



Review

Removal of Hydrophobic Contaminants from the Soil by Adsorption onto Carbon Materials and Microbial Degradation

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Abstract: The pollution of soil is a worldwide concern as it has harmful consequences on the environment and human health. With the continuous expansion of industry and agriculture, the content of hydrophobic organic pollutants in the soil has been increasing, which has caused serious pollution to the soil. The removal of hydrophobic organic contaminants from soil, aiming to recover environmental safety, is an urgent matter to guarantee sufficient food and water for populations. Adsorption has proven to be an effective and economically practicable method for removing organic contaminants. This paper summarizes the use of low-cost adsorbents, such as biochar and activated carbon, for removing hydrophobic organic contaminants from soil. Biochar is usually appropriate for the adsorption of organic contaminants via the adsorption mechanisms of electrostatic interaction, precipitation, and ion exchange. Biochar also has numerous benefits, such as being obtained from several kinds of raw materials, having low costs, recyclability, and potential for environmental treatment. This paper illustrates biochar's adsorption mechanism for organic contaminants and discusses the microbial degradation of hydrophobic organic contaminants.

Keywords: soil pollution; hydrophobic organic contaminants; adsorption; biochar; activated carbon; microbial degradation



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1. Introduction

Environmental pollution has become a worldwide concern. Both developing countries and developed nations are affected by environmental pollution and suffer the consequences. During the last century, there has been a large increase of industrialization, with a high demand for energy and the uncontrolled exploitation of natural resources, both of which aggravated the pollution problem, posing a serious threat to the biodiversity and ecosystems of the world [1]. Every year, demanding regulations for the control of pollution related to waste [2], air [3], atmosphere [4], and water [5] are proposed.

Recently, much attention has been paid to soil contamination. Ground contamination by chemicals is a worldwide problem [6], just like climate change and biodiversity loss [7]. Currently, with the incessant growth of industry and agriculture, the amount of organic pollutants has been increasing, which has caused severe pollution to the environment [8].

Hydrophobic organic contaminants (HOCs) mainly come from natural and anthropogenic sources. These organic pollutants are major environmental pollutants and have endangered the ecological environment and human health [9]. Organic contaminants are more widespread and complicated than heavy metal pollutants [10]. Soils and sediments are well-known natural sorbents and crucial sinks for several HOCs. Organic soil pollution ranges from single pollution to complex pollution [11]. The discharge of hydrophobic organo-xenobiotics from chemical, oil, wood, and coke industries has large impacts on soil quality [12]. The existence of HOCs in the soil is problematic since these compounds

show toxicity, mutation, are accumulated in the food chain, and present carcinogenic character [11,13]. The majority are persistent in soils because they are slow to degrade naturally or by biological, photo or chemical processes [14]. Such compounds, including hydrocarbons from petroleum, polychlorobiphenyls (PCBs), polychlorinated dibenzodioxins, dichloro-diphenyltrichloroethane (DDT), polycyclic aromatic hydrocarbons (PAHs), and most pesticides, are poorly soluble in water and show high contents of organic carbon, accumulating in soils through sorption [1]. Humans may be exposed to HOCs in soils may be by oral ingestion, inhalation, and/or dermal routes [15,16].

Of the abovementioned HOCs, the most common are PAHs (formed by hydrogen and carbon), which are universal harmful soil contaminants that cause cancer, mutations, and malformations [17,18]. PAHs are also highly resistant to natural degradation due to their highly hydrophobic characteristics. They are largely produced by the incomplete combustion of hydrocarbon-containing fuels [19]. The origin and distribution of PAHs in the environment are of crucial importance for the knowledge of their spread and persistence in the soil. PAHs commonly enter into surface water, sediments, or soils by wet or dry deposition, industrial effluents, roads, and dissolution from creosote-treated woods [20].

PAHs can come from either natural or anthropogenic sources (Figure 1). Natural sources include brush and forest fires, volcanoes, petroleum seeps, the decomposition of vegetative litter fall, bacterial and algal synthesis, and the erosion of sedimentary rocks with petroleum hydrocarbons. Anthropogenic sources include incinerators and some industrial processes with incomplete combustion, automotive emissions, wood-burning stove smoke, exhaust from jet aircraft, cigarette and cigar smoke, sewage sludge, petroleum product spills, and tarry or creosote waste materials [21].

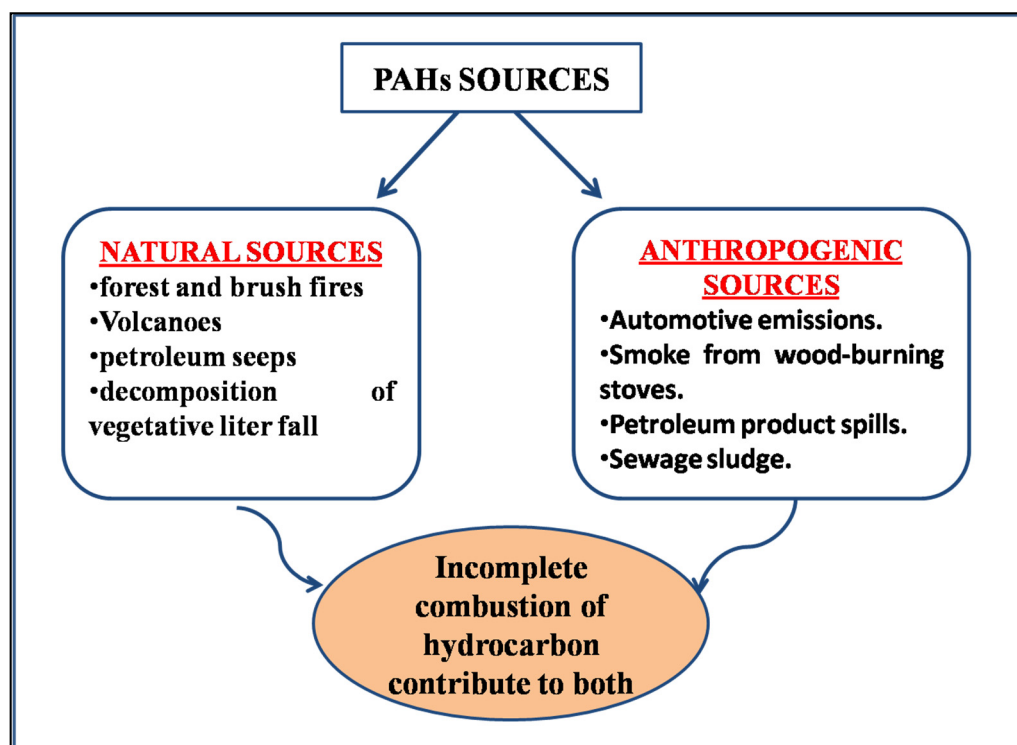


Figure 1. Sources of PAHs.

PAH concentrations in soils can vary significantly [22]. In agricultural soils, they are present in very low amounts of around 98–572 $\mu\text{g}/\text{kg}$ [23–25], while in forest soils their concentrations can vary from 95 to 9272 $\mu\text{g}/\text{kg}$, depending on the difference in soil depth [26,27]. Due to the high population in urban areas, such soils are often more contaminated, with PAH concentrations 467–51,822 $\mu\text{g}/\text{kg}$ [28–30].

In industrial areas, the amount of PAHs is very high, ranging from 724 to 7700 ppm, due to the combustion of hydrocarbon fuel [31], particularly in former manufactured gas plant (MGP) areas [32–34]. PAHs can also accumulate in soils, thus contaminating groundwater due to leaching and leading to the exposure of aquatic creatures to PAH [22,35]. Moreover, human and other living organisms can also be directly or indirectly exposed to PAHs coming from the soil through terrestrial food chains [36]. In fact, epidemiologic studies have shown an increase in lung cancer mortality in people who are highly exposed to these compounds, especially near industrial locations [37]. Therefore, it is important to clean up contaminated soils.

Environmental scientists have always faced challenges in the removal of soils contaminated with HOCs because hydrophobic molecules normally compactly bound to the soil, thus requiring costly energy solutions and/or chemical actions [19,38,39]. Several methods have been reported for the removal of HOCs from contaminated soils to decrease the possible risk of such compounds for nature and humans. The use of physical, thermal, chemical, phytoremediation, and biological processes (including total oxidation, radio frequency heating, oxidation, desorption by heat, photolysis, electrolysis, adsorption, ion exchange, natural attenuation, precipitation, bioaugmentation, biostimulation, phytoextraction, phytodegradation, and phytostabilization procedures) is an adequate method to remove HOCs from contaminated soil, sediments, and waters [40–45].

However, most of these techniques have disadvantages, such as high maintenance and investment costs and complicated operating procedures. Moreover, some produce unwanted by-products and others cause cancer and mutations (like trihalomethanes), adding additional harmful effects to public health [46–48]. Among them, sorption has proven to be an effective technique to remove HOCs in an environmentally accepted and economical way [49,50]. Therefore, numerous studies have been conducted to find the most economic and effective sorption media and to determine the factors that affect HOC removal [41,51–57].

2. Adsorption

Of the processes used for the removal of HOCs from soil, adsorption is the most useful because it is very simple in terms of operation, has low costs, requires little maintenance, and does not lead to the undesirable formation of by-products [58]. Because HOCs are poorly soluble in water and strongly adsorb on solids, adsorption is a choice technique [51–53,57,59,60] that is very efficient for the removal of HOCs from soil. Adsorption is defined as a process where ions or compounds are gathered on a liquid or solid surface (which is called the adsorbent; the adsorbed substances are called adsorbate). Often, the equilibrium concentration of the adsorbate in the adsorbent is plotted against its equilibrium concentration (in adsorbent) for a given temperature in studies [61].

2.1. Types of Adsorption

The adsorption processes can be classified as physical adsorption, also called van der Waal's adsorption, or as chemisorption (depending on intensity of the force of attraction between adsorbate and adsorbent).

2.1.1. Physical Adsorption

Adsorption resulting from van der Waals interaction forces is referred as physical adsorption or van der Waal's adsorption. It is a non-specific process only due to the weak attraction of van der Waals forces between molecules. The adsorbed molecule is not attached to a fixed site on the solid surface; instead, it can move freely. In addition, the material adsorbed on the adsorbent surface can condense and create several superimposed layers. The heat change found in such process is around 20–40 kJ/mol, with a decrease in both the entropy and free energy of the adsorption system [62]. Physical adsorption is quick and reversible. the process can occur as monolayer or multilayer adsorption.

2.1.2. Chemisorption

In the chemisorption process, chemical interaction or attractive electrostatic forces occur between the adsorbent surface and adsorbate molecules. Those molecules cannot freely to move from one site of the surface site to another when an adsorbed layer of material (one molecule thickness) is formed over the surface, and adsorbent capacity is totally used. The heat of adsorption is between 40 and 400 kJ/mol. A relatively high activation energy is associated with this process, so this is called activated adsorption. The process is relatively slow and seldom reversible.

2.2. Factors Influencing the Adsorption Process

There are several factors that can influence the rate and extent of adsorption for a particular solute.

2.2.1. Temperature

Temperature is one of the key factors that influences the adsorption process [63]. Following a temperature increase during the adsorption process, the adsorption capacity increases; this process is considered to be endothermic. This mechanism of change in the adsorption behavior in relation to temperature can be explained by considering thermodynamic parameters. The thermodynamic behavior shows whether the sorption process follows physisorption or chemisorption patterns.

The Gibbs energy change ΔG° is expressed as:

$$\Delta G^\circ = -RT \ln K$$

where R is the perfect gas constant, T is the temperature, and K is the adsorption equilibrium constant.

The relationship of (ΔG°) to enthalpy change (ΔH°) and entropy change (ΔS°) of adsorption is expressed as:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

A positive ΔH° value signifies that the process is endothermic, while exothermic processes usually have negative ΔH° values. On the other hand, a positive ΔS° value signifies increased randomness at the solid-solution interface during the adsorption process, whereas negative ΔS° values represent the opposite phenomenon (decreased randomness) [64].

2.2.2. Surface Charge

The adsorbent surface charge is dependent on the pH of the solution and the changes in the surface dealing with uneven charge distribution. An adsorption process can be enhanced when charged solutes present on the surface of the adsorbent are exchanged with counter ions.

2.2.3. Surface Area and Porosity

It is known that adsorption occurs at the surface and its efficiency has a direct relation with the surface area of the adsorbent material. Thus, increases in the surface area or porosity of the adsorbent increase adsorption [65].

The major advantages of adsorption compared to other conventional methods include [66]:

- High efficiency.
- Low operation cost.
- No additional nutrient requirements.
- Minimal chemical and biological sludge.
- Possible valuable metal recovery.
- Possible adsorbent regeneration.
- Successfully operation over a wide range of temperature and pH.

2.3. Adsorption Isotherms

An adsorption isotherm depicts the amount of solute that can be adsorbed per adsorbent weight, plotted against the bulk solution equilibrium concentration at a given temperature. Isotherms are divided into two models: Langmuir and Freundlich [67].

2.3.1. Langmuir Isotherm

The Langmuir assumes the uptake of metal ions, taking place via monolayer adsorption on a homogeneous surface, in the absence of interaction between the adsorbed species. The Langmuir equation is shown below:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m}$$

where C_e = concentration of the adsorbate (mg/L) in the solution at equilibrium; q_e = amount adsorbed on the adsorbent (mg/g) at equilibrium; q_m = monolayer adsorption capacity of the adsorbent (mg/g); and K_L = adsorption constant energy (L/mg) or Langmuir constant.

A straight line is obtained by drawing a graph of C_e/q_e versus C_e , and R_L is a dimensionless constant known as the equilibrium parameter or separation factor that expresses the important characteristics of the Langmuir isotherms. This term can be written as:

$$R_L = \frac{1}{1 + K_L C_0}$$

where C_0 = initial concentration of solute (mg/L) in the solution.

The value of R_L can indicate the isotherm shape to be unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$) [68,69].

2.3.2. Freundlich Isotherm

The Freundlich isotherm is an empirical relationship that enables the good modeling of experimental data [70]. It assumes that HOC uptake takes place on a heterogeneous adsorbent surface.

It can be expressed as:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e$$

where K_F is a constant linked to adsorbent capacity (mg/g) and $1/n$ is an empirical parameter dealing with the adsorbent sorption capacity ($n = 1-10$).

A straight line is obtained by plotting $\log q_e$ versus $\log C_e$.

2.4. Kinetic Adsorption Modeling

Understanding the kinetics of adsorption is vital for comprehending the transfer of an adsorbate to a solid adsorbent from a bulk solution. Kinetics data are often used in the development of adequate mathematical models that can explain the interactions between the solid adsorbent and molecules or ions of a pollutant [71].

If the dependent factors and reaction rates are unambiguously known, the results can be used to develop adequate adsorbent materials aimed for use at industrial applications. Several kinetic models can be utilized to understand the adsorption process and its complex dynamics [72].

Rate constants are calculated by using two kinetic models: pseudo-first-order and pseudo-second-order equations [73], which are based on solution concentration. The value of the correlation coefficient (R^2) can be determined by plotting a graph of the experimental data and the values predicted by the model. Relatively high correlation coefficients (R^2) show that the model is effectively able to describe the kinetics of an adsorbent.

The pseudo-first-order equation [74] is:

$$\log(q_e - q_t) = \log q_e - K_{ad} \times \frac{t}{2.303}$$

where K_{ad} = adsorbent rate constant (min^{-1}); q = quantity of adsorbed metal ions at t time (mg/g); and q_e = at equilibrium, quantity of metal ions adsorbed (mg/g).

The pseudo-second-order equation (PSE) [75] is given as:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t$$

where q_t = quantity of metal ions adsorbed at t time (mg/g); q_e = at equilibrium, quantity of metal ions adsorbed (mg/g); and K_2 = second-order adsorption rate constant (g/mg/min).

3. Removal and Adsorption of Hydrophobic Contaminants

3.1. Adsorption by Biochars

In recent times, focus has shifted to research on the biochar adsorption of organic molecules. Biochars have many benefits over activated charcoal, as they can be obtained from numerous kinds of raw materials, have low costs, and are recyclable [8]. Biochars also have porous structures, oxygen-containing functional groups and minerals [75,76]. They also possess increased adsorption efficiencies and can thoroughly adsorb several organic pollutants from environmental media, diminishing the environmental threats caused by organic pollutants [77]. Biochars are viable substitutes to activated carbon and can be used to eliminate various types of pollutants present in soil and water systems. Many studies have confirmed that biochars are especially efficient in the adsorption of PAHs [78,79], herbicides [80], insecticides [81], and antibiotics [82,83] in solutions. All of these organic pollutants can accumulate in soils for a long time [20], posing serious threats.

Biochar is a carbon-contained solid obtained via the heating of biomass in an oxygen-exhausted atmosphere, such as wood, with little or no oxygen [84–86]. The word “biochar” is a made up of “bio-” (as in “biomass”) and “char” (as in “charcoal”). Activated carbons are produced by higher temperatures and many activation processes, but biochar production is much cheaper and requires less energy. Biochars are considered effective adsorbents in the elimination of organic pollutants from aqueous solutions due to their large surface area, porous structure, abundant surface groups, and mineral components [87,88]. They are a novel type of low-cost adsorbents with high efficiency, typical for environmental technologies dealing with soil pollutant management, due to their cost-effective and environmental benefits [86].

3.1.1. Source, Type, Production and Properties of Biochar

Biochars are by-products of biomass waste that include crop (both field and processing) residues [89,90], fruit pits [91], bagasse [92], food and forestry wastes [93,94], animal manures [95], and sludge [96]. The time and temperature of pyrolysis, along with the types of material used, will determine the composition of the biochar [97]. Biochars can be divided into straw [98], shell [89,90], wood [93,94], sludge [96], animal fecal [99], and bamboo [100] biochars. Anila furnaces have been used for biochar production [8].

The potential of biochars as pollutant adsorbents depends on their physical and chemical structures. Pore characteristics are important physical properties that control how biochars adsorb contaminants and their interactions with soil [101]. Biochars are effective sorbents that immobilize organic contaminants and heavy metals [102,103]. The porosity and pore-size distribution of biochars significantly influences soil physical processes, and properties of biochar-amended soils [104–107]. The characteristics of biochars commonly depend on the feedstock biomass and production conditions. The feedstock materials and the pyrolysis conditions determine important functional properties, such as surface adsorption characteristics, surface area, porosity, and structural groups [108–111]. Biochars

have pore structures with broad pore-size distributions from the nanometer to micrometer scales depending on the feedstock and pyrolysis temperature [106,112]. Nanoscale biochar pores generally determine its chemical sorption properties. The surface areas of nanoscale pores could provide sorption sites for a wide variety of hazardous pollutants.

The most widely used methods to measure or assess pore structure are mercury intrusion porosimetry and nitrogen adsorption/desorption [112,113]. There are many sources of feedstock and numerous production technologies that can be used to produce biochars, which has likely led to the high variability in the pore properties of these materials. A detailed study of characteristics of biochars derived from different feedstocks and pyrolysis conditions was carried out [101]; in that study, 18 types of agricultural and forest waste were used as biomass feedstocks to produce biochar. These wastes were generally categorized as: (1) herbaceous plant wastes such as rice straw, rice husk, maize straw, maize cob, maize leaf, maize root, wheat straw, weed, sugarcane, and reed; (2) coniferous forest wastes like pine tree, golden larch, and slash pine; and (3) broadleaf forest wastes such as ginkgo, Chinese ilex, elegant maple, phoenix tree, and *Bretschneidera*. The results of this study showed that the biomass used for biochar production differently influenced the porosity and pore-size distribution of biochar. The BET surface areas of biochars derived from different feedstocks widely ranged from 1.06 to 70.22 m²/g, with a mean of 10.61 m²/g. The total pore volume of biochars was reported in a wide range of 0.48–7.25 cm³/100 g, with a mean of 3.19 cm³/100 g. The total pore volume increased in the order of herbaceous plant waste (on average: 2.30 cm³/100 g) < coniferous forest wastes (2.77 cm³/100 g) < broad-leaf forest wastes (4.60 cm³/100 g). The porosity of biochars was found to largely depend on feedstock types and range from about 58 to 80% [100]. Thus, the feedstock materials seem to be major factors determining biochar porosity. The porosity differences in biochars derived from different feedstocks has been attributed to differences in cell structure, shape, and size distribution in herbaceous plants, coniferous forests, and broad-leaf forests [101].

3.1.2. Adsorption Mechanisms for Hoc Removal by Biochar

Given its specific surface area, high porosity, and pH, biochar is a widely used material for organic pollutant adsorption [84,85]. The removal of organic pollutants by adsorption is influenced by the nature of the pollutants and the adsorbent surface [114]. For biochars used as adsorbents, the adsorbing mechanism of organic contaminants can be approximately divided into electrostatic attraction, π - π electron donor-acceptor interactions, H-bonding, pore-filling, complexes adsorption, hydrophobic interactions, the partition uncarbonized fraction, and spectrometer exchange [8]. The presence of oxygen-containing functional groups and π - π electron donor-acceptor interactions determine the quantity of organic pollutants adsorbed by the biochar. The adsorption of aromatic molecules is favored by the presence of the carboxylic acid, nitro, and ketonic groups on the surface of biochar, as they are considered to be electron acceptors, developing π - π interactions with aromatic molecules. Many types of biochar surface hydroxyl and amine functional moieties can also be considered to be π -electron-donor sites [82]. The adsorption mechanism of organic pollutants on biochars is shown in Figure 2 [8].

A biochar's surface is generally charged, which generates electrostatic attraction between the biochar and the organic compounds. The size of each atomic charge and the distance between two atoms play major roles in the magnitude of electrostatic attraction [114]. The hydrophobic nature of biochars is due to their low surface oxidation. Several types of biochars react with hydrophobic organic compounds via hydrophobic interactions to accomplish the elimination of organic pollution [115]. Chaukura et al. [116] showed that complex interactions between methyl orange (MO) molecules and ferric oxide-biochar nanocomposites can help in the removal of MO molecules in a single-solute solution.

In order to examine the adsorption of biochar on Thiacloprid (THI), maize straw and pig manure were used [87]. The results showed that THI positively interacted with biochar sorption affinity, surface area, and aromatic carbon content, as well as that H/C and (O + N)/C are negatively correlated. Biochar was mostly adsorbed by hydrophobic

interactions, pore-filling, partition uncarbonized fractions, and π - π electron donor-acceptor interactions [87].

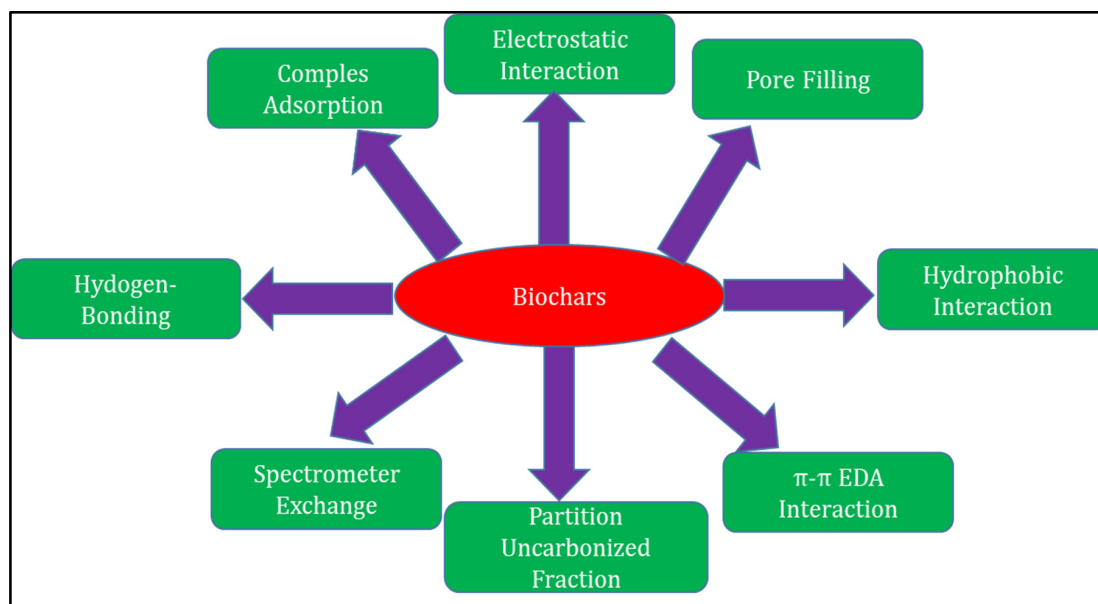


Figure 2. The mechanism of the adsorption of organic pollutants on biochars [8].

Another study showed that doxycycline was absorbed by a Cu(II)-impregnated biochar [117,118]. The surface of the biochar was enriched with a large number of active oxygenated moieties, such as C=O, C–O, –OH and –COO[−], that could interact with the Cu(II) surface complexes. This study revealed that the adsorption was the result of strong complexation and electrostatic interactions between the biochar and organic pollutants. A biochar with a negatively charged surface has electrostatic affinities with positively charged cationic organic compounds [117,118]. In order to study the adsorption mechanism of florfenicol (FF), a magnetic reed biochar (MRBC) was used, and the results showed interactions due to the formation of H-bonds between oxygenated moieties, such as the presence of –COOH and –OH and N-containing and F-containing groups on the surface of FF molecules. Simultaneously, FF’s high surface porosity and partially aromatic characteristics play important roles in the filling of pores and π - π electron donor-acceptor interactions during the process [119]. The adsorption efficiency of biochar produced from straw and pig manure can be modified by the use of H₃PO₄ to adsorb TC, establishing H bonds; however, π - π electron donor-acceptor interaction is the main adsorption mechanism [120]. Different types of biochars have diverse kinds of surface active and functional groups that are responsible for different mechanisms of the adsorption of organic pollutants [8].

3.1.3. Removal of Pesticides

Pesticides are the most common materials used to control pest and agricultural diseases. The extensive use of pesticides can raise crop yields and the economic profits of agricultural manufacturing [120]. Nevertheless, pesticides are very toxic and drifting. Their extensive use is a reason for air, soil, and water pollution, creating toxic effects in organisms, extinguishing ecological balance, and threatening human health [83]. Biochars are unique adsorbents due to their high porosity and surface area, high pH, profuse functional groups, and developed aromatic structure. Khorram et al. [121] confirmed the degradation and bioavailability of pesticides. Much research has been conducted on the biochar adsorption of pesticides in water and in soil. Different temperatures, such as 300, 500, and 700 °C, were used to produce biochars with maize straw as the raw material in order to study the adsorption effect on thiacloprid (THI) [87]; this study showed that the adsorption of THI by biochar is due to hydrophobic interactions, pore-filling, and π - π interactions.

To study the effects of numerous aspects on adsorption, sugarcane bagasse was used to adsorb organophosphorus pesticides, and it was found that the adsorption of the organic phosphorus pesticide dimethoate is a spontaneous exothermic process. The extent of adsorption and removal of dimethoate were found to be dependent on increasing amounts of bagasse carbon. Increases in the system temperature and the initial concentration of dimethoate decreased the efficiency of bagasse charcoal adsorption in the removal of dimethoate [122]. Researchers also examined the adsorption of imidacloprid at 600 °C using a biochar produced from swine manure [123]. The experimental results showed that pore-filling may be a key adsorption mechanism for regulating polar chemicals. In another study, bamboo, straw, and sawdust were used as raw materials to prepare biochar at 300–700 °C. These biochars were used to adsorb aqueous solutions of N-nitrosodimethylamine (NDMA), and the authors suggested the optimal adsorption potential and adsorption mechanism of three biochars. The experimental results showed that the bamboo charcoal biochar produced at 500 °C was very effective in removing NDMA from aqueous solutions. It was found that biochar has a high removal potential for nitrosamine disinfection, but the removal effect was independent of the solution chemistry [8,124].

3.1.4. Removal of PAHs

PAHs are kinds of persistent teratogenic, carcinogenic, and mutagenic organic pollutants [62]. Many studies have found that carbon materials, such as activated carbon and biochars, could very highly adsorb soil-bound hydrophobic organic contaminants (like PAHs) due to their large adsorptive abilities [125]. Sediments and organic matter in soils play important roles in the control of PAH adsorption. Adsorption capacity and organic matter affinity largely depend on soil composition [126]. Several studies [127,128] have found that the amount of adsorbed PAHs is related to the content of organic matter in soils and water systems. Moreover, the adsorption of HOCs via the organic matter of soil is related to the polarity and aromatic carbon of the latter [129]. It has been shown that organic matter aliphatic groups may play a major role on the sorption capacities of non-ionic organic pollutants, such as PAHs. Conversely, numerous studies have shown the important part played by aromatics and sediments present in soil organic matter in the adsorption of PAHs [126].

The effect of biochars in reducing PAH accumulation in rice was evaluated in the absence of air [130]; in this study, corn stalks and bamboo were selected as biochar materials and pyrolyzed at 300 and 700 °C. It was found that different types of biochar affected the adsorption mechanism of PAHs [130]. Aiming to show the influence of soil organic carbon (SOC) on the biochar adsorption of polychlorinated biphenyls from soil, a 120 day experiment was conducted [98]. The experimental results indicated that the presence of organic carbon may have affected adsorption with a range of interactions comprising competitive sorption, co-sorption, and cumulative sorption. Hence, the adsorption capacity of biochars on low-SOC soil for PCBs is significantly higher than that of biochar on high-SOC soil [98].

Biochars are characterized by high surface area and available porosity that enable the high adsorptive capacity of organic contaminants, making them advantageous adsorbents [131] in PAH elimination from aqueous solutions and PAH remediation from polluted soils. Similarly to activated carbon, biochars are produced via the pyrolysis of industrial, forest, and agricultural residues (such as wheat waste, rice husks, corn stover, pine needles, pecan shells, peanut hulls, apricot stones, and coniferous sawmill residues) in anaerobic or near-anaerobic conditions at temperatures ranging from 300 to 700 °C [17,132]. Biochars have been extensively used in soil modification because they can change soil properties, provide and keep nutrients and organics, and enhance microbial activities [133].

A study conducted by Oleszczuk et al. [134] found that approximately 40–50% of PAHs were removed from contaminated soil with a biochar, decreasing the toxicity to plants and microorganisms due to the capture of soil PAHs. Moreover, Wang et al. [135] reported that the use of biochars from wood allowed them to remove 60% of PAHs (pyrene, phenanthrene, and benzo(a)anthracene) from aqueous solutions. It has been revealed

that the adsorption capacity of PAHs is not affected by the particle size of biochar [136], although less time is required to achieve adsorption equilibrium when smaller particle sizes are used [137]. The biochar adsorption of organic contaminants depends on the production process, type of feed stocks, sorbate concentration, and age [135]. A previous study [138] showed that a biochar from wheat straw obtained at 400, 600, and 800 °C could remove 71.8–98.6% of PAHs from soil-washing waste. The adsorption capacity increased with the augmentation of the temperature for biochar production, and it was found that 136.8 mg/g of naphthalene was adsorbed by a pine needle biochar obtained at 700 °C [139].

The correlation between the manufacturing temperature and the adsorption capacity of a biochar is non-linear since ester and alkyl (aliphatic) moieties are destroyed when a biochar is produced. Moreover, the used high temperatures increase carbonization, which leads to the formation of high microporosity in biochar surfaces [140,141]. Accordingly, further studies on biochar production processes for PAH removal should be carried out. A biochar comprises rubbery and glassy fractions. The latter has presented the competitive non-linear adsorption of organic pollutants, while the former has presented the non-competitive linear separation of organic pollutants [141]. Surface coverage, multilayer and polymeric matrix adsorption, and condensation in capillary pores are additional procedures that can be included in the biochar adsorption processes [142].

3.2. Adsorption by Activated Charcoal

Removal of PAHs

Activated carbon is another popular and useful adsorbent for PAHs since it shows high surface areas (from 300 to 3000 m²/g) [143]. Activated carbon can be made out of a large number of materials, such as petroleum coke, bituminous coal, sewage sludge, fruit shells, and plant materials [143–145] via carbonization and subsequent activation. It is available as powder, granules, or briquette, depending on the intended application. Powder and granular activated carbon are more common for the PAH adsorption and removal processes. Granular activated carbon (GAC) is the most commonly used porous media for the adsorptive elimination of organic contaminants [146]. Amstaetter et al. [147] conducted adsorption tests of several molecules, such as anthracene, phenanthrene, pyrene, fluorene, chrysene, from aqueous solutions, and they found very high adsorption capacities for activated carbon.

Similarly, the 99% removal of PAHs from the drainage water of moderately contaminated soils was reported with the addition of 2% powdered activated carbon (PAC) [148]. An activated carbon produced by a rice husk agricultural residue showed a larger adsorption capacity compared to other industrial and agricultural adsorbents (such as chitin, chitosan, coconut shells, sugar bagasse, mesoporous organo silica, and leonardite) for phenanthrene, naphthalene, and pyrene PAHs [149]. Similarly, activated carbon produced from agricultural-based soybean stalk waste was able to provide a 95.6–100% PAH removal efficiency from aqueous solutions [144]. Furthermore, activated carbons with diverse adsorptive properties can be obtained by changing the activation process parameters such as temperature, activation agents, and oxidant flow rate [150]. Similarly, the removal efficiency of activated carbon from soybean stalk could be enhanced by raising the activation temperature, which resulted in an increase of the surface area [144]. The well-developed porous structure and large surface area of activated carbon improve its adsorption capacity [151]. The normalized specific surface area capacity might be different, depending on the kinds of activated carbon used. Petroleum coke activated by CO₂ has shown a maximum adsorption of naphthalene of 112.6 mg/g with a larger normalized surface area of 0.27 m²/m², while a commercial activated carbon derived from coal with a surface area of 0.19 m²/m² adsorbed 196.4 mg of naphthalene (per gram of carbon) [143]. All these studies demonstrated that activated carbon is a good adsorbent that can remove PAHs from contaminated soils. Hence, adsorption can be an efficient and economically viable method for removing HOCs [61]. Different adsorption mechanisms for HOCs with different adsorption media are provided in Table 1.

Table 1. Details of the adsorption of HOCs on different adsorbents, their characterization, and removal mechanisms.

Hydrophobic Organic Contaminants	Types of Adsorbents	BET Surface Area (m ² /g)	Total Pore Volume (cm ³ /g)	Pore Size (nm)	Surface Groups	Removal Efficiency and/or Adsorption Efficiency	Adsorption Mechanism	References
Dimethoate	Sugarcane bagasse Biochar	-	-	-	-	-	Physical sorption and intraparticle diffusion	Sun et al. [122]
Thiacloprid	Maize straw Biochar	-	-	-	-	-	Hydrophobic interaction, pore-filling, and π - π interaction	Zhang et al. [87]
Imidacloprid	Swine manure Biochar	0.68–8.45	-	Rougher and more porous	(-COOH and -COH)	-	Pore-filling	Jin et al. [123]
N-nitrosodimethylamine	Bamboo biochar	33.50–39.25	-	-	O-containing moieties (-C-O, C=O, -COOH)	61.68%	Hydrophobic interaction	Chen et al. [124]
2,4-Dichlorophenol	Sewage sludge/wood Chip Biochar	25.6–360	-	-	Hyrophobic surface	99.95%	Electrostatic interactions and π -electron donor-acceptor interaction	Kalderis et al. [152]
Bisphenol A	Potato peels Biochar	0.907–1041.43	0.004–1.216	-	C-OH, C=O moieties in aromatic carboxyl groups, C=C of the aromatic ring structures and conjugated systems such as diketone, ketoester, quinone	454.62 mg g ⁻¹	π - π interaction	Arampatzidou and Deliyanni [153]
Carbamazepine	Eucalyptus wood and bamboo Biochar	64.728–85.07	0.057–0.069	-	-	104.85 to 861.70 mg L ⁻¹	π - π interaction	Chen et al. [154,155]
Benzophene (BZP) Benzotriazole (BZT) Bisphenol A (BPA) 17 β -estradiol (E2)	Pine chips	1360	0.307–0.643	-	Alkyl (0–45 ppm), methoxyl (45–63 ppm), carbohydrate (63–108 ppm), and carboxyl carbons (165–187 ppm)	6.79 mg L ⁻¹ 9.22 mg L ⁻¹ 28.4 mg L ⁻¹ 30.2 mg L ⁻¹	Hydrophobic interaction	Kim et al. [156]
Tetraethyltin	Sawdust	17.35	0.038	8.85	-	91.6%	π - π interaction Complexation	Zhou et al. [157,158]
Tetracycline	Saw dust 600	-	-	-	-	10 to 25 mg L ⁻¹	Hydrogen bonding and π - π EDA	Zhou et al. [157,158]
Phenanthrene Pentachlorophenol	Poplar and coniferwood chips	76.88 114.67	0.046 0.067	24.08 23.23	C-H (3050 cm ⁻¹), C=C and C=O stretching (1707 cm ⁻¹), aromatic C=C and C-H alkenes (1591–1455 cm ⁻¹), C=O stretching (1080 cm ⁻¹)	11.9 mg kg ⁻¹ 132 mg kg ⁻¹	π - π interactions	Rao et al. [159]

4. Degradation of Hydrophobic Contaminants

Biodegradation is the transformation of chemical constituents through the action of living organisms that determines the fate of organic chemicals in soil, and it is particularly important in the case of HOCs. The slow biodegradation of organic contaminants may cause bioaccumulation, which results in primary and secondary food poisoning or a reduction of soil quality. Generally, biodegradation involves conversion into relatively harmless simple molecules and ions, such as CO₂, H₂O, CH₄, and other inorganic compounds. The process is known as biodegradation or mineralization and can be considered to be a sink in aerobic soil compartments. The transformation and mineralization mainly depend on the environmental conditions of the soil [31,160–165]. HOCs (such as PAHs) and pesticides are very harmful for soils because their presence leads to resistance towards biodegradation and increases bio-accumulation and carcinogenic activity. The excessive usage of these pollutants can degrade the fertility and quality of the soils and lead to toxicity in living beings found nearby. Such compounds do not easily naturally degrade [165]. Usually, they undergo volatilization, adsorption on soil, chemical and photo-oxidation, microbial degradation, and leaching [31].

The hazardous effects of HOCs can be reduced by the alteration, removal, or separation of the pollutant via digging in the contaminated soil and its containment or incineration. These are costly technologies that only move pollutants between phases [165]. Those conventional methodologies have shown several disadvantages because they are expensive and the remediation they provide is often incomplete, as the compounds are converted to metabolites that more persistent and similarly or even more noxious than the parent molecules [166]. At present, there are some chemical, physical, enzymatic, and biological approaches used to reduce HOCs. Among these, microbial degradation was found to be more thermodynamically reasonable and cost-effective [167].

Although the degradation of HOCs depends on many factors, such as the amount and nature of the microorganisms, environmental conditions, and the chemical structure and nature of the compound to degrade, HOCs can be biodegraded into simple metabolites such as H₂O, inorganic minerals, CH₄ (anaerobic), and CO₂ (aerobic). Several factors such as temperature, pH, oxygen, degree of acclimation, microbial population, chemical structure, the accessibility of nutrients, and cellular transport properties can affect the biodegradation process [165].

4.1. Microbial Degradation of PAHs

It is possible to achieve the microbial degradation of PAHs with algae, bacteria, and fungi. Bacteria and fungi have been widely studied because they are able to degrade xenobiotics, such as PAHs [165–167].

4.1.1. Bacteria

Bacteria comprise a type of microorganisms often associated to the degradation of organic pollutants present in contaminated soils. Several bacteria are able to degrade PAHs, as depicted in Table 2.

Table 2. Bacteria used for the biodegradation of PAHs.

PAHs	Bacterial Species	References
Benzo(a)pyrene	<i>Sphingomonas paucimobilis</i> , EPA 505 strain	Ye et al. [168]
Phenanthrene	<i>Pseudomonas aeruginosa</i>	Romero et al. [169]
Pyrene	<i>Mycobacterium</i> spp., KR2 strain	Rehmann et al. [170]
BaP.	<i>Pseudomonas</i> , <i>Agrobacterium</i> , <i>Bacillus</i> , <i>Burkholderia</i> , and <i>Sphingomonas</i> species	Aitken et al. [171]
Acenaphthene, fluorene, phenanthrene, anthracene, and pyrene	<i>Pseudomonas fluorescens</i> and <i>Haemophilus</i> spp.	Yuan et al. [172]
Pyrene Anthracene	<i>Mycobacterium flavescens</i> and <i>Rhodococcus</i> spp.	Dean-Ross et al. [173]

Most bacteria show biodegradation efficiency and can be isolated from sediments or contaminated soil [165]. Among PAHs, benzo(a)pyrene (BaP) is the most toxic and carcinogenic. Many scientific studies have shown that bacteria grown in liquid culture experiments with an alternative carbon source can efficiently degrade BaP. Ye et al. [168] showed that BaP concentration decreased by 5% following 168 h of incubation with *Sphingomonas paucimobilis*. The resting cells of *S. paucimobilis* produced $^{14}\text{CO}_2$ (28%), indicating the ring cleavage hydroxylation of the 7,8,9,10-benzo moiety. *Pseudomonas aeruginosa*, coming from a highly polluted stream near a petroleum refinery, was found to be able to steadily grow over phenanthrene, thus allowing for the total removal of the pollutant in 30 days [169]. The KR2 strain of *Mycobacterium* spp., isolated from soil contaminated with PAH next to a gas work plant, was found to be able to use pyrene as a source of carbon and energy, metabolizing up to 60% of the added pyrene (0.5 mg/mL) at 20 °C within 8 days. It was found that 4,5-phenanthrene dicarboxylic acid, cis-4,5-pyrene dihydrodiol, 1-hydroxy-2-naphthoic acid, phthalic acid, 2-carboxybenzaldehyde, and protocatechuic acid were produced; the degradation path is shown in Figure 3 [165,170].

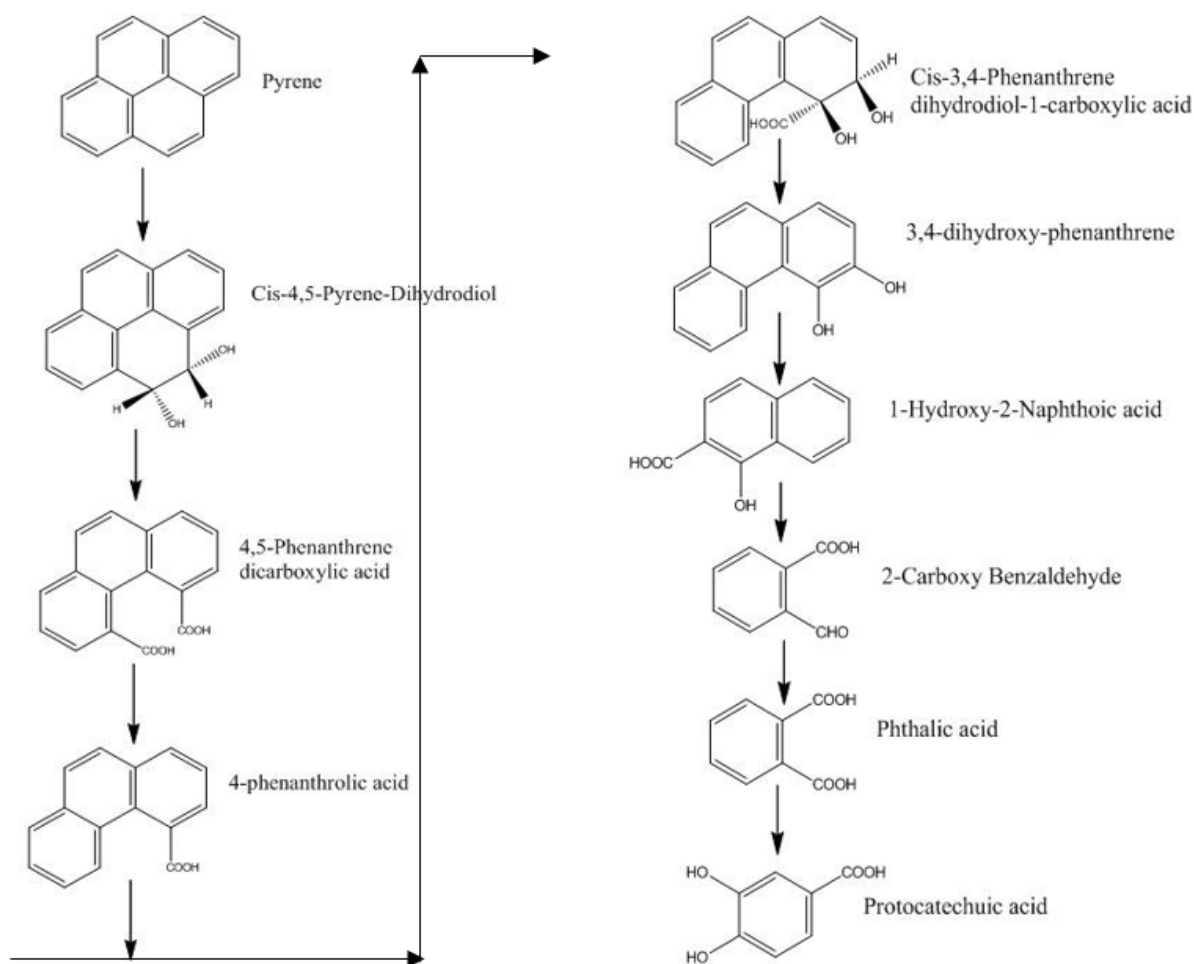


Figure 3. *Mycobacterium* spp., KR2 strain bacterial degradation path of pyrene [165,170].

4.1.2. Fungi

Numerous fungi have been recognized to efficiently degrade PAHs [165]. The fungus *Cunninghamella echinulata* var. *elegans* has been reported to degrade PAHs following a first-order reaction, where the change rate of PAH amount is directly proportional to time and the amount of soil contaminant [174]. Microbial degradation by ligninolytic fungi is also suitable for different PAHs because lignin shows a non-regular structure and the fungi can generate extracellular enzymes with lignin peroxidase, phenol oxidases (like laccases

and tyrosinases), Mn-dependent peroxidase, and H₂O₂-producing enzymes without much specificity to the substrate [164,175]. Ligninolytic enzymes accomplish radical oxidation with one electron, forming cation radicals from PAHs [176]. The degradation of PAHs was studied with ¹³C deuteromycete ligninolytic fungal strains, and it was concluded that degradation depended on the variation of ligninolytic enzymes [177]. Strain 984 with Mn peroxidase activity showed the maximum degradation of naphthalene (69%), followed by strain 870 (17%), which showed activities for lignin peroxidase and laccase. The latter strain presented a phenanthrene degradation of 12%, while strain 710 presented a 65% degradation of anthracene [177].

Recently, soil fungi were found to generate ligninolytic enzymes in low to very low oxygen concentrations and to be able to degrade PAHs [178]. Species such as *Trichocladium canadense*, *Aspergillus* sp., and *Fusarium oxysporum* most efficiently degraded 2–3 fused-ring PAHs, while *Aspergillus* sp., *T. canadense*, *Achremonium* sp., and *Verticillium* sp. degraded 4–7 fused-ring PAHs [178]. Hence, under low-oxygen conditions, fungi can have good capacity to degrade a wide range of PAHs. A systematic route for the degradation of phenanthrene and anthracene by ligninolytic fungus *Irpex lacteus* is shown in Figure 4 [164,165].

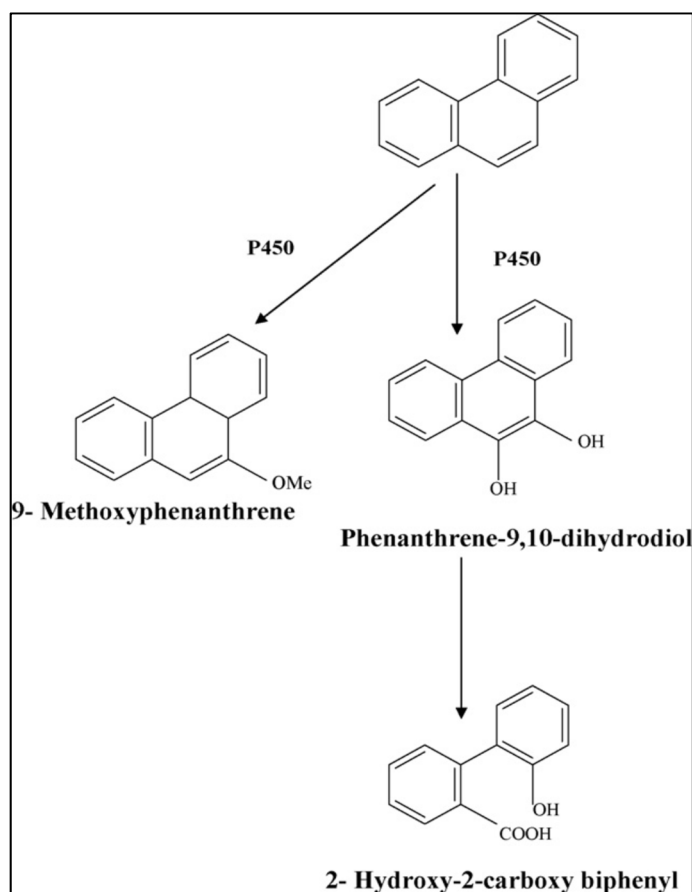


Figure 4. Fungal degradation pathway of phenanthrene by *Irpex lacteus* fungus [164,165].

4.1.3. Algae

Several studies have shown that algae can also be used for the degradation of PAHs. Naphthalene is converted into a series of metabolites by eukaryotic and prokaryotic photoautotrophic marine algae (such as green algae, cyanobacteria, and diatoms) [179–181], with naphthalene cis-hydroxylation performed by cyanobacteria, *Agmenellum* spp., and *Oscillatoria*. The pathways are analogous to those of fungi [179–183]. Marine algae were found to be able to degrade BaP into diols and quinones in over 5–6 days. The *Selenastrium capricornutum* green freshwater alga can turn BaP into cis-dihydrodiols with the help

of a dioxygenase enzyme [184]. This alga forms 9,10-dihydrodiol using white light and 11,12-dihydrodiol under gold light. BaP quinone production was found to increase when light energy was augmented from gold to white and UV-A in the region of PAH absorbance. It was also proven that only the green algae could almost totally process BaP into dihydrodiols, as blue, green, and yellow algae were not able to do so [185]. The removal of fluoranthene and pyrene by algae increased with the presence of bacteria. The biodegradation of PAHs enhanced by photosynthesis performed by alga and bacteria microcosms was reported to occur in a one-stage treatment [186]. Salicylate, phenol, and phenanthrene were chosen for algal–bacterial microcosm biodegradation. *Sphingomonas yanoikuyae* and *Pseudomonas migulae* were also used for the degradation of phenanthrene. *Chlorella sorokiniana* green alga was grown among pollutants with different concentrations, with the following inhibition effect ranking: phenanthrene > phenol > salicylate. Maximum degradation (>85%) was reported with bacteria and algae cultivated under light, showing synergistic relationships between algae and bacteria [186]. Research on pyrene, fluoranthene, and their mixture by *Scenedesmus platydiscus*, *Scenedesmus quadricauda*, *Chlorella vulgaris*, and *Selenastrum capricornutum* showed that elimination depends on the algal species and toxic compound [187]. It was found that approximately 48% and 78% of PAHs were removed by *S. capricornutum* and *C. vulgaris*, respectively, in 7 days. The removal efficiency of a mixture of pyrene and fluoranthene showed that the existence of a PAH increased the elimination of another PAH. Thus, algae are adequate for PAH degradation and can co-metabolically assist bacteria [187].

4.2. Microbial Degradation of Pesticides

Pesticides are organic chemicals used for improving the agricultural yields, product quality, soil productivity, the control of insect vectors to avoid the occurrence of human and animal epidemics, and the minimization of agricultural losses due to crop pest [166]. Organophosphates, organochlorines, neonicotinoids are pesticides often used in India. They can cause harmful effects to ecosystems and are a possible threat to humans and animals [167,188–190]. There are different ways to decrease the effects of pesticide on health and the environment, remediate contaminated sites, and treat pesticide residues [167]. Among them, microbial degradation has proven to be cost-effective and simple for the remediation of pesticides [167].

Microorganism such as actinomycetes, bacteria, and fungi can help to biotransform and detoxify pesticides. *Pseudomonas*, *Bacillus*, *Moraxella*, *Flavobacterium*, *Arthrobacter*, *Acinetobacter*, *Paracoccus*, *Alkaligenes*, *Aerobacter*, *Sphingomonas* and *Burkholderia* are among the most important bacterial species used for transformation of pesticides. Fungi such as *Fusarium*, *Aspergillus niger*, *Penicillium*, *Lentinula edodes*, *Lecanicillium*, and *Oxysporum* can also detoxify pesticide degradation. Among those, *Actinomycetes* and *Streptomyces* have been considered to be the best [167]. When these microbes are placed in soil, they rapidly become able to destroy pesticides because those chemicals provide suitable carbon sources and electron donors [191], consequently allowing for the management of contaminated soils [192]. These microbes have pesticide-degrading enzymes capable of transforming the pesticides into harmless by-products [166]. The biotransformation of those contaminants is related to the microorganisms with suitable degrading enzymes and several other environmental aspects [193], such as pH, temperature, available nutrients, and water potentials. Moreover, some other parameters such as ecological, physiological, molecular, and biochemical factors, can have important roles in the microbial transformation of pesticides [167,194,195].

4.2.1. Bacterial Degradation of Organochlorine Pesticides

Organochloride pesticides are organic molecules containing a Cl atom covalently bonded to carbon and hydrogen. They include chlorinated hydrocarbons, chlorocarbons, organochlorides, chlorinated solvents, and organochlorines. It was found that organochloride pesticides are difficult to biotransform [196–198], as they are extremely carcinogenic

and toxic composites that can persist in nature for several years [167]. The most commonly utilized organochlorine pesticides are aldrin; dieldrin; α -, β -, δ -, and γ -BHC (Lindane); endosulfan; heptachlor; aroclor and dichloro diphenyl trichloroethane (DDT); and methoxychlor [199,200]. Bacteria include the soil inhabitants *Pseudomonas*, *Micrococcus*, *Bacillus*, and *Arthrobacter* with potential to promote organochlorine degradation [201]. These bacterial species play major roles in the elimination of those xenobiotics from polluted soils. Their active, multifaceted, and complex enzymatic systems transform these contaminants via the removal of their functional groups. Matsumura et al. [202] described the breakdown in the soil of dieldrin by *Pseudomonas* sp. The organochlorine molecules are degraded by two main routes: reductive dechlorination (without oxygen) and dehydrochlorination (with oxygen). Liu et al. [203] showed that the chlorinated pesticide hexachlorocyclohexane can be completely removed from soils with *S. japonicum*, which showed an efficiency of 2 mg/L/h.

Numerous reports dealing with endosulfan degradation have shown that it can be degraded by either oxidation or hydrolysis reactions, which form endosulfan sulphate and endosulfan diol as major metabolites. Jayashree and Vasudevan [204] carried out systematic studies on endosulfan diol remediation with the Tween 80 synthetic surfactant and *P. aeruginosa* at pH values of 7 and 8.5. They showed that the bacterial degradation of endosulfan was clearly stimulated in the presence of the surfactant. At a pH of 8.5, bacteria could remove 94% endosulfan, forming less toxic endodiol and endosulfan sulphate [204]. Kumar et al. [205] demonstrated that 73% of α -endosulfan and 81% of β -endosulfan could be removed through mixed cultures of *Rhodococcus erythropolis* and *Stenotrophomonas maltophilia*. The toxicity of the degraded by-products was tested against nuclear cells of human polymorphs detected by a micronucleus assay, revealing that metabolites formed by mixed culture degradation were less harmful than endosulfan [205].

4.2.2. Bacterial Degradation of Carbamate

Carbamate-derived pesticides are esters of this carbamate and organic derivatives of carbamic acid. These compounds were used as pesticides in 1950s for pest control with good efficiency and wide-ranging biological activity [167].

The carbamates are converted into several products through several procedures such as biodegradation, hydrolysis, photolysis, oxidation, metabolic reactions in microorganisms, and biotransformation [167,206]. The degradation of carbamates takes place through the methylcarbamate linkage by a carbofuran hydrolase enzyme traced on a plasmid in *Achromobacter* sp. [207]. Numerous bacteria are able to degrade carbamate using carbofuran hydrolases such as *Mesorhizobium*, *Pseudomonas*, *Rhodococcus*, *Ralstonia*, *Bacillus*, and *Ochrobactrum* [208,209]. The metabolic transformation pathway for carbofuran, a type of carbamate through bacterial *Sphingomonas* sp., was previously proposed [209]; carbofuran is firstly degraded to carbofuran phenol and then transformed into 2-hydroxy-3-(3-methylpropan-2-ol) phenol. *Pseudomonas* isolates were shown to be able to convert carbamate carbendazim to 2-aminobenzimidazole (Figures 5 and 6) [209].

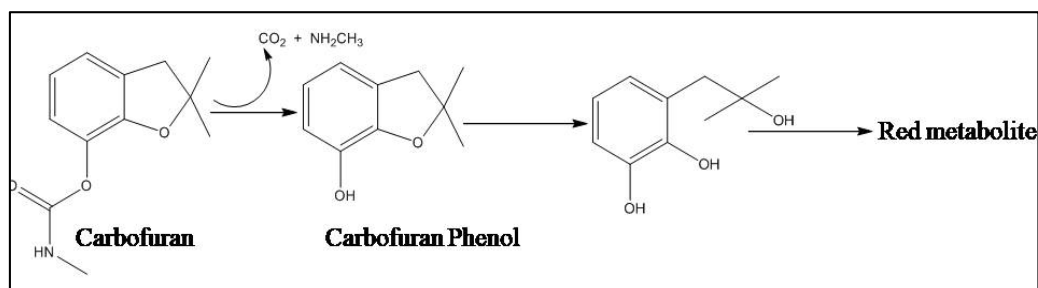


Figure 5. Bacterial degradation pathway of carbofuran by *Pseudomonas* [209].

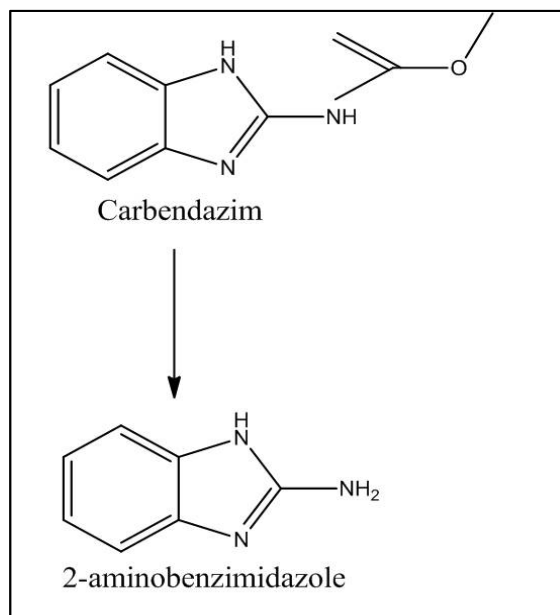


Figure 6. Bacterial degradation pathway of carbendazim by *Pseudomonas* [209].

4.2.3. Fungal Biodegradation of Pesticides

The biotransformation of numerous pesticides using fungi has received substantial attention. Fungi such as *Aspergillus sydowii*, *Penicillium miczynskii*, *Penicillium mraistrickii*, *Trichoderma* sp., and *Bionectria* sp. have been successfully used for degradation proficiency in (solid) culture media. A study on heptachlor and heptachlor epoxide fungal degradation was conducted on several species of white rot, and possible degradation pathways were identified in five species, including *P. brevispora*, *P. tremellosa*, and *P. acanthocyst*, in which 71%, 74%, and 90% of heptachlor were, respectively, removed after 14 days. The most common heptachlor metabolites were heptachlor epoxide, 1-hydroxy-2,3-epoxy-chlordene, and 1-hydroxy-chlordene (Figure 7), while *P. brevispora*, *P. acanthocystis*, *P. aurea* and *P. lindtneri* removed from 16% to 25% of heptachlor epoxide, following 2 weeks of incubation. 1-hydroxy-2,3-epoxy-chlordene and heptachlor diol were detected as metabolic products, showing that the hydroxylation and hydrolysis reactions took place in the heptachlor epoxy deposition 1 and the epoxide ring, respectively [210,211]. It was also reported that organochlorines degrade through an oxidative system via a strain of *Trichoderma harzianum* [212].

Aspergillus niger was shown to be able to bioremediate endosulfan, which largely affects water systems and soil environments. It was found that these fungal cultures could endure 400 mg/mL of endosulfan and that this compound was completely removed after 12 incubation days, as shown by the evolution of CO₂ [213]. Thin layer chromatography (TLC) results showed the formation of many endosulfan metabolic intermediates and biological transformations containing endosulfan sulfate, endosulfan diol, and another non-identified compound. The degradation rate increased when using a mixture of fungi [214]. The degradation efficacy of DDT and chlorpyrifos was 26.94% and 24.94%, respectively [214]. The fungal degradation of carbamates has also been reported in many studies. Several N-methylcarbamate insecticides are removed through an *Aspergillus niger* novel hydrolase. It was demonstrated that carbamate degradation is initiated by hydrolysis ester linkage [215,216].

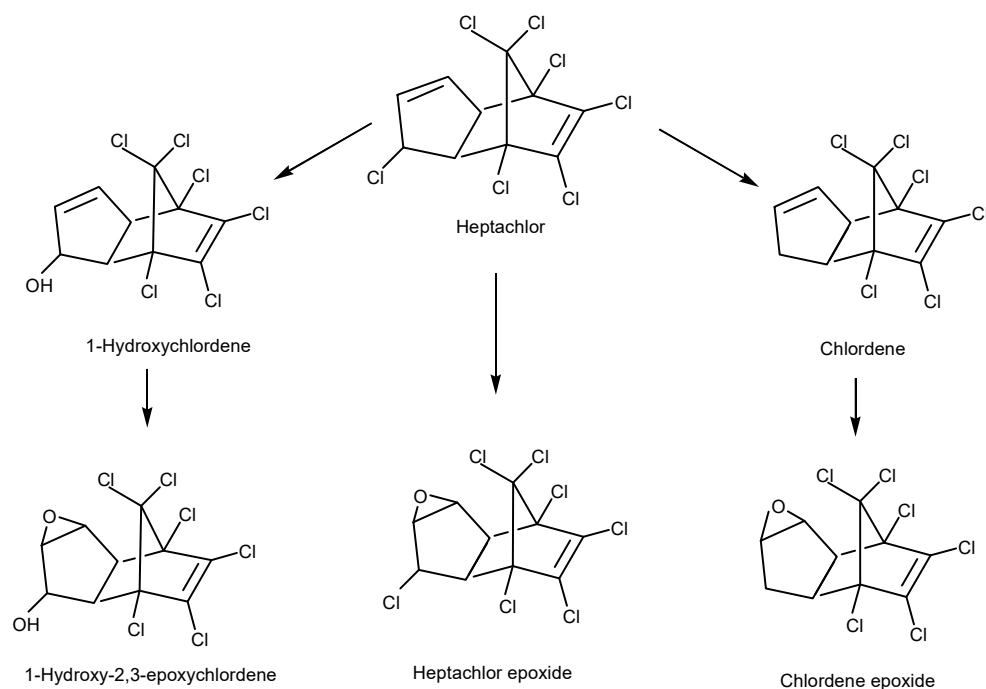


Figure 7. Metabolic pathway of heptachlor through fungal degradation [167,211].

5. Conclusions

Sadly, in the last few years, the amount of hydrophobic organic contaminants in the environment has increased due to the continuous development of industry and agriculture, which has led to serious environment pollution. HOCs such as polychlorobiphenyls (PCBs), petroleum hydrocarbons, polychlorinated dibenzodioxins, polycyclic aromatic hydrocarbons (PAHs), dichloro-diphenyltrichloroethane (DDT), and almost all pesticides found in the environment can cause serious threat to soils. The existence of HOCs in soils is a major scientific, societal, and regulatory concern because these compounds present toxicity, mutation, carcinogenic character, and accumulation in the food chain. Due to these harmful effects on human health, efficient and accessible HOC removal procedures are needed to treat contaminated soils.

Adsorption was found to be an economically viable and effective method for removing organic contaminants. This study was dedicated to the elimination of HOCs from soil using adsorption and different types of adsorbents. Adsorption is influenced by properties of the adsorbate and adsorbent, operating parameters such as ionic strength, pH, the presence of organic or inorganic complexes, temperature, and contact time. This study has shown that a removal efficiency of up to 100% can be attained, depending on the good selection of the adsorbent media and operating factors. The removal of HOCs from soils by biochar and activated carbons is worth considering because they are low-cost, high-efficiency, and renewable adsorbents. Moreover, the biotransformation of HOCs can be used as a tool to convert HOCs to less harmful/harmless forms by using algae, bacteria, and fungi microorganisms, separately or in combination; this is an eco-friendly methodology to degrade/remove HOCs from soil. Additionally, this study presents comprehensive perspectives on the future management of HOCs.

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