PAH capture
Aromaticity	Degree of carbonization and presence of conjugated $\pi$ -electron systems	Enhances $\pi$ - $\pi$ interactions with aromatic PAH compounds
Functional Groups	Oxygen-containing (hydroxyl, carboxyl), nitrogen, sulphur groups	Influence hydrophobic interactions and hydrogen bonding with PAHs
Surface Charge (pH-Dependent)	Zeta potential varies with pH and pyrolysis temperature	Affects electrostatic interactions with PAHs in different soil conditions
Hydrophobicity	Determined by degree of carbonization and surface oxidation	Promotes partitioning of PAHs onto biochar surface
Cation Exchange Capacity (CEC)	Capacity to retain and exchange cations	Can influence adsorption of metal-PAH complexes
Ash Content	Inorganic residue, including minerals such as Si, Ca, Mg, and K	High ash content may reduce PAH adsorption by blocking pores
Pyrolysis Temperature	Usually falls within the 300 °C to 900 °C range, affecting surface chemistry and porosity	Higher temperatures increase aromaticity and stability but may reduce functional groups
Feedstock Type	Biomass source (e.g., wood, agricultural waste, manure)	Determines biochar properties such as porosity, surface area, and functionalization
Activation Methods	Chemical (acid/base treatments), physical (steam, CO <sub>2</sub> activation)	To improve adsorption, increase surface area, pore formation, and functional groups.

## 5.2. Production methods and influence on adsorption capacity

The adsorption performance of biochar for PAH removal is significantly influenced by its production method, particularly pyrolysis conditions, feedstock type, and activation techniques [1]. One important element influencing the physicochemical characteristics of biochar is the pyrolysis temperature. While high-temperature pyrolysis (>600 °C) yields biochar with greater porosity, increased aromaticity, and enhanced hydrophobic interactions, which makes it more

effective for PAH adsorption, low-temperature pyrolysis (<400 °C) usually produces biochar with fewer surface areas and more oxygen-containing functional groups [31]. The choice of feedstock also has a significant impact on the characteristics of biochar [46]. Agricultural wastes (such as rice husks and corn stover), forestry waste (such as sawdust and wood chips), and materials generated from animals (such as manure and bone char) are examples of common feedstocks [92]. Animal-derived biochars contain more inorganic components that could contribute to additional adsorption mechanisms, while plant-based biochars typically have a bigger surface area and a higher carbon content [36, 107].

The adsorption capacity of biochar can be further increased by activation techniques including chemical activation (using acids, bases, or salts) and physical activation (using steam or gas treatment) [92]. Superior PAH removal effectiveness is often achieved by activated biochars because of their enhanced surface area, better pore structure, and higher surface functionalisation [108]. Optimising the use of biochar in environmental restoration requires an understanding of the connections between its adsorption capability and manufacturing characteristics [83, 109]. A study by Li et al. [110], used meta-analysis to show that biochar modifies the persistence of PAHs in soils via altering the physicochemical parameters and microbiological diversity of the soil. A meta-analysis utilising 56 published studies was carried out to assess the impact of biochar on the concentration of PAHs, soil physicochemical properties, and microbial diversity in PAH-contaminated soils, as well as to identify the factors affecting biochars capacity to alter PAH persistence. Applying biochar resulted in a significant decrease in soil total carbon (C<sub>tot</sub>) PAH concentrations (15.4 %), as well as a reduction in free carbon (C<sub>free</sub>) PAH and bioaccessible carbon (C<sub>bioacc</sub>) PAH levels of 55.6 % and 46.5 %, respectively. Furthermore, biochar enhanced the variety of microorganisms and improved the physicochemical characteristics of soil contaminated with PAHs. There was a notable increase in the relative abundance of PAH degraders (43.7 %), suggesting that PAH biodegradation was greatly improved. Overall, the findings demonstrated that pyrolysing woody biochar at 300–500 °C reduced the persistence of PAHs in soils with a high content of soil organic matter (>20 g/kg) [110].

A study by Geng et al. [83] investigated the efficacy of biochar as a PAHs adsorbent and microbially immobilised carrier. By encouraging  $\pi$ - $\pi$ /n- $\pi$  electron donor-acceptor interactions, hydrogen bonds, and electrostatic interactions, and hydrophobic interactions, acid/alkali modification enhanced the phenanthrene removal ability in an aqueous solution of biochars, according to the results of the surface characterisation and adsorption studies [83].

Following the successful immobilisation of the degrading bacteria *Rhodococcus* sp. DG1 on the rice husk-derived biochar using nitric acid oxidation (RBO), the biochar demonstrated the highest phenanthrene adsorption efficiency and a greater specific surface area. After 30 days, the microbes immobilised on RBO using the adsorption method generated a notable clearance rate of 80.15 % of phenanthrene, which was 38.78 % higher than the control [83].

The effectiveness of biochar as a material for sediment remediation of PAH contamination was investigated in a study by Chen et al. [41]. The effect of biochar as a capping material on the removal of PAHs from sediments was examined. The high adsorption capacity of the biochar was responsible for the 1.6-fold increase in pyrene that resulted from the amendment of biochar. The porosity and biological affinity of biochar allowed PAH degradation bacteria to establish a stable niche, even though it did not change the predominant microbial community. As per the findings, biochar enhanced the likelihood of PAH-degraders encountering PAHs in sediments. The adsorbed pyrene was quickly destroyed by the pyrene-degraders in the charcoal pore (+103 %) when electron acceptors were available. Biochar may therefore be a useful substance for removing PAHs from sediments [41].

### 5.3. Surface chemistry and functional groups involved in PAH adsorption

The interaction between biochar and PAHs is primarily governed by surface chemistry, including aromaticity, porosity, and functional group composition [111]. Because biochar is very aromatic, especially when made at high temperatures, it can interact with the aromatic rings of PAHs through  $\pi$ - $\pi$  bonds, increasing the adsorption affinity [104]. The vast pore network of biochar allows for size-exclusion effects and many adsorption sites, which permits the selective retention of various PAH molecules according to their chemical structure [29]. A study by Zhou and colleagues, used biochar made from wood waste to examine the adsorption mechanism of PAHs [111]. To examine the adsorption performance of PAHs, they generated two types of oxygen-rich biochar from waste wood. They also utilised molecular modelling to construct an adsorption model for 16 prioritised PAHs, 23 nitrated PAHs, and 9 oxygenated PAHs. The pyrolysis conditions have a substantial impact on the oxygen-rich biochars surface adsorption performance. The primary results showed that naphthalene molecules were the first to adsorb, and that oxygen-rich biochars ideal adsorption sites were strongly attached to carboxyl and hydroxyl functional groups. Furthermore, the primary adsorbed functional groups for PAH adsorption were the benzene ring, -COOH, and -CH<sub>3</sub> of biochar [111].

Additional functional groups that increase PAH adsorption efficacy can be introduced via surface changes of biochar, such as oxidation, amination, or metal impregnation [111]. The efficiency of biochar as an adsorbent for PAHs in polluted soils can be greatly increased by modifying its surface characteristics through post-treatment changes and controlled pyrolysis [112, 113]. A study by Boguta and colleagues examined the effects of modifier type and concentration on the sorption and structural characteristics of chemically modified biochar made from wood waste [114]. The study's primary goals were to: a) prepare chemically engineered biochars (BCs) using a variety of reagents, such as base (NaOH), organic ( $\text{CH}_3\text{COOH}$ ) acids and mineral ( $\text{HCl}$ ,  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$ ), b) identify the type and concentration of modifiers that affect the BCs' surface properties; and c) evaluate the best modification conditions in terms of environmental factors. According to their results, the modifiers utilised at the lowest concentrations did not significantly alter the BCs' characteristics. Acidic functional groups, mostly lactonic ones, were increased by acidic modifiers at 0.1–1.0 M. BCs treated with  $\text{CH}_3\text{COOH}$  and  $\text{H}_2\text{SO}_4$  showed the greatest improvement, with an increase in acidic structures of 13–17 % and 9–15 %, respectively. The BCs that were exposed to increasing concentrations of  $\text{CH}_3\text{COOH}$  (by 2–50 %) and NaOH (by 21–154 %) showed the greatest augmentation of basic groups [114].

Recent research has shed light on the surface chemistry and functional groups that control PAH adsorption onto biochar, showing that adsorption is influenced by both electron-donating and electron-withdrawing functional groups in addition to the more conventional  $\pi$ - $\pi$  interactions [115, 116]. It has been demonstrated that novel techniques such biomass mixing during pyrolysis and heteroatom doping (such as N, S, and P functionalization) can adjust surface polarity and electron density, increasing PAH affinity [117, 118]. Furthermore, the introduction of oxygenated and nitrogenous groups through in-situ surface modification using green oxidants or bio-based agents enhances hydrophobic interactions and chemical bonding. Targeted and effective PAH remediation can be achieved by optimizing the surface chemistry of biochar in uncharted areas, such as the dynamic alteration of functional groups under different environmental conditions and their long-term stability in field applications [118].

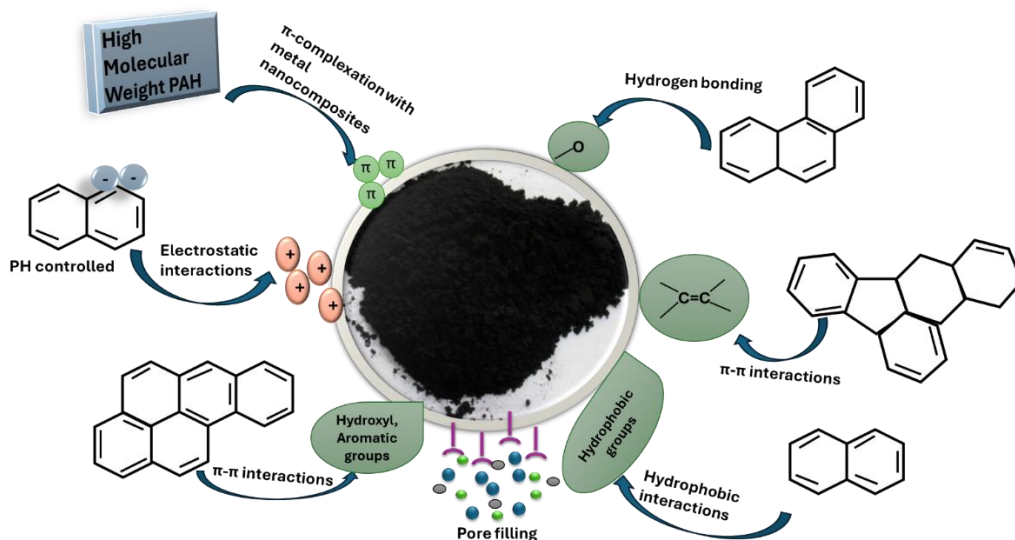
## **6. Mechanisms of PAH Adsorption onto Biochar**

### **6.1. The $\pi$ - $\pi$ stacking and hydrophobic interactions**

The  $\pi$ - $\pi$  stacking and hydrophobic interactions have a significant impact on the adsorption of PAHs onto biochar surfaces [83]. Due to the nonpolar character of both PAHs and biochar

surfaces, hydrophobic interactions are important in the adsorption of PAHs onto biochar [119]. Because they are hydrophobic organic molecules, PAHs prefer to bind to nonpolar, carbon-rich surfaces over watery ones. The carbon content and aromaticity of biochar, which rise at increasing pyrolysis temperatures, affect the strength of the hydrophobic interaction [31]. Additionally, because biochar and PAHs both contain conjugated  $\pi$ -electron systems,  $\pi$ - $\pi$  stacking interactions are essential in PAH adsorption [120]. Strong adsorption affinities result from these interactions between the graphitic-like structures on the surfaces of biochar and the aromatic rings of PAHs. High-temperature biochars are especially good at adsorbing high-molecular-weight PAHs because their highly developed aromatic structures improve  $\pi$ - $\pi$  interactions [119, 121].

Due to its abundance of aromatic carbon structures, biochar offers delocalized  $\pi$ -electron systems that can participate in  $\pi$ - $\pi$  electron donor acceptor (EDA) interactions with the aromatic rings of PAH molecules [122]. These interactions are enhanced by the level of aromaticity and graphitization of the biochar surface, especially in high temperature ( $\geq 600$  °C) biochars with a more organized carbon structure [123, 124]. By pushing nonpolar PAH molecules toward the hydrophobic areas of biochar surfaces and reducing their accessibility to aqueous phases, hydrophobic interactions further facilitate PAH adsorption. Under neutral pH and low polarity circumstances,  $\pi$ - $\pi$  stacking and hydrophobic partitioning are the predominant mechanisms for PAH sorption because of the strong, non-covalent connections that are frequently produced by this dual process [125, 126]. The mechanisms of PAH adsorption onto carbon-based adsorbents are depicted in **Figure 9**. The mechanisms demonstrated include pore filling within micro- and mesoporous structures, surface complexation involving oxygen-containing functional groups, hydrophobic contacts caused by PAH non-polarity, and  $\pi$ - $\pi$  electron donor-acceptor interactions between PAH aromatic rings and graphitic surfaces.



**Figure 9:** PAH adsorption mechanisms on carbon-based adsorbents.

Castan et al. [127] examined the impact of ionic strength and interactions with pyrene on the aggregation of biochar particles in soil pore water. The researchers examined the aggregation of biochar particles in solutions with varying ionic strengths (0.1 M CaCl<sub>2</sub>, 0.01 M CaCl<sub>2</sub>, and ultrapure water) using both biochar particle suspensions. This effect was more noticeable after 28 days of equilibration than after just 24 hours. The aggregation of biochar particles in solutions with 0.01 M CaCl<sub>2</sub> and pyrene was significantly higher than in solutions without pyrene. However, at high doses of CaCl<sub>2</sub> (0.1 M CaCl<sub>2</sub>), the impact of pyrene evaporated. To ascertain the fate of biochar in soil, it is necessary to consider both the presence of PAHs and the impact of the ionic strength of the pore water [127]. Chen et al. [117] investigated the effects of incineration and oxygen-limited pyrolysis on the transport of biochar. Their research examined the mechanisms of transport and retention for three varieties of traditional biochar and three varieties of oxygen-limited pyrolytic biochar in saturated porous media. As demonstrated by the results, the specific surface area of the three oxygen-limited pyrolysis biochars (180–200 m<sup>2</sup> · g<sup>-1</sup>) was greater than that of the conventional biochar (50–60 m<sup>2</sup> · g<sup>-1</sup>). As a result, the permeability of pyrolytic biochar is less than 0.1 and its retention capacity is strong. Traditional biochars zeta potential was more than 30 mV in absolute value, and it generated stronger electrostatic repulsion [117].

## 6.2. Pore-Filling and surface adsorption

Through pore-filling and surface adsorption processes, biochars porous structure facilitates the removal of PAHs by offering a large surface area and adsorption sites. Because of size-exclusion effects, PAH molecules can diffuse into the micropores and mesopores of biochar,

where they are physically confined [93]. Weak van der Waals forces also contribute to surface adsorption, especially in biochars with considerable surface roughness [86]. Defects, cracks, and edge sites on the surface of biochar can improve PAH retention by adding more adsorption sites. Biochar porosity, which is impacted by the kind of feedstock and pyrolysis conditions, increases the efficiency of pore-filling mechanisms [128].

Two important physical processes controlling the retention of PAHs in the porous matrix of biochar are pore-filling and surface adsorption [129]. PAH molecules can be confined or distributed into a variety of adsorption sites made possible by the hierarchical pore structure, which consists of micro, meso, and macropores [67]. Because of their size compatibility, micropores (less than 2 nm) are essential for the adsorption of low-molecular-weight PAHs, whereas mesopores (2–50 nm) may hold bigger, multi-ring PAHs. The growth of micro- and mesoporosity is facilitated by high-temperature pyrolysis, which increases the surface area and adsorption capacity. Pore-filling is enhanced by surface adsorption, especially for bigger PAHs that are difficult to enter micropores [130]. The overall adsorption effectiveness is greatly influenced by the interaction of these two processes, especially when the biochar has a large specific surface area and well-developed pore connectivity [83].

A study by Kleemann and colleagues assessed the adsorption of PAHs onto biochar derived from sewage sludge [131]. Their study used sewage sludge from a treatment plant to create biochar, which was then used as an adsorbent in a complicated system that contained 16 priority PAHs. Functional groups (FTIR), crystallinity (DRX), thermogravimetric degradation (DSC/DTG), morphology and elemental composition (SEM/EDS), specific surface area, and pore size were used to characterise the biochar. When SSB was  $2 \text{ g L}^{-1}$ , 90 % of the PAHs were eliminated, according to the dose effect. Various SSB doses were used in kinetic tests. The Elovich model was the best fit for the kinetic results. The US EPA reported 16 developing organic PAHs, each of whose adsorption capability and elimination % was assessed separately. The material's electivity for fluoranthene, pyrene, and phenanthrene was demonstrated by the highest adsorption capacities that were confirmed for these chemicals, respectively [131].

### 6.3. Role of functional groups and surface modifications

Functional groups on the surfaces of biochar affect PAH adsorption through electrostatic, hydrogen bonding, and dipole interactions [132]. However, for low-molecular-weight PAHs and biochars made at lower pyrolysis temperatures, where oxygen-containing groups are more prevalent, these interactions are more noticeable [117]. Chemical activation (oxidation,

amination, or metal doping) and other surface modifications can change the surface charge of biochar or add additional functional groups, increasing its adsorption ability. Metal-modified biochars can enhance adsorption efficiency by promoting  $\pi$ -complexation with aromatic rings, while oxidised biochars exhibit higher polarity and affinity for slightly polar PAHs [120]. For biochar to be optimised as an adsorbent, it is essential to comprehend how functionalisation and PAH elimination interact [121].

Chemical alteration or surface oxidation (e.g., with  $\text{H}_3\text{PO}_4$ , KOH, or metal oxides) can improve adsorption selectivity by adding more functional sites, increasing surface acidity, and changing electronic characteristics [133]. Additionally, surface modification may promote  $\pi$ - $\pi$  EDA interactions and increase wettability, especially for polar PAHs. On the other hand, severe oxidation might decrease hydrophobicity, which lowers the nonpolar PAHs' adsorption capacity. For biochar to perform at its best, surface functionality and hydrophobicity must be balanced [134]. Yao et al. [135] examined PAHs removal mechanisms in biochar and their impact on plant growth. In their study, biochar was produced by pyrolysing distillers' grains, pig dung, and sewage sludge at 300, 500, and 600 degrees Celsius, respectively. To examine the mechanism of PAH elimination in biochar and assess its impact on plant growth, the manufactured biochar was put through hydrothermal, water washing, and thermal treatments. Results indicated that hydrothermal treatment, thermal treatment, and water washing removed PAHs from biochar at rates of 36.79 % to 86.09 %, 80.00 % to 80.90 %, and 19.15 % to 72.40 %, respectively. PAH elimination processes include thermal desorption and weaken hydrophobic interaction [135].

Pore filling, hydrophobic interactions, and  $\pi$ - $\pi$  electron donor-acceptor interactions all influence the adsorption of PAHs onto biochar; surface functional groups and aromaticity are crucial in determining affinity and selectivity [136]. This study advances current understanding by critically linking biochar structural evolution and modification strategies to adsorption performance rather than treating mechanisms in isolation. One important lesson is that specific adsorption of PAHs with varying molecular weights is made possible by adjusting the surface chemistry and pore architecture of biochar, providing a logical design framework for soil remediation [7, 32]. Through mechanism-driven development of effective and sustainable biochar-based remediation methods, these findings advance the science beyond empirical data [137].

#### 6.4. Influence of environmental factors on PAH adsorption and biochar properties in soil

Temperature, pH, and soil composition are some of the environmental variables that affect PAH adsorption onto biochar [63]. Surface charge and interactions between functional groups on biochar are influenced by the pH of the surrounding environment [63]. Even though PAHs are non-ionic, changes in pH can change the surface chemistry of biochar, which can impact how well it adsorbs substances. For example, whereas alkaline circumstances might decrease surface polarity and favour hydrophobic interactions, acidic ones may increase hydrogen bonding [138]. Temperature affects molecule diffusion speeds and interaction energies, which are important factors in PAH adsorption. Higher temperatures can improve adsorption kinetics by increasing biochar surface activity and PAH mobility [112].

Environmental conditions strongly influence the adsorption behaviour of biochar toward PAHs, largely through effects on biochar surface properties, PAH speciation, and soil–water interactions [7]. Soil pH alters the ionization state of functional groups on both biochar and soil organic matter, affecting  $\pi$ – $\pi$  interactions and hydrophobic partitioning that govern PAH affinity. Under acidic conditions, protonation of surface oxygen groups can reduce electrostatic repulsion and enhance hydrophobic domain exposure, whereas alkaline conditions may increase negative surface charge and competition with dissolved organic matter, reducing PAH uptake [7, 139]. Pore accessibility and diffusive transport are determined by moisture content; moderate water coatings promote PAH diffusion into micropores, whereas saturation restricts mass transfer rates and gas-phase transfer [1]. Temperature affects the thermodynamics and kinetics of sorption: higher temperatures can improve diffusion into biochar pores and typically increase desorption from soil matrices, leading to complex temperature-dependent sorption isotherms. Variation rules in adsorption capabilities are influenced by aromaticity, surface area, and functional group distribution, which are further modulated by biochar feedstock, pyrolysis temperature, and age under environmental circumstances [98]. Hydrophobic partitioning,  $\pi$ – $\pi$  electron donor–acceptor interactions, hydrogen bonding, and pore filling are the mechanisms that control adsorption; the relative importance of each mechanism varies depending on soil composition, competitive sorbates, and environmental stressors [127].

Nevertheless, by decreasing intermolecular contacts, high temperatures may also decrease PAH retention. PAH adsorption onto biochar is also influenced by the make-up of the soil, which includes the amount of organic matter, clay minerals, and competing pollutants [140]. The efficacy of PAH removal may be decreased by organic materials in the soil competing for biochar adsorption sites. Conversely, by offering more adsorption surfaces, clay minerals may

improve PAH retention. Optimising the use of biochar in actual soil remediation situations requires an understanding of these environmental conditions [141]. Furthermore, adsorption selectivity may be impacted by competing hydrophobic chemicals and natural organic matter altering surface polarity or blocking active sites. Therefore, to accurately forecast PAH bioavailability and optimize the use of biochar in field circumstances, it is imperative to comprehend these environmental impacts [63, 134].

## 7. Factors influencing the adsorption efficiency of biochar for PAH removal

### 7.1. Biochar physicochemical properties on PAH adsorption efficiency

The effectiveness of biochars adsorption of PAHs is largely determined by its physicochemical characteristics [142]. The amount of adsorption is directly influenced by surface area and pore structure; biochars with a high surface area have higher adsorption capabilities because there are more active sites available [139]. While mesoporous biochars offer superior adsorption for bigger PAHs, microporous biochars, which are created at high pyrolysis temperatures are more efficient for small PAH molecules [48]. Hydrogen bonds, dipole-dipole interactions, and electrostatic forces are among of the ways that functional groups on the surface of biochar affect PAH interactions [142]. Because of their increased aromaticity and decreased oxygen-containing functional groups, high-temperature biochars are more effective against nonpolar PAHs [143]. The selectivity and adsorption capability of biochar can be further enhanced by modifications such oxidation, amination, and metal doping [42, 144]. A study by Guo et al. [144] used both magnetic and non-magnetic biochars generated from rice husks to investigate the sorbent removal of phenanthrene from aqueous solutions. Phenanthrene (PHE) was removed from aqueous solutions using magnetically modified rice husk biochar (MBC), which was successfully made using a hydrothermal process from original biochar. The BC's porosity, specific surface area, and hydrophobicity all increased following magnetic treatment. The adsorption data was well-fitted to Langmuir and pseudo-second-order kinetic models. In comparison to BC, MBC exhibited a larger adsorption capacity of PHE and a faster adsorption rate. Based on the Sips model analysis, PHE's maximum adsorption capacity on MBC was 97.6 mg/g, which was noticeably more than that of other BC sources. The  $\pi$ - $\pi$ -conjugated processes and surface functional groups were primarily responsible for the two BCs' adsorption mechanism. PHE was primarily adsorbed in the functional groups of C–O and Fe<sub>3</sub>O<sub>4</sub> on MBC, whereas it was primarily adsorbed in the functional groups of –OH, N–H, C=C, and C–O on BC [144].

## 7.2. PAH characteristics

The physicochemical characteristics of PAHs, specifically their molecular weight, polarity, and solubility, have a major impact on the adsorption efficacy of biochar [96, 145]. Low-molecular-weight PAHs (such as naphthalene and phenanthrene) are more susceptible to desorption and leaching due to their greater solubility and mobility in soil [138, 146]. The behaviour of PAH adsorption is also influenced by polarity. While slightly polar PAHs may create hydrogen bonds with the oxygen-containing functional groups of biochar, nonpolar PAHs mostly interact with it through van der Waals forces and  $\pi$ - $\pi$  stacking. The total adsorption efficiency and the possibility of PAH retention in contaminated soils are determined by the balance between these interactions [100].

## 7.3. Soil conditions

The adsorption effectiveness of biochar can be changed by the ambient conditions of contaminated soil [147]. The pH of the soil influences the surface charge and functional group activity of biochar, which in turn impacts the interactions between PAHs [63]. Even though PAHs are non-ionic, changes in pH can influence how the functional groups in biochar are protonated or deprotonated, which can alter hydrogen bonds and dipole interactions [148]. The overall removal effectiveness may be decreased if organic matter in the soil competes with PAHs for adsorption sites on biochar [94]. Organic matter can also increase the solubility of PAHs, which might lead to increased bioavailability and possible adsorption onto biochar [149]. PAH mobility is influenced by moisture content; a higher water content promotes PAH transport but may also result in competing adsorption with water molecules [138]. Microbial activity in soil can aid in the breakdown of PAHs, enhancing the adsorption capacity of biochar. However, adsorption sites may be blocked by extensive microbial colonisation on biochar surfaces, which would decrease efficacy. Optimising the use of biochar in actual remediation situations requires an understanding of soil characteristics [142].

A study by Ukalska-Jaruga et al. [145] examined how PAHs dissipate and sorb to organic matter in soils that have been modified with exogenous rich-carbon material. To accurately observe the behaviour of PAHs in soils, the investigation was conducted as a sorption experiment under carefully regulated air and water conditions. After nine months of ageing, the average decrease in PAH-tot levels in soils without biochar was 92 %, but the average decrease in soils with biochar was 41 %. Flu, Ant, Phe, and Pyr showed comparable  $T_{1/2}$  (43–59 days) in soils devoid of biochar, however Chry showed a significantly greater and wider  $T_{1/2}$  than other hydrocarbons (67–280 days). The half-life modifications for all PAHs were

considerably impacted by the addition of biochar to the soils. The behaviour and sorption potential of PAHs in the soil are considerably altered by the addition of exogenous carbon material, such as biochar. Higher PAH persistence, longer ageing times, and decreased sorption affinity by native organic matter structures are characteristics of biochar-enriched soils [145].

#### 7.4. Competition with other contaminants in soil

Heavy metals, petroleum hydrocarbons, and other organic compounds are among the many contaminants found in contaminated soils that might compete with PAHs for biochar adsorption sites [150, 137]. Co-contaminants can disrupt PAH adsorption by changing the surface chemistry of biochar or by directly competing with it. For instance, metal ions could attach to the functional groups of biochar, decreasing the number of PAH adsorption sites that are available [151, 152]. Biochar can occasionally be made more selective for PAHs while reducing interference from other pollutants by functionalising it with chelating agents or multi-sorbent composites. Enhancing biochars efficacy in intricate environmental systems requires an understanding of competing adsorption mechanisms [148, 153]. A study by Li et al. [154] used biochars made at various pyrolytic temperatures to selectively remove PAHs from soil washing effluents. To selectively adsorb PAHs from soil washing effluents, wheat straw biochars (BC400, BC600, and BC800) were generated at 400, 600, and 800 °C. For soil washing effluents containing Triton X-100 (TX100), PHE, FLU, and PYR, biochars at 2 g L<sup>-1</sup> (for BC800) or 6 g L<sup>-1</sup> (for BC400 and BC600) can recover more than 87 % of TX100 while removing 71.8–98.6 % of PAHs. The removal of PAHs increases as the dose of biochar increases. As the pyrolytic temperature rises for a given dose of biochar, PAH elimination and TX100 loss rise as well. The sorption affinity of biochars for PAHs is significantly higher than that of TX100. Therefore, it is proposed that biochar is a good substitute for TX100 recovery and selective PAH adsorption in the soil washing process [154].

Chen et al. [86] conducted a study on the enhanced sorption of PAHs by soil modified with biochar. They assessed how various types of biochar influenced the sorption of PAHs into agricultural soil that had been modified with biochar [86]. Pine needle biochar was made at a range of pyrolytic temperatures (P100–P700; 100 °C, 300 °C, 400 °C, and 700 °C) and added to a variety of paddy soil compositions. Biochars have varying impacts on the sorption of PAHs by soil that has been modified with biochar. Because P100 has a linear-type isotherm, adding it to soil boosted the sorption isotherm's linearity. High pyrolytic temperature-produced biochar showed great efficacy in increasing the sorption affinity of biochar-amended soil. When the P300 level exceeded 0.5 % and the P400 and P700 contents above 0.1 %, biochar considerably

regulated the total sorption. According to the results, adding biochar to soil may improve the sorption of PAHs to the soil [86].

Biochar characteristics (pore size distribution, aromaticity, surface area, and functional groups), PAH properties (molecular weight and hydrophobicity), and soil environmental factors interact to determine the effectiveness of PAH adsorption onto biochar [155]. This work provides a novel perspective by combining these variables into a single framework that explains performance variability across studies rather than evaluating them separately. The key takeaway is that system-specific biochar design and application strategies are necessary for effective PAH remediation, going beyond one-size-fits-all methods in favour of predictive, context-driven optimization [63, 156].

## **8. New developments in the alteration of biochar for improved PAH adsorption**

### **8.1. Surface functionalization and activation techniques**

Recent advances in biochar modification have focused on improving its adsorption capacity for PAHs through surface functionalization and activation techniques [156]. Surface functionalisation is the process of adding different functional groups, including amine (-NH<sub>2</sub>), carboxyl (-COOH), or hydroxyl (-OH), which can improve the polarity of the biochar and produce certain interactions with PAHs [142]. Through the formation of hydrogen bonds or electrostatic interactions with PAHs and an increase in surface reactivity, these functional groups enhance the biochar's capacity to adsorb hydrophobic contaminants. Similarly, the specific surface area of biochar can be increased and the pore distribution optimised through physical activation through pyrolysis at high temperatures [123]. These changes increase the overall effectiveness of biochar in contaminated soils and make it more selective in its adsorption of various PAH types [63].

### **8.2. Composite biochar materials**

Another significant advancement in biochar modification involves the development of composite biochar materials, such as biochar-nanoparticle hybrids [157]. The incorporation of nanoparticles, such as iron oxide, zinc oxide, or carbon-based materials, into biochar has been shown to enhance its adsorption properties for PAHs [133, 158]. The porous structure of biochar and the high reactivity of nanoparticles are combined in these composite materials to produce synergistic effects that enhance the overall effectiveness of pollution removal. For instance, because of the metal ions' additional interaction sites and the nanoparticles' large surface area, biochar combined with metal nanoparticles may show enhanced adsorption of

PAHs [123]. Additionally, biochar-nanoparticle hybrids can have catalytic qualities that could aid in the breakdown or modification of adsorbed PAHs, fulfilling the twin purposes of remediation and adsorption. When treating heavily contaminated soils, when improved adsorption and removal are required for efficient pollution mitigation, these composite materials are very helpful [159, 160].

Although many biochar modification techniques, including metal or metal-oxide loading, acid/alkali functionalization, and composite creation with clays or polymers, have been reported to improve PAH adsorption, their quantitative effectiveness varies significantly [114, 161]. Due to increased surface area and oxygen-containing functional groups, acid-modified biochars usually exhibit 20–60% improvements in PAH adsorption capacity. Higher removal efficiencies (>80–90%) can be attained by metal-loaded biochars (e.g., Fe-, Mn-, or Mg-based), but they frequently come at a 2-4 times higher manufacturing cost and carry the danger of secondary metal leaching [162, 163].

The highest adsorption capabilities (often >250–300 mg/g) and enhanced selectivity are generally found in composite biochars that incorporate clays, graphene, or polymers [164]. However, these biochars come with complicated synthesis processes, higher material costs, and larger life-cycle environmental footprints. While advanced composites are very effective, they might not be as viable for large-scale field applications without additional techno-economic and sustainability optimization [165]. In general, simple chemical functionalization provides the optimal balance between efficiency, cost, and environmental impact [157]. **Table 4** shows the adsorption performance of biochar modification techniques for removal of PAHs. Along with the related surface and structural changes, it provides an overview of important kinetic and equilibrium characteristics, such as adsorption rate, equilibrium time, and maximum adsorption capacity. The comparison shows how various modification techniques affect adsorption mechanisms, efficiency, and practical application, enabling a methodical assessment of their benefits, drawbacks, and appropriateness for long-term PAH remediation.

**Table 4.** Comparative adsorption performance of different biochar modification strategies for PAH removal.

Biochar Modification Strategy	Main Surface/Structural Changes	Typical Adsorption Rate	Equilibrium Time	Maximum Adsorption Capacity ( $q_{max}$ )	Dominant Adsorption Mechanisms	Key Advantages	Key Limitations	Reference
Pristine biochar	Moderate surface area; native oxygenated functional groups	Moderate	12–48 h	Low–moderate (10–80 mg/g)	Hydrophobic interaction, pore filling	Low cost; environmentally benign	Limited capacity; slow kinetics	[166]
Physically activated biochar (steam/ $CO_2$ )	Increased microporosity and surface area	Fast	6–24 h	Moderate–high (50–200 mg/g)	Pore filling, $\pi$ - $\pi$ interactions	Improved kinetics and capacity	Energy-intensive activation	[167]
Chemically activated biochar (KOH, $ZnCl_2$ , $H_3PO_4$ )	Highly developed pore structure; high surface area	Very fast	2–12 h	High (150–500 mg/g)	Pore filling, $\pi$ - $\pi$ interactions	Excellent adsorption performance	Chemical cost; secondary pollution risk	[168]
Metal/metal oxide-loaded biochar (Fe, Mn, Al oxides)	Enhanced surface reactivity; heterogeneous nucleation sites	Fast	4–24 h	Moderate–high (80–300 mg/g)	Surface complexation, $\pi$ - $\pi$ interaction, co-adsorption	Improved selectivity; multifunctionality	Possible metal leaching	[163]
Magnetic biochar ( $Fe_3O_4$ -modified)	Magnetic separability; increased surface heterogeneity	Fast	3–12 h	Moderate–high (100–350 mg/g)	$\pi$ - $\pi$ interactions, pore filling	Easy recovery and reuse	Added synthesis complexity	[169]
Composite biochar (biochar-clay, biochar-polymer)	Improved mechanical stability and sorption synergy	Moderate	12–48 h	Variable (60–250 mg/g)	Combined adsorption and partitioning	Structural stability; reduced leaching	Lower adsorption rate than activated biochar	[170]

### 8.3. Multi-pollutant removal approaches

Recent studies have also explored biochars potential in multi-pollutant removal, which is particularly relevant for soils contaminated with a range of environmental pollutants, including PAHs, toxic elements, and other organic pollutants [90, 123]. Because of its adaptability, biochar may absorb multiple contaminants at once, which makes it a great option for all-encompassing soil remediation techniques [171]. Optimising the surface chemistry and pore structure of biochar to increase its capacity to absorb various contaminants is necessary to modify it to target diverse pollutants [172, 173]. Functionalised biochar, for example, can be designed to specifically target PAHs while simultaneously promoting heavy metal adsorption via electrostatic or ion exchange interactions [98, 174]. Additionally, the creation of composite biochar materials that combine Metal-Organic Frameworks (MOFs) or other sophisticated materials can improve the multi-pollutant adsorption capacity of biochar by improving its ability to interact with both organic and inorganic contaminants [175]. In addition to increasing biochars effectiveness in polluted soils, these multi-pollutant removal techniques also lessen the need for intricate treatment procedures, which makes biochar-based solutions more affordable and environmentally friendly for widespread use [176, 169]. **Table 5** shows comparative evaluation of the economic impact of various types of biochar for PAH adsorption. The comparison sheds light on the trade-offs between economic viability and adsorption efficiency, offering guidance on the best biochar choices for extensive and long-term PAH remediation.

**Table 5:** Comparative economic analysis of various biochar types for PAH adsorption

Biochar feedstock	Production method	Typical pyrolysis temperature (°C)	Estimated production cost (ZAR/ton)	Adsorption efficiency for PAHs (% Removal)	Remarks	References
Wood-based biochar	Slow pyrolysis	450–600	6,500 – 8,000	75–90	High surface area and aromaticity; relatively costly due to feedstock sourcing.	[177]
Agricultural residue biochar (e.g., corn stalk, rice husk)	Slow pyrolysis	400–550	3,500 – 5,500	65–85	Low-cost and sustainable; adsorption efficiency depends on feedstock composition.	[82, 178]
Sewage sludge biochar	Hydrothermal carbonization	180–250	2,800 – 4,500	60–80	Low cost; contains mineral phases enhancing adsorption; may require post-treatment to reduce toxicity.	[179]
Manure-derived biochar	Slow pyrolysis	400–600	4,000 – 5,800	70–88	Nutrient-rich; beneficial for soil amendment but may have higher ash content.	[180]
Industrial waste biochar (e.g., paper sludge, sawdust)	Slow pyrolysis	500–600	3,000 – 4,800	68–82	Good cost-performance balance; potential for circular economy use.	[181]
Activated biochar (chemically modified)	Activation (H <sub>3</sub> PO <sub>4</sub> , KOH, etc.)	600–800	8,500 – 12,000	85–98	Highest adsorption efficiency; higher energy and reagent costs.	[182]
Composite biochar (e.g., biochar–clay or biochar–metal oxides)	Co-pyrolysis or surface modification	500–700	9,000 – 13,000	88–99	Superior PAH removal efficiency; costly due to additives and synthesis complexity.	[183]

## 9. Comparison of biochar and other adsorbents for the removal of PAHs

### 9.1. Comparison with activated carbon, clay minerals, and zeolites

PAHs in contaminated soil can be adsorbed using zeolites, clay minerals, activated carbon, and biochar [138, 184]. Activated carbon is believed to be the most effective of these due to its vast surface area and well-developed microporous structure, which allow for strong hydrophobic interactions and  $\pi$ - $\pi$  stacking with PAHs [185]. However, activated carbon's extensive use in environmental remediation is restricted by its high cost and energy-intensive manufacturing method [162]. The strong cation exchange capacity and layered structures of clay minerals, like kaolinite and montmorillonite, make them an affordable substitute with good adsorption potential [186]. However, because to weaker hydrophobic interactions and a lack of pore architectures that are appropriate for PAH adsorption, their removal effectiveness is frequently lower than that of charcoal [150, 187]. A study on the adsorption of PAHs by natural, synthetic, and modified clays was carried out by Satouh et al. in 2021. The removal of 16 PAHs was evaluated and compared in their study using the adsorption capacities of natural (montmorillonite (Mt)), synthetic (Na-Mica-4), and modified (containing octadecylamine and octadecyltrimethylamine (ODA-Mt, ODA-Mica-4, ODTMA-Mt, and ODTMA-Mica-4)) clays. Zeta potential, FTIR, and XRD were used to synthesise and characterise the materials. Following the adsorption tests, the results demonstrated proper preparation and the absorption of PAHs into the clays' structure. The recommended materials have adsorption percentages close to 100 %, making them effective PAH adsorbents. Specifically, those utilising Mt. Mt and Na-Mica-4 demonstrated superior adsorption capacity compared to their organofunctionalized derivatives, suggesting that PAH adsorption may take place in both the interlayer and the surface portion. The suggested adsorbents benefit from their low cost and excellent efficiency [186].

A study on the removal of PAHs from soil using a composite material that contains iron and activated carbon in the freeze-dried calcium alginate matrix was carried out by Funada et al. [162]. The development of a new clean-up technique that uses a composite consisting of activated carbon as an adsorbent and iron powder as a magnetic material in a freeze-dried calcium alginate matrix (Fe-AC-alg) has allowed for the magnetic separation of PAHs from solid samples. This approach was used to determine the number of PAHs that were extracted

from the glass beads. The Fe-AC-alg (1.0 g) was combined with a roadside soil sample (10 g) for two weeks. Over 96 % of the PAHs were removed [162].

Zeolites also show good adsorption capabilities for PAHs due to their tunable porosity and well-defined crystalline structures [188]. For locations that are co-contaminated with both organic and inorganic contaminants, their ion-exchange capabilities may be beneficial [189]. However, zeolites are more costly than charcoal due to the additional processing needed for their manufacture and modification for optimal PAH removal [190]. In contrast to these adsorbents, biochar provides a balance between cost-effectiveness, environmental sustainability, and adsorption efficiency [151]. Its porosity, functional groups, and surface properties can all be altered by pyrolysis and post-treatment modifications, making it a versatile material for PAH remediation [35]. PAHs sorption by functionalised humic acids immobilised in micro- and nano-zeolites was examined in a study conducted in 2021 by Robles-Mora and colleagues [190]. To entrap PAHs, they proposed a hybrid sorbent that combines functionalised humic acids (HAs) and nano-zeolite. To overcome the instability of HAs in solution, which has already been documented, functionalized HAs immobilised in a porous support are used. To increase HAs' non-polarity and the production of aliphatic groups, HA functionalisation was done. Anthracene and pyrene were removed at percentages greater than 90 % because of hybrid support; fluoranthene, which has an angular molecular structure, was adsorbed at 85 % [190].

## 9.2. Cost-effectiveness and sustainability considerations

For large-scale clean-up applications, an adsorbent's cost-effectiveness is a crucial consideration [191, 192]. Despite being very effective, activated carbon is costly because it is made from non-renewable resources and requires energy-intensive activation procedures [123]. Biochar, on the other hand, is a more economical and sustainable substitute because it is made from forestry and agricultural waste [45]. Pyrolysis's ability to produce biochar also makes it possible to use biomass scraps, which lowers waste and promotes a circular economy. Clay minerals and zeolites are relatively inexpensive but require mining and processing, which can have environmental impacts [19, 175, 190]. Biochar is a sustainable adsorbent for PAH clean-up because of its low production costs, renewable feedstock sources, and potential for carbon sequestration. Additionally, biochar application in contaminated soil can improve soil health, promote microbial activity, and provide long-term environmental benefits beyond pollutant removal [151]. A succinct comparison of the sustainability and cost-effectiveness of biochar and other adsorbents for the removal of PAHs from polluted soil is given in **Table 6**.

**Table 6:** Comparison of the sustainability and cost-effectiveness of biochar and other adsorbents for the removal of PAHs from polluted soil.

Adsorbent	Cost-Effectiveness	Sustainability	Regeneration & Reusability	Limitations	References
Biochar	Low-cost, produced from waste biomass	Renewable, carbon-negative, enhances soil fertility	Can be regenerated but may degrade over time	Variable adsorption efficiency depending on feedstock and activation	[127, 151]
Activated Carbon	High cost due to production and activation processes	Non-renewable (if coal-based), high carbon footprint	Effective regeneration possible, but costly	Expensive, energy-intensive production, limited large-scale use	[162]
Clay Minerals	Low-cost, naturally abundant	Environmentally friendly, widely available	Limited regeneration capability	Lower adsorption capacity for PAHs compared to biochar and activated carbon	[186, 193]
Zeolites	Moderate cost, synthetically produced or mined	Naturally occurring but some types require energy-intensive synthesis	Good regeneration potential	High production cost for synthetic zeolites, lower efficiency for hydrophobic PAHs	[188]

### 9.3. Regeneration and reusability of biochar in PAH adsorption

Improved long-term cleanup techniques and lower operating costs depend on an adsorbent's reusability. However, repeated regeneration cycles may result in structural degradation and decreased adsorption effectiveness [17, 136, 194]. Activated carbon can be regenerated chemically or thermally [162]. Chemical regeneration procedures, which can be expensive and result in secondary waste, may also be necessary for zeolites and clay minerals [186, 190]. Biochar, depending on its composition and surface modifications, can be regenerated through thermal desorption, solvent extraction, or biological treatments [78]. However, the regeneration

efficiency varies based on the nature and extent of PAH adsorption [46]. According to studies reported in literature, biochar may be able to maintain its adsorption ability for several cycles, especially when combined with microbial degrading techniques that promote the breakdown of PAHs [74, 111]. Although research is ongoing to determine whether biochar can regenerate, its low cost of manufacture and environmental advantages make it a viable choice for one-time or limited-reuse treatments in soils contaminated with PAHs [27]. Because of its tiny particle size and intense interaction with soil components, biochar is difficult to separate from soil for regeneration [175]. Regeneration is frequently evaluated in lab settings as opposed to field settings [76]. Regeneration of biochar for practical uses may entail on-site reactivation via chemical or thermal treatment of excavated soil biochar mixtures [78, 195].

In 2023, Jia and colleagues investigated the regeneration of a novel high-performance biochar mercury adsorbent that had been directionally modified through multimetal multilayer loading [78]. They employed temperature-programmed desorption and adsorption kinetics to explore the microscopic characteristics of the regenerated materials and the underlying mechanism of  $Hg^0$  removal and regeneration. Their results revealed that introducing multiple metals reduced the pyrolysis reaction barrier of the modified biomass. The formation of aggregated metal oxides on the altered biochar surface enhanced the oxidative activity of the carriers and amplified the Ce oxide threshold effect. Furthermore, optimal regeneration conditions (5 %  $O_2$  at 600 °C) effectively balanced deep carbonisation with the restoration of adsorption and oxidation sites, establishing clear structure-performance relationships between the physicochemical properties and  $Hg^0$  removal efficiency of the regenerated biochar [78]. Biochars potential as a sustainable remediation material will be further increased by research into enhancing its structural stability and regeneration effectiveness [148].

## **10. Practical applications and field studies**

### **10.1. Laboratory vs. field-scale performance of biochar for PAH removal**

Biochars ability to effectively remove PAHs from polluted soils under controlled settings has been shown in laboratory-scale research; high removal efficiencies for different PAH compounds have been noted [111, 196]. However, there are many obstacles in converting these findings into field-scale applications [197]. Complex soil properties including moisture content, microbial activity, and organic matter concentration may have an impact on biochars efficacy at the field scale by affecting its adsorption capacity [198]. Furthermore, environmental factors including temperature fluctuations, seasonal variations, and interactions

with other contaminants in the soil can affect the long-term effectiveness of biochar [199, 200]. Since field studies give a more accurate picture of how biochar interacts in dynamic, heterogeneous environments, they are required to evaluate the practicality of biochar for PAH elimination.

Comparative long-term field performance data show that while laboratory studies often report high static adsorption capacities under controlled conditions, field performance is subject to dynamic environmental influences that can attenuate or sustain remediation efficacy over time [111, 201]. For instance, multi-season monitoring at old industrial sites demonstrates that biochar-amended soils remove PAHs quickly at first, followed by varying stabilization stages where sorption dynamics are altered by microbial degradation, biochar aging, and organic matter accumulation [202]. Biochar aging increases affinity for higher-molecular-weight PAHs due to increased surface oxidation and micropore development, but it may decrease adsorption rates for lower-molecular-weight compounds due to pore blockage or competitive sorption with soil organic matter, according to field studies comparing aged biochar to its fresh counterparts [139]. Longitudinal datasets show that plant-microbe interactions, wet-dry alternations, and freeze-thaw cycles all have a significant impact on the long-term retention and re-mobilization of PAHs, with some sites maintaining reductions of  $\geq 70$ –85% compared to untreated controls over multi-year periods [11, 83]. The need to incorporate environmental variability into mechanistic models to more accurately forecast the actual performance of biochar-based remediation techniques is highlighted by such field data [203].

Geng et al. [202] conducted a pilot-scale study on the bioaugmentation of PAH-contaminated soil using a locally sourced bacterial consortium in soil-slurry bioreactors. Both laboratory- and pilot-scale experiments were performed to explore the degradation mechanisms involved in this bioremediation approach. In laboratory-scale bioreactors, the indigenous PAH-degrading consortium, initially isolated from the soil, achieved an 80.5 % total PAH degradation rate. Subsequently, a 410-day pilot-scale trial was implemented using two 1.5 m<sup>3</sup> bioreactors to evaluate key operational parameters and determine optimal conditions. The critical factors influencing PAH removal were identified within the first 200 days. Once optimal conditions were established, an average PAH removal efficiency of 93.4 % was achieved over 15 consecutive treatment batches spanning 210 days. Low-Molecular-Weight (LMW) PAHs degraded at a pace that was noticeably faster than that of High-Molecular-Weight (HMW) PAHs under ideal operating conditions; however, their degradation behaviours did not differ appreciably when mass transfer was constrained [202].

The effects of nanoscale zero-valent iron loaded biochar on the destiny of phenanthrene in the soil-radish (*Raphanus sativus* L. var. *radculus pers*) system were investigated by Shen et al. [204]. It has been demonstrated that using nanoscale zero-valent iron loaded on biochar (nZVI@BC) to activate persulfate can effectively remove organic contaminants from soil [204]. The widely distributed phenanthrene was chosen as the model pollutant in their study, which involved ball-milling nZVI@BC, nZVI, and nanoscale biochar (nBC) and applying them as amendments in pot experiments with PAH-contaminated soil to examine their effects on soil-crop (radish, *Raphanus sativus* L.) systems. The findings showed that, in comparison to the control treatment, nZVI@BC might cause a greater (75 %) build-up of Phenanthrene in radish; however, there were no appreciable changes in plant biomass or enzyme activity. Radish shoots' Fe concentration rose from  $86.87 \pm 5.61$  mg/kg DW without material application to  $125.20 \pm 11.93$  mg/kg DW with nZVI@BC in Phe-uncontaminated treatments, while roots showed no discernible changes [204].

#### 10.2. Case studies on biochar application in PAH-contaminated sites

Several case studies that have investigated its usage for PAH elimination at contaminated locations has demonstrated biochars potential as an efficient remediation method [95, 205, 206]. For example, biochar has been used to lower the content of PAHs in the soil in urban and industrial regions with high levels of pollution [207, 208]. In one such example study, PAH-contaminated soils next to an industrial complex were treated using biochar made from agricultural waste [127, 209]. The results demonstrated a notable decrease in PAH concentrations, and the pyrolysis settings and feedstock type had an impact on biochars adsorption capacity [111]. In a different case study in China, biochar was used to clean up PAH-contaminated soils in a mining region [110]. It was found to be an excellent adsorbent of PAHs and other co-contaminants, such as heavy metals [195]. The effectiveness of biochar in the removal of PAHs from polluted soil at the laboratory and field scales is contrasted in **Table 7**. These case studies demonstrate the usefulness of biochar in actual contaminated areas, but they also emphasise the necessity of site-specific modifications to optimise its effectiveness [210, 211].

**Table 7:** Comparisons of laboratory- and field-scale performance of biochar for PAH removal from soil and sediment.

Location	Scale	Biochar Type	Pyrolysis Temperature (°C)	Soil/Sediment Type	PAH Type(s)	Efficiency (% Removal)	Key Findings	References
Serbia	Laboratory	Wood-based biochar	740	Sandy loam	16 USEPA PAHs	–	Biochar reduced the bioavailability of PAHs in sediment that has been historically contaminated.	[81]
Poland	Field experiment	premium grade biochar	650	loamy sand	16 USEPA PAHs	–	The largest PAH losses were observed over the first 105 days of the experiment.	[212]
Taiwan	Laboratory	Wood biochar	300	sediment	16 USEPA PAHs	90%	Wood based biochar effectively removed PAHs from contaminated sediment.	[177]
Poland	Laboratory	sewage sludge-derived biochars	500 & 700	Contaminated soil	16 USEPA PAHs	–	Sewage sludge biochars successfully reduced the bioavailable PAHs in	[85]

							contaminated soil.	
Poland	Laboratory	Activated biochar	800	Contaminated industrial soil	16 USEPA PAHs	70-86%	The efficiency of immobilising PAHs was increased by the activated biochar.	[213]
China	Laboratory	metallic biochar	500	Sediments	Phenanthrene	39.6-87.5%	Metallic biochar improved Phenanthrene removal efficiency.	[214]
China	Laboratory	Biochar	500	River sediments	Pyrene	103%	Biochar could be a useful substance for removing PAHs from sediments.	[41]
China	pilot-scale	biochar-supported nanoscale zerovalent iron	700	Contaminated soil	Aromatic hydrocarbons	86.9-99.2%	Biochar was effectively used on an in-situ pilot scale to remediate contaminated soil.	[215]
China	Laboratory	Rape straw biochar	500	Contaminated soil	16 USEPA PAHs	-	The rhizosphere soil treated with 2% biochar showed the greatest PAH reduction.	[216]

China	Laboratory	Woody biochar	400	Contaminated soil	Phenanthrene, pyrene and benzo(a)pyrene	5.96-106%	The removal of PAHs was greatly enhanced by the combination of plants and biochar.	[84]
Taiwan	Laboratory	Bamboo biochar	800	marine sediments (loamy)	16 USEPA PAHs	76-90%	Bamboo biochars demonstrated a high removal effectiveness of PAHs.	[165]

### 10.3. Potential hazards and long-term stability of biochar in soil

The sustainability of biochar as a PAH elimination method depends critically on how stable it is in soil over the long term [41, 217]. Although biochars high carbon content and resistance to microbial destruction make it generally stable, environmental conditions including rainfall, temperature changes, and soil pH can affect its efficacy and durability over time [218]. Research has indicated that the adsorption capacity of biochar may diminish with time as a result of soluble component leaching or modifications to its surface chemistry, which may impact its capability to retain PAHs [126, 198]. Furthermore, it is important to carefully evaluate the possible dangers connected to the application of biochar, such as the modification of soil microbial populations or the leaching of harmful substances [219]. To make sure that the use of biochar does not have unforeseen ecological repercussions, ongoing field research is required to evaluate its long-term stability and environmental impact. Enhancing biochars role as a sustainable and safe adsorbent for soil remediation requires addressing key challenges [35]. The feedstock, production conditions, and environmental interactions all affect the long-term stability and possible risks of biochar in soil [7, 172]. Biochar may experience oxidation, structural deterioration, or microbial transformation over time, which could change the stability and effectiveness of its adsorption. Biochar can also contribute pollutants such heavy metals or PAHs if not properly produced [42]. In contrast, biochar typically shows strong long-term stability and low environmental risk when properly optimized and characterized, which improves soil health and immobilizes pollutants [125].

In 2024, a study by Chen and colleagues investigated the remediation of PAH-contaminated soil using activated persulfate in combination with carbonylated activated carbon-supported nanoscale zero-valent iron (nZVI-CAC) [16]. The nZVI-CAC composites were synthesized and employed to activate persulfate (PS) for the degradation of PAHs in contaminated soils. The catalyst was thoroughly characterized using SEM, XRD, FTIR, and XPS techniques. Among the tested oxidant systems, the PS/nZVI-CAC combination demonstrated superior performance for phenanthrene degradation, outperforming PMS/nZVI-CAC and H<sub>2</sub>O<sub>2</sub>/nZVI-CAC systems [16]. It was also effective in degrading the other six PAHs with varying molar weights and structures. The chosen PAHs had the lowest and highest degradation efficiencies, respectively, of 60.8 % and 90.7 %, under ideal circumstances. A theoretical foundation for the remediation of PAH-polluted soil may be provided by the results, which showed that the

heterogeneous process utilising activated PS with nZVI-CAC was successful in PAH breakdown [16].

### **11. Limitations and Future Research Directions**

There are still several unanswered questions about the basic mechanisms behind the adsorption of PAHs onto biochar, despite tremendous advancements in our understanding of this process [7, 220]. Among these is a more thorough examination of the function of biochar surface chemistry, particularly about certain functional groups and how they interact with various PAH compounds [221]. The intricate interconnections involving hydrophobic contacts,  $\pi$ - $\pi$  stacking, and surface charge effects in the adsorption process require more investigation [10, 222]. Further research is required to examine the kinetics and thermodynamics of PAH adsorption under various settings, as well as the impact of environmental parameters, such as soil pH and temperature, on PAH adsorption efficiency [223]. By filling these gaps, biochar-based adsorbents for PAHs will be better designed, and their use in contaminated soils will be maximised [224, 225].

Although it has been demonstrated that biochar may successfully absorb PAHs, its long-term stability in polluted soils is still a problem [226]. Weathering, microbial deterioration, or leaching can cause biochar to change chemically or physically over time, which could lower its adsorption capacity [227]. The durability of biochar in soil ecosystems and its possible long-term interactions with other pollutants require more investigation [228]. Furthermore, it is important to thoroughly assess how applying biochar would affect the environment, especially about how it will affect microbial communities, soil health, and the ecosystem as a whole [229]. Examining biochar's long-term stability and potential environmental impacts will be beneficial in ensuring that it is a practical and effective soil repair method [32, 230]. The expense of producing, transporting, and using biochar on a broad scale presents further practical challenges, especially when addressing extensive contamination [202]. Furthermore, as the legal framework for the use of biochar in environmental applications is still developing, regulatory obstacles can prevent the broad adoption of biochar-based remediation solutions [198, 231].

Although biochar is generally thought of as an eco-friendly sorbent, its use in contaminated soils may present secondary contamination issues that need to be carefully considered [31]. When pH and redox conditions change, modified biochars especially those made by chemical activation or metal loading may contribute residual acids, alkalis, or trace metals that could

seep into soil and groundwater [231]. Furthermore, competitive sorption with dissolved organic matter or microbial degradation may cause aged biochar surfaces to liberate previously adsorbed PAHs, which could result in pollutant remobilization [116, 232]. Additionally, fine biochar particles could move through soil profiles, changing the physicochemical characteristics of the soil and influencing microbial communities. Therefore, to guarantee that biochar-based remediation reduces unforeseen environmental impacts while providing sustainable pollution control advantages, thorough leaching testing, long-term field monitoring, and life-cycle assessments are crucial [44].

Stakeholders and industry leaders can encourage the use of biochar by funding demonstration projects at the pilot stage, encouraging industry-academia cooperation, and creating commercial incentives for environmentally friendly soil remediation techniques [1, 233]. Creating public-private collaborations can hasten the commercialization and transfer of technology. Green innovation funds, climate resilience efforts, and environmental restoration programs might also provide funding options to support the production and implementation of biochar on a wide scale [233, 234]. To connect academic breakthroughs with useful, real-world applications, such concerted efforts are crucial [63].

New developments in biochar-based soil remediation present intriguing chances to increase the efficiency of PAH removal and broaden the range of biochars uses [235]. Recent advancements in biochar modification techniques, including chemical activation, functionalisation, and hybrid composites, can improve the adsorption capacity and selectivity of biochar for PAHs [236]. Research into biochars potential as a multipurpose adsorbent, which includes the capacity to absorb not just PAHs but also toxic elements and other organic contaminants, could expand its use [237, 238]. Soil remediation techniques that are more economical, sustainable, and efficient will be made possible by ongoing innovation in biochar materials, manufacturing techniques, and hybrid approaches [239, 155].

While surface modification methods like chemical activation and plasma treatment improve  $\pi$ - $\pi$  interactions and hydrophobic affinity for PAHs, magnetic biochars facilitate simple recovery and reuse [123, 240]. Additionally, coupled remediation systems that combine biochar with electrochemical, or bioremediation techniques are showing promise for large-scale soil decontamination, and machine learning and modelling tools are being used to forecast adsorption behaviour and improve design parameters [67]. Collectively, these developments

show how biochar-based PAH treatment is moving toward more effective, sustainable, and data-driven methods [136].

## 12. Conclusion

Biochar has emerged as a promising solution for remediating PAH-contaminated soils due to its high surface area, porous structure, and tunable surface chemistry. The main processes in PAH adsorption that enable biochar to efficiently absorb and hold onto PAHs in contaminated soils have been emphasised in this review, including pore-filling,  $\pi$ - $\pi$  stacking, and hydrophobic interactions. Surface functionalisation, activation methods, and the creation of composite biochar materials are only a few of the developments in biochar modification that have improved the material's adsorption capacity and selectivity for various PAH compounds. The removal of PAHs is governed by important adsorption mechanisms, which can be improved by chemically or physically altering biochar. These mechanisms include  $\pi$ - $\pi$  stacking, hydrophobic interactions, pore-filling, and the effect of surface functional groups. The potential for increasing adsorption capacity and reusability is demonstrated by emerging technologies such as engineered, magnetic, and composite biochars.

Moreover, biochar's capability to handle complicated soil contamination situations has been shown by its combination with other treatment techniques, such as multi-pollutant removal schemes. Despite these developments, there are still several obstacles to overcome before laboratory results may be applied on a large basis. These include the need for more biochar production method optimisation to guarantee cost-effectiveness and scalability, the long-term stability of biochar in soil, and variations in biochar performance brought on by environmental conditions. A bibliometric analysis showed limited research on biochar for PAH adsorption in polluted soil, emphasizing the need for further studies and innovation. Future studies should concentrate on filling up these gaps by investigating novel methods of biochar modification, comprehending how biochar affects microbial populations and soil health, and creating legal frameworks that would enable its widespread use. Ultimately, biochar offers a viable, adaptable, and affordable way to remove PAHs from polluted soils, with great promise for improving soil quality and lowering the dangers of PAH pollution.

### CRedit authorship contribution statement

**Motlatle Moshalagae:** Writing – review & editing, Resources, Investigation, Data curation, Conceptualization. **Mkhohlakali Andile:** Visualization, Software, Methodology, Investigation. **Mokoena Lebohang:** Writing – review & editing, Visualization, Validation,

Supervision, Project administration, Investigation. **Mogashane Tumelo:** Writing – review & editing, Writing – original draft, Software, Methodology, Investigation, Data curation, Conceptualization. **James Tshilongo:** Visualization, Investigation, Funding acquisition.

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### Conflicts of interest

The authors declare no conflicts of interest.

### Data availability

No data was used for the research described in the article.

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### **Declaration of Interest Statement**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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