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Review

Biochar a Promising Strategy for Pesticide-Contaminated Soils

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Abstract: Soil pesticide contamination induced by modern agriculture has become a serious global issue. Its uncontrolled and inefficient application is among the main reasons for their enrichment in plants and animals subsequently transferred to humans and providing a public health risk. Biochar as a renewable and economical carbonaceous material provides a natural solution for immobilizing pesticides and improving soil health. The biochar impact in agricultural contaminated soil is governed by various factors such as the physico-chemical properties of biochar, pyrolysis, soil conditions, and the application method, which can lead to significant gaps in the removal or mitigation of toxic substances. The current study summarizes the negative effects of pesticide use and the advantages of biochar according to other remediation techniques, succeeded by the mechanism and controlling factors on minimizing pesticide leaching and bioavailability in soil. In addition, the role of biochar on fundamental processes of adsorption, desorption, biodegradation, and leaching is discussed. Ultimately, the major future research regulation and key strategies that are fundamental for pesticide-contaminated soil remediation are proposed.

Keywords: pesticide; agriculture; biochar; sorption; remediation

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1. Introduction

The conflict between a growing global population and limited arable land imposes immense pressure on agricultural productivity [1]. Pesticides and fertilizers improve agricultural production, and their usage corroborates with improper management drives the aggravation of environmental contamination [2]. Over the last few decades, pesticide demand and consumption surpassed 4 million tons per year worldwide [3]. Between 2000 and 2019, global production of primary crops (wheat, maize, sunflower, rice) enhanced by 53%, reaching a new high of 9.4 billion tons, particularly to pesticides and fertilizers, increased irrigation usage, and secondary to conservative practices and larger cultivated areas [4]. With the wide use of agricultural inputs, agricultural production is improved, whereas environmental quality is negatively influenced [1].

Pesticides are essential chemicals required for crop growth with privative action on soil quality driven by changes in chemical and biological parameters. Likewise, pesticides damage soil microbial biodiversity and enzymatic function, along with soil organic matter decay [5]. Surface and ground water sources contamination has intensified given inadequate pesticide management; weather events and water management have also contributed to pesticides leaching through the soil. As a result, agriculture activities induce considerable changes to the complete ecosystem, leading to less healthy arable land, and affecting the global economy, food safety, and security. The pesticide persistence and extensive properties which have caused prejudice against biodiversity are mainly responsible for the associated environmental concerns [5]. Therefore, research trends focused on procedures that can attenuate pesticide threats in water and soil and also maximize crop yield.

At present, physical and chemical remediation (oxidation/reduction, washing with extractants, adsorption), bioremediations, and phytoremediation are techniques frequently used for the removal of toxic substances from the soil. Each remediation technique has its advantages and limitations in the application, costs, leaching, fertility depletion, and high environmental risks [6]. Microbial remediation and phytoremediation are viable and cost-effective alternative approaches but depend on the strength and availability of pesticide residues and the ability of the detoxifying agent to break down the pesticide molecules [7]. The advanced oxidation process has a faster reaction and generates fewer slush, but the maintenance and investment costs are high [8]. However, the physical remediation of pesticides is effective but discouraged because of poor environmental safety. As a result, developing safe, high stability, economical and eco-friendly methods for removing pesticides from the environment is required.

Biochar as a carbon-rich solid material derived through the thermochemical process of biomass has received considerable attention over the last decades [9]. It is regarded as an environmentally friendly alternative for pesticide remediation because of its unlimited availability, low cost, and constancy features. Biochar displays a large specific surface area, porous micromorphology, high cation exchange capacity, and chemical and biological stability which can immobilize contaminants and minimize the risk of soil contamination [10]. Due to its particular properties, biochar has been reviewed for various practices, such as adsorption [11], nutrient source [12], energy storage [13], and carbon sequestration [14]. It is particularly applied as a soil amendment to promote nutrient supply and crop yield, enhance soil properties and texture, reduce greenhouse gas emissions, and improve the adsorption effect of organic contaminants by modifying or making composites. Applying biochar to agricultural soil can enhance seed germination, biomass and yield growth, and nutritional quality while stimulating plants in absorbing micronutrients [12].

The characteristics of biochar are governed by the feedstock's nature and pyrolysis conditions [15]. The ability of biochar to remediate/immobilize pesticides in the soil is influenced by the types of pesticides and soil, biochar dosage and application methods, solution pH, and environmental conditions. For example, the optimum pH for maximum glyphosate sorption was 82% in biochar obtained from rice husk, whereas a higher solution pH (10) decreased the sorption capacity to 56% [16]. The outcomes of various investigations on pesticide remediation by biochar are still in their infancy and heterogeneous [1,7].

Based on the literature and linked to keywords such as "pesticide, biochar, agriculture, remediation", from MDPI, Web of Science, Scopus, and ScienceDirect databases, we systematically review the aspects of the current state and existing issues related to biochar and pesticide remediation. From the selected databases, it was reported that the number of articles published increased by 30% between 2010 and 2022, with the most articles per year observed in late 2020. As a result, the use of biochar on pesticide-contaminated soils is growing in popularity. Therefore, an exhaustive and critical review underlining the current involvement of biochar in pesticide behavior might be a valuable addition to the existing literature. It also provides an overview of the diverse biochar content on the remediation effect and mechanism with soil limiting factors, which might serve as a guide for large-scale biochar application.

Based on the motivations stated above, the general objective was to systematically review the current knowledge concerning the potential use of biochar in agricultural remediation soil from the following perspectives: (i) pesticide global consumption and public concerns, (ii) remediation techniques of pesticides-contaminated soil, (iii) biochar mechanisms for pesticides immobilization, and (iv) factors which influence the polluted pesticide-contaminated soil.

2. Pesticide Use and Health Concerns

Pesticides and fertilizers form an indispensable item of agricultural production, which helps farmers to grow more crops on less land. Globally, pesticide consumption grew constantly from 1990 to 2020, with approximately 20,000 commercial products for plant protection, applicable worldwide [17]. According to various reports [18], nearly 4.2 million tons are used every year in the agricultural industry. Globally, China was the top contributor to pesticide use, trailed second by USA, Brazil, and followed by Argentina [19]. In 2022, the predicted pesticide volumes were 1763 thousand tons for China followed by USA and Brazil, with 407,780.000, and 204,560.000 tons, respectively. Figure 1 displays the global pesticide consumption among the worldwide leading countries.

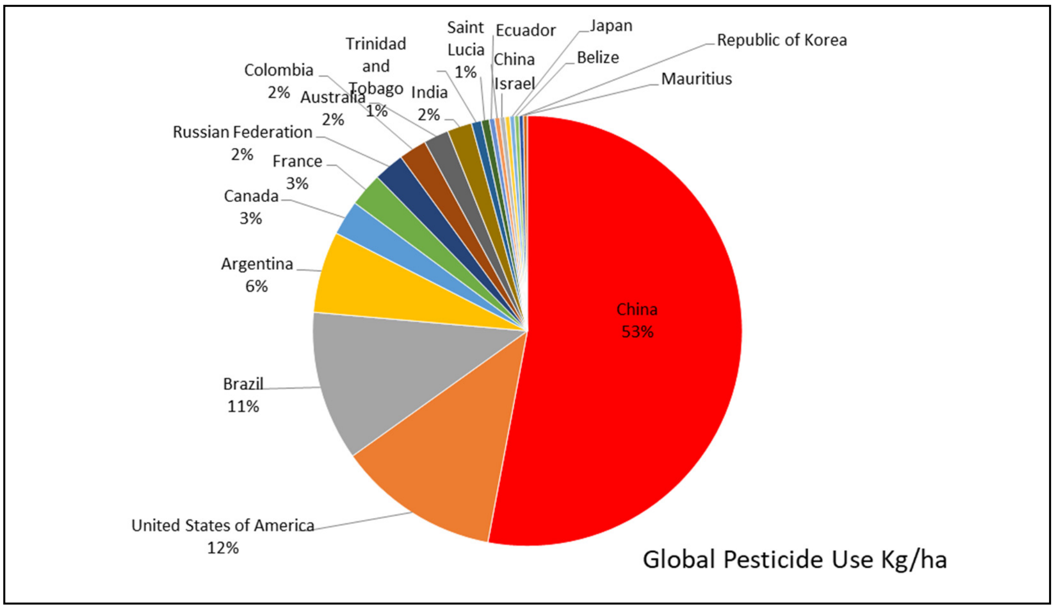

Figure 1. Global pesticide use (kg/ha) (data were taken from FAO-STAT 2022).

Despite the discussion on the sustainability of agriculture and the pesticides that can be used at low doses, on average, the use of pesticides in Europe did not decrease. The pesticide database schedule of the European Commission comprises more than 400 a. i. authorized for use in member countries, with almost 350,000 tons of active substance sold [20]. Between 2011 and 2020, Germany, Spain, France, and Italy contributed 2/3 of all EU pesticide sales.

According to recent market data [21], the global agrochemical market was USD 243,1 billion in 2019, and it is expected to increase to nearly USD 300.0 billion by 2024. Geographically, The Asia–Pacific region accounts for the largest agrochemical market in terms of production and consumption, generating almost 51% of the global market's growth every year. Based on pesticide type, herbicides account for 40% of the market share, followed by insecticides (18%) and fungicides (10%).

The most extensively applied pesticides are organophosphorus (chlorpyrifos, malathion, diazinon, parathion) and carbamates (carbaryl, carbofuran, aldicarb) which represent 34% of global pesticide sales [22]. On the other hand, organochlorine pesticides are extremely persistent in the environment and less frequently utilized. Heptachlor, endosulfan, aldrin, dichlorodiphenyltrichloroethane (DDT), and hexachlorocyclohexane (HCHs) were used in the agricultural and public sectors to eliminate mosquitos and termites [23]. As a result of their solubility in lipids and the fact that they are not completely degraded, they accumulate in tissues and amplify further in the food chain. Triazine and glyphosate, as herbicides are used for weed management. However, their properties and mode of action may affect unintended species and accumulate over time in the environmental compartments [24].

To achieve high yields, the excessive usage of pesticides has led to food and soil contaminations and ecosystem damage, because 90% of the applied pest do not reach the target species [16,25]. As per World Health Organization (WHO) over 300,000 deaths worldwide arise each year as a consequence of pesticide intoxication [26]. Pesticide intoxication is characterized by a state in which a person ingests or inhales pesticides, in quantities that exceed the pesticide control limits, resulting in negative outcomes [27]. Supplementary this can be defined as either occupational or unintentional. Professional exposure or occupational poisoning affects employees who operate in agricultural areas or in manufacturing industries and are subject to toxic chemicals daily. In this area, humans can be exposed to the pesticide through a variety of pathways including skin, inhalation, ingestion, and contact [26]. Unintentional exposure is caused by people's ignorance or concern about the dangers of pesticide ingestion/inhalation. The pesticide type, the length of time and method of exposure, as well as each person's health status, will have an impact on the risk of poisoning [28]. Even human breast milk samples showed pesticide residues, whereas variations in weight at the time of birth have also been noted [29].

The majority of health effects of pesticide exposure were associated with neurological disorders, accompanied by other health risks (14%) and chronic renal disease (6%). Other health concerns covered cancer (13%) and poisoning (8%), as well as respiratory issues (7%) and reproductive disruption and genotoxicity (6%) [28].

3. Remediation Techniques for Pesticide-Contaminated Soil

It is widely admitted that the agricultural sector considerably boosts the expansion of regional financial management. Unfortunately, economic expansion correlates with environmental injury and destruction. Agriculture is one of the main drivers of environmental deterioration, being linked to soil erosion and acidification, water eutrophication, global climate change, and CO_2 emission [30]. One of the key processes of land degradation is soil erosion, where the soil fertile layer is removed due to the excessive water supply. As a result, soil macro and micronutrients are lost, which also causes global warming due to the release of soil carbon. Additionally, agriculture is characterized by the addition of artificial substances such as nitrates and phosphate through fertilizers, resulting in nutrient enrichment, and subsequent eutrophication phenomena in bodies of water [31].

Due to global change forces, the temperature and precipitation patterns hinder (disturb) agricultural production with associated pest pressure, consequently requiring more widely and frequently used and higher levels of pesticides [32]. Rising temperatures could extend crop yields and shift crop growth to northern areas, whereas the pest generation and growth rates are increased [33]. Additionally, the modification of the pest schedule might request to modify the pesticide application doses or new pesticide active ingredient formulations, which are connected to increased environmental toxicity [34].

Overall, agriculture activities have a greater impact on water supplies, soil quality, and foodstuff and possibly generate political, social, and economic threats (Figure 2). Therefore, creating innovative methods for the remediation of pesticide-contaminated soil is a relevant task and also a critical demand. Remediation technologies through the application of phyto, physico-chemical and biological processes, modify the contaminants properties to reduce their quantity and mobility. In terms of large-scale application, the available technologies present advantages and disadvantages which are based on contaminant type and concentration, the physico-chemical properties of soil, etc. [1].

Phytoremediation is a plant-based green technology used for producing carboxylesterase, peroxidase, peroxygenase, or cytochrome p450 enzymes which can mineralize and degrade diverse pesticide classes. This low-cost technology takes advantage of plant capacity to eliminate or reduce pesticides to less toxic and hazardous [35]. Rhizodegradation, phytodegradation, phyto transformation, and phytovolatilization are among the processes involved in the breakdown of pesticide residues. Plants extract pesticide molecules from the soil by roots, translocate them to stem and leaves, and then accumulate or degrade/mineralize in the metabolic process. These phases facilitate the microorganism institution and bacterial diversity increase which advances pesticide degradation [36]. *Medicago sativa* L., *Zea mays*, *Lolium perenne* L., and *Curcubita pepo* are among the plant species that are frequently proposed to address pesticide phytoremediation [7]. Additionally, a variety of parameters such as soil pH, moisture, temperature, organic matter, and pesticide quantity, and plant species, all limit pesticide uptake, whilst time the dependent reduction in availability can be linked to the residues aging. Therefore, agricultural soil amendment with biochar can minimize the availability and pesticide leaching, the greenhouse gas emissions, and also can act as a slow-release fertilizer [1]. Integrating biochar with phytoremediation may be a helpful alternative to environmental restoration.

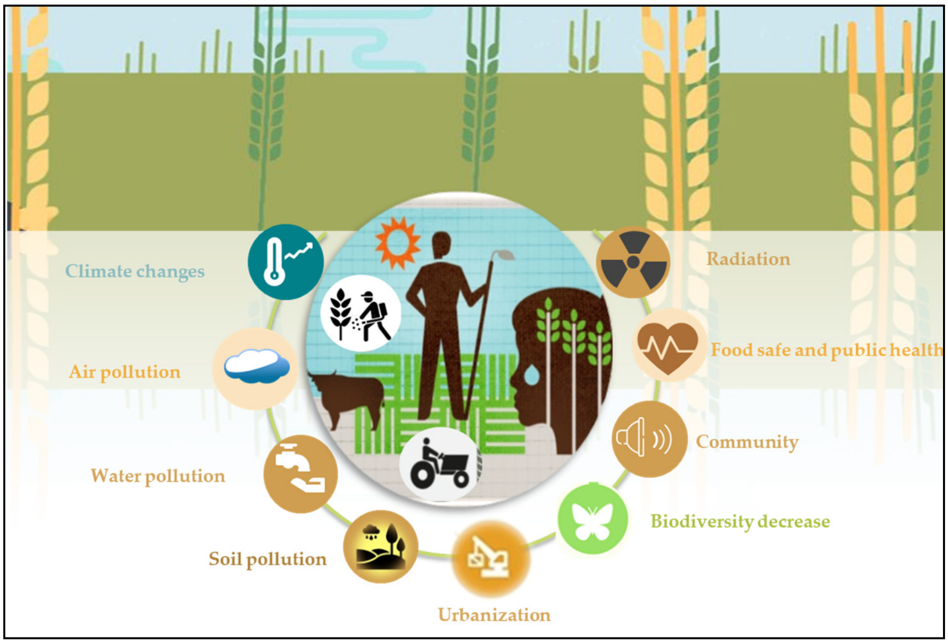

Figure 2. Agriculture's impact on the environment.

Bioremediation is based on a living organism, particularly a microbe to detoxifying and degrading pesticide molecules from the environment [37]. Pesticide microbial remediation is a cost-effective and thermodynamically responsible technology that uses natural biological activity [38]. Given optimal circumstances, soil fauna uses pesticide molecules as a nutrient source (carbon, sulfur) and electron donors. The main reaction of the bioremediation process is hydrolysis, conjugation, and degradation which determine the partial or complete mineralization of pesticides to H_2O and CO_2 [37]. Microorganisms enzymatically have the capacity to convert certain pollutants to fewer toxic products or perhaps abolished them. However, to effectively use microbes for bioremediation, it is important to have a better comprehension of the ecologically, physiologically, biochemically, and molecularly factors that affect pollutant transformation [39].

As physical methods, containment and immobilization processes are regarded as a form of waste disposal, due to temporary measures achieved for the polluted sites. These methods comprise techniques that remove or isolate the source of contamination, excavation, and landfilling both inside and outside the site as well as sealing that prevents infiltration and leaching [40]. Soil washing is the remediation of contaminated soils using different types of extractants, where the excavated soil is mixed with aqueous solutions containing organic compounds or acids. The washing fluids can be recycled or disposed of wastelands. According to researchers, this technology has limitations related to the low effectivity of the solvent extraction of high molecular pesticide weight and the toxicity of solvent to soil microbial population [41]. The electrokinetic soil flushing method initiates many physical (heating, viscosity changing), electrochemical (water oxidation and reduction), and electrokinetic transport processes (electro-osmosis, electrophoresis) which encourage the transport and removal of pollutants from soil [42].

During chemical remediation, a variety of reactions take place (ionization, hydrolysis, or oxidation-reduction, which are typically associated with pH values) to reduce the mobility and bioavailability of pesticides [43]. Chemical reduction/oxidation and immobilization constitute the majority of this remediation technique [44]. The fundamental of chemical immobilization technology is to mitigate the leaching and bioavailability of pesticide molecules through the addition of soil amendments. Currently, immobilization agents or soil amendments such as clays, compost, and biochar are frequently applied. A modern advanced oxidation process for soil remediation is ozonation which can oxidize pesticides directly or by $HO^{\bullet}$ radicals produced during the decomposition of ozone reaction [45]. Pesticide-contaminated soils by chemical treatment can be achieved within minimal timetables while presenting certain environmental risks restricting future land use.

In summary, although all of the aforementioned techniques provide some positive impacts on soil remediation, it is also essential to address their drawbacks. The appropriate remediation technique should be selected based on pesticide concentration and nature, soil physico-chemical properties, environmental conditions, or cost of implementation. Additionally, the use of biochar associated with other remediation techniques may generate significant findings because is an effective agent for pesticide molecules remediation that is safe for the environment and promotes the development of soil conservation.

4. Biochar for Remediation of Pesticide Contaminated Soil

In agricultural and environmental fields, biochar provides an integrated solution with the purpose of soil recovering function and agricultural product quality improving [46]. Consequently, biochar has received increasing attention as an alternative for contaminants sorption [16] (Figure 3).

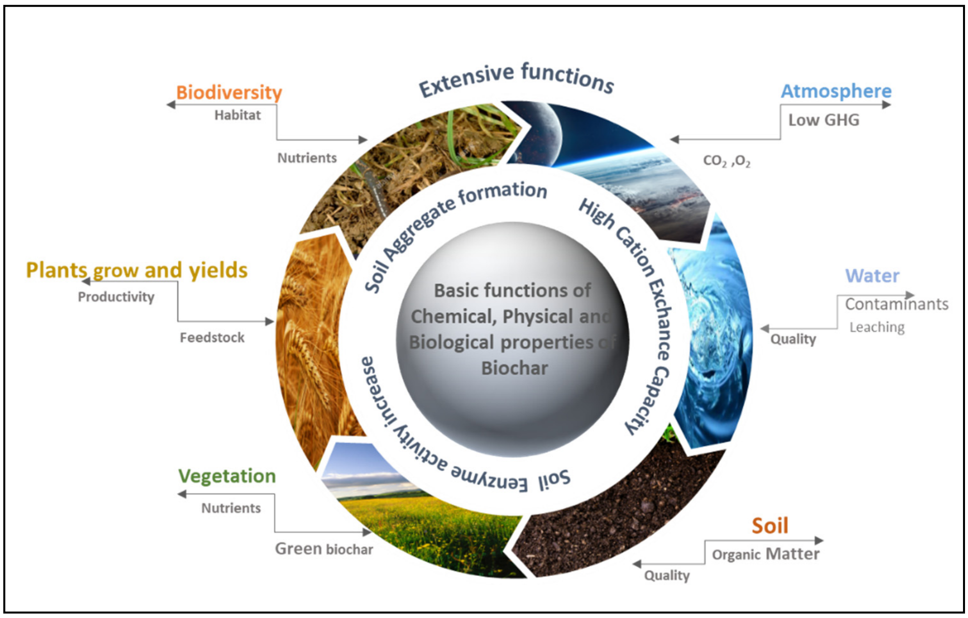

Figure 3. Environmental benefits of biochar.

4.1. *Biochar Effects as Soil Amendment*

Biochar the "black gold", is the organic solid char product, obtained through crop straw or animal and municipal wastes aromatization under anoxic circumstances and elevated temperature, which optimizes organic residues while reducing environmental pollution [47]. The use of biochar is mainly reflected in soil agricultural improvement of soil erosion and acidity, moisture retaining, soil loosening, and increase of soil organic matter and nutrient content. The porous structure of biochar enhances soil aeration, consolidates soil aggregate, and improves soil water holding capacity. According to the majority of research, biochar could be linked to soil particles without obstructing the available pores, maximizing the system's total porosity [48]. As a result of greater root respiration and water assimilation, crop yields may be improved. Soil water holding capacity—SWHC is the basis for understanding soil water movement and solute transport [49]. The microporous structure of biochar influences the SWHC of sandy soils, the advantages of biochar amendment to sandy soil outweigh those of clay soil [50]. Overall, applying biochar to arid, coarse-textured, or sandy soils has greater potential in improving water holding capacity than adding to other soil types [51,52].

Biochar maintains soil nutrients by preventing soil nitrogen, potassium, magnesium, calcium and sodium leaching. This phenomenon is often associated with several physico-chemical and biological reactions [53]. The increased biochar ion exchange capacity sites reduce the loss of nutrient ion, induces the increase of water holding capacity which corroborates with the physical retention of dissolved nutrients from the soil solution [54].

By modifying soil microbial community enrolled in the geochemical cycle, the applied biochar might promote nutrient storage through biological pathways. Moreover, the main constituent elements of biochar structure include C, N, P, K, and Ca, are important supplemental nutrients for soil fertility and crop yield increase [55]. Adding biochar frequently has a greater impact on boosting the fertility of sterile soils, including extensively leached and acidic soils. Following pyrolysis, the majority of biochar nature is alkaline, since functional groups on the surface of biochar can hold inorganic compounds and alkali elements that can be used for the acidic soil improvement [56]. The application of biochar can enhance soil microorganism's habitat, which directly influences the variety, morphology, and microorganisms' behavior [57]. The low temperature preparation process of biochar was more convenient for microbial development than the high temperature processes, due to nitrogen and dissolved organic carbon content [58]. Biochar porous structure increases soil biological activity and variety supplies living space for microorganisms and soil organisms and stimulates soil aggregates formation. Thus, biochar influences soil chemical processes, of cation exchange of C and N, which enhance soil nutrients, increase crop yield, and decrease greenhouse gas emissions.

4.2. Biochar Effects on Pesticide Behavior in Soil

Recently, biochar effects have become increasingly significant for the fate and behavior of pesticides. Pesticides in the soil can interact with biochar through sorption, desorption, degradation, and leaching processes to limit their availability and mobility [59]. Properly, biochar has a high capacity for binding pesticides, which minimizes the concentration of the active ingredient in the soil solution. Biochar causes variability in pesticide fate and behavior and involves competition since various organic and inorganic pollutants coexist in the soil. As suggested by studies, the quantity of carbofuran and chlorpyrifos in the soil was significantly reduced in presence of biochar as compared to the control soil [10]. Similarly, the addition of 5% of corn cob and straw biochar increased the removal rate of 1 mg L^{-1} atrazine solution from 27.02 to 76.65% [60]. The presence of biochar in soil hinders pesticide plant activation and reduces the uptake of pesticides by plants. Due to the high porosity of biochar which facilitates more adsorption sites, this may retain pesticide molecules which could decrease the uptake by growing plants. After the application of biochar, the phenomenon of toxicity and phytoaccumulation in plants grown in sewage sludge was considerably reduced. This might be due to the presence of macro and micro pores corroborating with functional groups, which may have furnished adequate sites for pesticide sorption [47].

4.2.1. Mechanisms of Pesticide Adsorption by Biochar

The adsorption mechanism of pesticide molecules by biochar in soil contaminated with pesticides is complex due to the diversity of the soil matrix. From Table 1, it could be seen that several mechanisms control the adsorption of pesticides onto various types of biochar. Essentially, biochar can adsorb pesticides in two ways based on sorbate-sorbent interaction strength. In the start, physisorption is performed due to diffusion, hydrophobic interactions, π–π bonds, van der Waals forces, and hydrogen bonding which are reversible weak intermolecular physical interactions. Secondly, chemisorption is often performed through covalent bonding or complex formation which are irreversible monolayer chemical interactions; these mechanisms can react independently or synergistically [61] (Figure 4).

Each potential mechanism of pesticide adsorption on biochar is strongly dependent on biochar chemical and physical features (functional groups, mineral content, surface area, and pore structure) and soil properties.

Table 1. Possible adsorption mechanism of pesticides with different biochar types.

Pesticides	Feedstock Type	Pyrolysis Temperature	Mechanisms	References
Oxyfluorfen	Bamboo, maize straw, rice hull, peanuts, chestnut	300–500	Hydrophobic interactions, π-π interactions	[61]
Atrazine carbaryl	Pig manure	350–700	Pore filling, Hydrophobic effect, π-π interactions	[62]
Thiacloprid Nitenpyram Dinotefuran	*Tenebrio molitor* frass	650–850	Micropore filling, π-π electron donor-acceptor, interactions, H-bonding, covalent bonding hydrophobic interactions	[63]
Glyphosate	Birchwood	450	π-π interactions, hydrophobic interactions	[64]
Metolachlor	Soak walnut shell powder	700	Hydrogen bond,π-π interactions	[65]
Paraquat	Swine manure	400	Ion exchange	[66]
Atrazine, Imidacloprid Azoxystrobin	Rice straw	-	Non-bonding interactions, electrostatic interactions, pore filling, partitioning mechanism	[67]

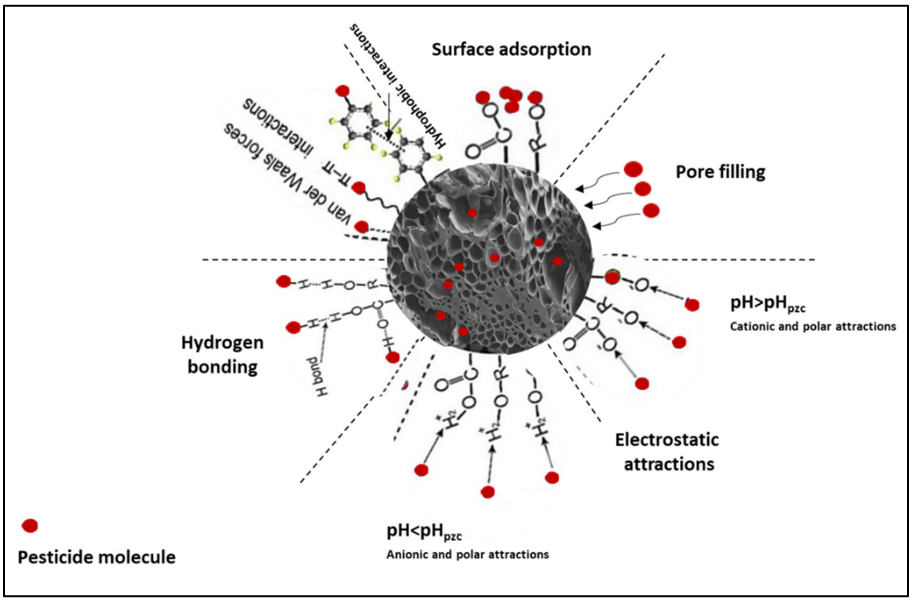

Figure 4. Presumed mechanism for pesticide molecules adsorption on biochar.

Hydrophobic Interactions

Hydrophobic interactions are non-specific, entropy-driven interactions that take place in water and influence the efficiency of pesticide adsorption on biochar [68]. Pesticide molecules and other hazardous organic contaminants could be easily adsorbed on biochar structure due to their hydrophobicity which is connected to the octanol–water distribution coefficient (K_{ow}) [69]. In the case of non-polar pesticides, the adsorption of biochar by hydrophobic interactions would be proportional to K_{ow} values. Pesticide molecules with high K_{ow} values may be adsorbed onto the hydrophobic solid phase, which increases the biochar capacity to absorb organic pollutants [70]. The contaminants aromaticity might be correlated with the hydrophobic interaction mechanism [71]. The soluble pesticides or pollutants can be retained by biochar with hydrophobic functional groups or precipitate on the alkaline biochar surfaces [15]. According to [62] the adsorption of atrazine and carbaryl on pig-manure-derived biochar might be related to a range of processes including the hydrophobic effect. [72] reported that the hydrophobic interaction is the fundamental mechanism implicated in ionizable organic pollutants adsorption. The surface of new brand biochar contains macromolecules with H high density, which can remove neutral ionic organic chemicals or hydrophobic organic compounds by these interactions [73]. According to [74], biochar pyrolyzed at high temperatures has more hydrophobicity than biochar that has been pyrolyzed at a lower temperature.

Hydrogen Bonding

Hydrogen bonding is a strong dipole interaction between hydrogen donor (bonded to nitrogen or oxygen atoms present within -NH_2, -OH, -COOH, functional group and electron-rich π systems) and acceptor [69]. The polar functional groups on the biochar surface which comprises oxygen, carbonyl and carbohydrates react with hydrophilic or/and positively charged pesticides by generating strong hydrogen bindings. According to [75], the sorption of polar pesticides on biochar may be facilitated by the hydrogen forces, whose strength is greater than van der Waals forces but lower than covalent bonds. Recently, it has been discovered that a unique hydrogen bond plays a significant role in the adsorption of anionic ionizable organic compounds by biochar under basic environments, particularly when the ionizable organic pka values are similar to biochar pHpzc values [76]. It has been found that the high sorption capacity of biochar for pesticides could be due to hydrogen bonding among oxygen-containing moieties of biochar and pesticides [10]. In response to repulsive forces between biochar and pesticides is promoted the adsorption due to hydrogen bonding. Through this interaction, pesticides (imidazolinones, a-triazines, and amine/heterocyclic nitrogen atoms of pyridines) typically operate as electron donors. Numerous oxygen containing functional groups are present on the surface of biochar produced from a variety of feedstocks, and these groups can behave as hydrogen bond donors [75]. As a consequence, pesticides and other organic contaminants containing electronegative components may bind to the functional groups of biochar which include O, by hydrogen bonding [77]. The adsorption mechanism of 2,4 D and MCPA on witchgrass-derived biochar can undergo a variety of interaction types based on polar functional groups present on the biochar surface [78]. The constant van der Waals and π–π interactions promote the adsorption of herbicide molecules even at high pH levels where there is a strong repulsion between the carboxylate and phenolate anion of biochar and pesticide carboxylate. Due to hydrogen bonds, organic pollutants may not be able to react with the hydrophobic structure of the biochar surface, supporting the adsorption of water on the oxygen containing functional groups, which favors the water cluster formation while being disadvantageous to the adsorption of organic pollutants [79].

Electrostatic Interactions

Electrostatic interactions are responsible for adsorption mechanisms that depend on the distance between atoms, as well as the size of the charge of each atom [80]. The primary mechanism of ionizable organic pollutants adsorption is the electrostatic interactions, which were confirmed by linkages among the pH values and the capacity of biochar to adsorb organic contaminants [73]. It has been demonstrated that one mechanism by which biochar removes different classes of pesticides is through electrostatic interactions [81,82]. Additional research reveals that the protonated molecule behaved more like a strong π-electron acceptor instead of a neutral molecule due to the positively charged amino group, whereas in aqueous solutions, the cationic molecules of organic compounds such as pesticides or dyes encouraged the electrostatic attractions with biochar surface negatively charged [76,83]. The electrostatic strength changes with the pH and ionic strength, in which the pH manage the biochar surface charge [84,85]. An essential index of the biochar surface charge is the degree of pHpzc which is measured by plotting the adsorbent baseline pH towards conclusive pH values [86]. Because at low pH, the functional groups on the surface of the biochar become protonated, the surface is electropositive at pH < pHpzc, which promotes the adsorption of anionic pesticides, whereas when the pH > pHpzc, the surface of biochar is electronegative increases the adsorption of cationic pesticides [87]. Adsorption may increase with an increase in the adsorbent ionic strength when the electrostatic interaction between the ionic organic adsorbate and biochar are repellent, whereas adsorption may decrease with an increase in the ionic strength when the electrostatic interactions are favorable. This could be due to the ions competing for space in the negatively charged sites of the biochar [73].

Pore Filling

Pore filling is regarded as one of the dominant mechanisms responsible for the adsorption of organic contaminants and pesticide molecules by biochar [10,85]. The pore network of biochar with the macro-, meso- and micropores which comprise the specific surface area of biochar are responsible for organic pollutants adsorption on biochar. For example, the adsorption mechanism of triazine herbicide might be attributed to biochar mesoporosity and microporosity [67]. The nonlinear Langmuir adsorption isotherm is followed by the pore filling mechanism, which acts mostly in biochar with minimal volatile compounds [85]. Remarkably, pore blocking frequently coexists alongside the pore filling mechanism [88].

4.2.2. Mechanism of Pesticides Desorption by Biochar

The desorption process of pesticides is the release of pesticides adsorbed into biochar, generally associated with bioavailability, bioaccessibility, efficacy, leaching, degradation, and toxicological impact, being a more difficult mechanism than sorption [10].

In soil amended with biochar, through the pesticide sorption–desorption process, reversible and irreversible sorption may develop based on the process of interaction with biochar. According to several studies reversible adsorption can be performed by two mechanisms: (1) the sorbent swelling during adsorption process, which causes the deformation of macro/micropores structure and (2) the interactions of weak bonds between the pesticide's molecules and elemental composition of biochar [89,90]. Assessing the hysteresis coefficient values, among unamended and biochar amended soil is one of the main paths to establishing the reversibility of pesticide adsorption. This hysteresis coefficient is the ratio between adsorption and desorption exponents [91]. An increase in the coefficient values could be regarded as a suggestion of partial reversibility. According to [92], the reversible adsorption of isoproturon in soil with 2% biochar could have occurred as a result of micropore displacement since the hysteresis coefficient value of biochar amended soil was greater than the value of control soil. The one-step desorption revealed that a part of the fomesafen molecules adsorbed, were desorbed since in soil amended a higher hysteresis coefficient was measured [90]. In the same way, the kinetic impact of rice-husk-derived biochar with a lower specific surface area, demonstrates the weak adsorption of fomesafen by biochar. In soil amended with biochar derived from red gum wood chips, [93] reported reversible adsorption, which may have been caused by the presence of larger micropores as the primary active centers for pesticide molecules retaining.

Nevertheless, an irreversible sorption process of pesticides molecules might occur, that involves the surface specific adsorption, micropore immobilization, and separation onto condensed structure [6]. It has been reported that biochar, can reduce the pesticide dissolved concentration associated with the increase of irreversible sorption [94]. According to [95] adding 1% biochar derived from wheat straw to the soil reduced the desorption rate of MCPA herbicides from 64.2% to 55.1% in the amended soil.

4.2.3. Mechanism of Pesticides Biodegradation by Biochar

Generally, biodegradation, hydrolysis, and oxidation are the basic pathways of pesticide decomposition and dissipation in soil [6]. Additions of biochar as an amendment could decrease their biodegradation owing to the sorption mechanism. For instance, [96] and [97] found that the degradation molecules of benzonitrile and acetamiprid were delayed in soil treated with biochar. The strong binding of pesticides to biochar elemental composition reduces their availability to the soil microbial population, in addition to their effectiveness and phyto availability [98].

Currently, is accepted that the concentration of degradable pesticides in soil diminishes with the application of biochar. Depending on the quantity applied, biochar has different effects on pesticide mineralization. According to [92], after the application of 0.1% biochar, a first rapid degradation was related to phenyl ring mineralization. After the addition of 1% and 2% biochar to soil, the pesticide molecules were sequestered and were less accessible for the consequent microbial breakdown. Furthermore, [99] reported that the biochar addition frequently increases microbial activity and proliferation, resulting in more substantial pesticide degradation. For example, biochar derived from corn stalks provided an easily accessible source of energy for soil microorganisms. According to [61] biochar derived from rice hull and maize straw corroborate microbial degrading bacteria, increased oxyfluorfen molecules dissipation.

When biochar is linked to plant roots, it can promote microbial activity for hexachlorobenzene degradation and other xenobiotic compounds [100]. Microbial activity is typically stimulated by plants through enzymes and low molecular weight organic acids in plant exudates [101]. Ref. [102] showed that both soil-plant treatments with biochar had a lower concentration of carbofuran and chlorpyrifos than in the control treatment, due to the combined effect of phyto-uptake by plants and enhanced decomposition.

Moreover, the temperature of pyrolysis can impact the biochar effect on pesticide biodegradation. [103] investigated carbaryl degradation in sterile and non-sterile soils treated using maize and rice biochar produced at low (350 °C) and high (700 °C) temperatures. For soil treated with biochar at temperatures of 350 °C, it resulted from an improvement in the biotic removal rate of carbaryl, whereas at temperatures of 700 °C the rate of degradation was reduced. The low temperatures biochar contains easily degradable substances which encourage microbial population. [104] reported identical tendencies for imidacloprid and clothianidin degradation as a consequence of pyrolysis temperature.

4.2.4. Mechanism of Pesticides Leaching by Biochar

Pesticide leaching is a major environmental and health issue [105]. The use of biochar in agricultural system has improved pesticide adsorption and reduced the desorption process and consequently reduces the mobility of pesticides.

Most of the studies display a decrease in pesticide leaching or run-off due to the addition of biochar in soil. For instance, [64] studied the leaching of diuron and MCPA using wood-based biochar as an adsorptive layer directly on or close to the soil surface. The leaching phenomenon was reduced with biochar application through values of retention coefficients linked to biochar layer thickness. Similar results were found by [106] for metolachlor and imidacloprid, which confirmed the reducing leaching potential, as illustrated by the values of GUS (the groundwater ubiquity score) indices in unamended biochar soils. Ref. [107] observed a lower leachability potential of deltamethrin in sandy loam soils amended with different doses of wheat straw biochar, caused by the strong binding and sorption of pesticide molecules inside biochar particles. A possible mechanism of pesticide leaching decrease is the process of pore deformation or the existence in biochar structure of macro-pores which facilitate the retention of pesticide molecules. Therefore, the sorption capacity and performance of biochar towards pesticides depends on the type of feedstock and conditions of pyrolysis, and characteristics of pesticide molecules [108].

5. Factors Influencing the Biochar Impact on Soil Contaminated with Pesticides

5.1. Composition and Chemical Structure of Biochar

The unique physical–chemical properties of biochar affect the pesticides sorption strength and play an essential role in the development of porous soil connections. Biochar elemental composition, functional group, pH and surface area, and porosity are the main factors that may influence the pesticide fate in environment compartments.

5.1.1. Elemental Composition

Elements are the foundation of biochar's chemical structure, and the elemental composition gives biochar high cation exchange capacity which is believed to perform a significant role in the soil sorption process of pesticides [109,110]. Biochar can lower the pesticides availability through multiple mechanisms such as surface chelation and acidity that can act simultaneously. The trend of biochar elemental composition is consistent with the pyrolysis conditions and the type of feedstocks. With the increase in pyrolysis temperature, the ash content increases, whereas the total content of biochar functional groups decreases [111]. According to [10], biochar derived from crop residues has high mineral ash content and high pH. The feedstock may influence the properties of biochar. The content of phosphorous in bio solid biochar is (1.82–3.60%) much higher than those in oak wood biochar (0.03–0.06%), whereas biochar obtained from poultry litter and pig manure has a higher content of potassium (1.6–5.9%) than biochar derived from different raw materials [112]. The feedstock and temperature variation leads to differences in the elemental composition (ash content) and functional chemistry of biochar, which in term affects pesticide sorption. Additionally, the higher pyrolysis temperature increases the biochar surface area and micropores, providing more sites for pesticide sorption [113]. While simultaneously lowering functional groups on the surface, it might result in less pesticide sorption. Overall, it is currently challenging to reveal and understand the adsorption mechanism of biochar and the ideal parameters for pesticide removal.

5.1.2. Functional Group

Following pyrolysis, the lignin and cellulose from the feedstocks are converted into aromatic and fatty carbon, which are suitable for biochar structure achievement [114]. Functional groups on the biochar surface such as hydroxyl groups (-OH), carboxyl groups (-COOH), carbonyl Groups (-C = O), and ester groups (-COOR) provide biochar ability to adsorb pesticide molecules [114]. Generally, biochar surface functional groups are greatly influenced by the pyrolysis temperature and type of feedstock. The high temperature increases the aromatic structure, and the alcohol groups are converted to phenolic hydroxyl groups, thereby increasing the O/C and H/C ratio and biochar specific surface area [115]. According to [116], raising the pyrolysis temperature from 100 °C to 600 °C enhances the C content of biochar-derived maize straw to 84.29% while decreasing the H and O contents to 2.60% and 11.95%, respectively. As a result, the biochar O/C and H/C ratios decrease at high pyrolysis temperatures suggesting that the plant-based feedstock undergoes a reaction of dehydration and deoxygenation [117]. Low H/C ratios are typically associated with aromatic compounds, which suggest biochar stability and resistance to degradation [118]. The pesticide sorption effectiveness is generally influenced differently by variations in the temperature of pyrolysis. High-temperature biochar has more specific surface areas, as demonstrated by [119], whereas decreasing functional groups can limit the pesticide sorption capacity. Furthermore, [120] balanced the pyrolysis behaviors of biochar derived from maize and wheat straw and rice husks and straw at temperatures ranging from 300 °C to 450 °C. For the highest bio-oil yield from maize and rice husk, the optimum temperature is 450 °C, whereas 400 is preferable for rice and wheat straw. Among these available low-cost resources, the biochar derived from rice husk has the highest conversion rate of organic carbon (56.62%).

5.1.3. Biochar pH

The biochar pH values derived from different types of feedstocks and pyrolysis temperatures are completely distinctive. In general, biochar samples are alkaline as a result of basic functional groups that hold inorganic minerals and alkaline components, after the pyrolysis process. With the enhancement of temperature, the ash content increase, the content of O and H decrease, whereas the aromatic structure and biochar pH increase [121]. Through an alkali catalysis mechanism, biochar with a higher pH can stimulate the organophosphorus and carbamate insecticide breakdown [122]. The majority of biochar derived from agricultural wastes have a pH between 7.0 and 10.4 because of the decomposition of acidic functional groups and the volatilization of organic acids during pyrolysis [47]. Nevertheless, certain biochar are slightly acidic when biochar is produced at 300 °C and 400 °C.

5.1.4. Surface Area and Porosity

The surface area and porosity are essential factors determining the adsorption performance of biochar for pesticides and other organic contaminants through pore filling and surface adsorption [119]. The higher surface area and porous structure will produce a greater adsorption capacity of biochar. Biochar porosity may develop through raw material pyrolysis as a result of volatilization of organic matter and water loss during the dehydration process [123]. The SEM (Scanning Electron Microscopy) image, which has been used to characterize different types of biochar pores, showed as the carbonization process intensifies, the porosity and specific surface area growth. The porosity of biochar is a key component in determining its specific surface area, which affects its ability to absorb pesticides. Biochar pores, according to their size, can be categorized as micropores (<2 nm), mesopores (2–50 nm), and macropores (>50 nm) [124]. Consequently, given the surface charge or polarity, the micropores cannot retain large pesticide molecules due to their difficulties in accessing the biochar inner porous structure [125]. Many studies have shown that the high temperatures caused raw materials internal pores release and new and disordered pores were also formed, enhancing the biochar surface roughness and porosity. Once the temperature is raised, the biochar pore volume and surface area increased from 0.056 to 0.099 $cm^3\ g^{-1}$ and 25.4 to 67.6 $m^2\ g^{-1}$, respectively [126]. In the same way, the temperature interference on the maize straw biochar surface area was improved to 265 $m^2\ g^{-1}$ as the pyrolysis temperature increased from 350 to 700 °C [16]. Similarly, [127] reported higher specific surface and porosity of rice husk biochar at higher temperatures.

Additionally, to the temperature of pyrolysis, the composition of raw material significantly influences the biochar properties. [128] reported a better sorption performance of maize straw biochar compared to biochar from corn cob, when the soil was mixed with 5% biochar at an initial concentration of atrazine solution of 1 mg L^{-1}. For instance, biochar derived from plants is reported to have the highest surface areas (140.41–448.2 $m^2\ g^{-1}$) compared to that of pig, dairy, or poultry manure (6.6–83.4 $m^2\ g^{-1}$) [79,117,129]. Generally, biochar with microporous structures is produced through pyrolysis of biomass with a high rate of lignin (coconut shell and bamboo), whereas the microporous structures are obtained from biomass with a high content of cellulose (husks).

The rich pore structure and large surface area of biochar might potentially contribute to a variety of adsorption responses of pollutants from water and soil, depending on prospective applications.

5.2. Pesticide Characteristics

The physico-chemical properties of pesticides such as their aromaticity and polarity have significant importance in the biochar adsorption–desorption process. Pesticide aromaticity might have an impact on the electron donor-acceptor interactions among biochar and organic compound, consequently affecting the adsorption process [80]. The highly conjugated ring system or π electron cloud of the aromatic compound could interact non-covalently with π electron of other aromatic compounds; therefore, the π–π EDA interactions might be the mechanism for pesticide remediations with biochar [130]. It is suggested to use biochar generated at high pyrolysis temperatures for the adsorption of aromatic molecules. Adsorption sites and π–π interactions between biochar and adsorbates were improved since high pyrolysis temperatures could improve the biochar aromaticity [131].

An increase in cation exchange capacity, as well as the interaction development with biochar, exhibited certain functional groups of organic compound advantages. To strengthen the adsorption process, the oxygen-rich biochar could be linked to a hydrogen bond present in pesticide structure that also contains a H acceptor or ligand [130]. Atrazine's electron-withdrawing chlorine substituents may induce adsorption preference through π–π EDA interactions with biochar aromatic carbon [85]. According to [132] the introductions of halogens as substitute as well as the position of substituent appears to produce pesticides resistant to degradation and persistence.

The presence of ionizable functional groups such as -NHR, $-NH_2$, -NHCOR, $-CONH_2$, -OH often causes an increase in adsorption process [5]. Pesticide ionizability is controlled by the soil pH, where in acidic conditions, basic pesticides generate cations, increasing adsorption, whereas non-ionic pesticides may be momentarily polarized, facilitating adsorption on a charged surface. Acidic pesticides are proton donors and at high pH become anions due to the dissociation [5].

Pesticide lipophilicity and hydrophilicity influence the adsorption desorption on biochar. Water solubility highlights the hydrophilicity, which is the attraction of pesticide molecules to water, whereas the ability of pesticides to dissociate into lipids, oils and non-polar solvents, etc., assessed by the octanol–water partition coefficient (K_{ow}), serves to determine pesticide lipophilicity [10]. Usually, the interaction of biochar with water soluble pesticides is weakly compared with lipophilic compounds [5].

5.3. Soil Characteristics

In addition to the direct effects of biochar properties and pesticide characteristics, different soil parameters (soil organic content, microbial community, and soil pH) have been investigated in order to affect pesticide adsorption in soil.

5.3.1. Soil Organic Content

Soil carbon structure comprises soil organic and inorganic carbon [133]. Soil organic carbon is the major adsorbent for pesticides and other pollutants. According to [133], each modification in soil organic carbon structure and quantity based on biochar addition may have a great influence on the pesticide sorption-desorption process.

Soil oxidation/reduction reactions as well as sorption/desorption processes are mainly controlled by the soil organic carbon from biochar structure. The cation exchange capacity and soil pH have been demonstrated to change as a result of these reactions, which then decrease/increase soil capacity to adsorbs and remove pesticide molecules [134]. The presence of reactive functional groups such as hydroxyl, carboxylic, phenolic, and carbonyl in soil organic carbon structure, facilitates the formation of various complexes with pesticides.

5.3.2. Soil pH

Soil pH is the most variable factor in the biogeochemical process of different types of pesticides and organic/inorganic pollutants in soil. Similar to soil organic carbon, each variation in soil pH has a significant influence on soil chemical reactions such as oxidation/reduction, sorption, and desorption. According to [135] adding biochar to soil can significantly change the pH of the soil depending on the pH value of biochar. The oxidation degree, pyrolysis temperature, and type of feedstock affect the biochar pH, which can range from high acidic (<4) to high alkaline (>12) [136].

5.3.3. Soil Microbial Community

Following the addition of biochar, the soil microbial community might behave differently. According to [137], biochar amended soils showed an increase in soil microorganisms, whereas [138] no changes were detected in soil microbes. Soil fluorescein diacetate hydrolytic activity is an indicator of total microbial activity and corroborates with a higher respiration rate, indicating the mineralization of carbon soil microorganism in addition to the reduction of organic pollutants such as pesticides [139]. The high content of nutritive elements from biochar structure increases the microbial activity that degrades pesticides such as atrazine or promotes an atrazine adapted microflora which increase the mineralization of different types of pesticides [140,141]. Based on the biochar type and its chemical and physical features linkages between microbial activity and the microbial breakdown of pesticides have been reported [142]. Ref. [143] reported that the application of wheat straw biochar and the fomesafen herbicide increased the colonization of alpha diversity of *Zygomycota*, *Ascomycota*, *Basidiomycota*, *Chytridiomycota*, and *Glomeromycota*. The variation in the composition of the microbial community has been stated by the biochar nutrient availability, organic carbon content, and water holding potential which provides favorable conditions as well as a biodiversity habitat [138]. Ref. [98] reported that the soil amended with biochar increased the abundances of *Proteobacteria* and *Actinobacteria* bacterial groups.

The dynamics of soil microbial community related to various forms of biochar application including pesticide degradation require to be investigated thoroughly.

6. Final Consideration and Perspectives

Biochar is an effective adsorbent for pesticide removal from different environmental structures. This research conducted a systematic literature review aiming to highlight the potential of biochar remediation for pesticide-contaminated soils with a comprehensive analysis of biochar sorption mechanism towards different parameters impacting the performance of biochar treatment. This review primarily presented the pesticide global consumption with associated environmental and health concerns as well as the involved specific remediation techniques. Generally, the main drivers influencing biochar adsorption performance for pesticide remediation comprise biochar, pesticide, and soil characteristics and properties. Furthermore, adsorption–desorption, leaching, or mineralization processes involve different specific interactions and mechanisms which govern the fate of pesticides in soil. Overall, the specific considerations that emerged are as follows: (i) biochar improves soil quality, restores soil physical, chemical, and biological properties, and increase soil carbon storage; (ii) biochar decreases pesticide leaching and bioavailability as a consequence of sorption capacity; and (iii) feedstock type and pyrolysis conditions are dominant biochar factors influencing pesticide fate.

However, the effects of biochar on pesticide sorption still require additional research, primarily because of various inadequacies (restrictions) and shortcomings such as:

- Establish unitary guidelines specifications and protocols for biochar manufacturing. The physico-chemical properties of biochar are strongly affected by the pyrolysis rates, temperature, and type of feedstock. Due to the current cost of biochar production, universal biochar standards must be established. A future direction in biochar development is the combined use of biochar in order to maximize biochar utilization which provides a methodological base for subsequent applications.
- Perform long-field research effects of biochar application. The majority of biochar applications on pesticide fate are lab-scale experiments or greenhouses studies where the progressive process of soil contamination and degradation is not quantified. Soil physico-chemical properties and ecological balance have diverse long-term consequence and more studies are required to understand how biochar affects the environment. Extensive and prolonged field tests should be carried out in order to investigate the mechanism of long-term biochar addition to soil and to highlight the harmful effects of biochar on the environment.
- Boost the microbial modified biochar-derived usage. It is known that biochar can increase microbial activity in soils and current research on biochar inoculated with particular microorganisms is limited. The biochar-derived modified microbial enhance the soil quality due to the pore structure which can provide living conditions for microorganisms.
- Pertinent studies about the biochar aging process. The intricacy of physico-chemical reactions as well as the impact type of soil and climatic conditions (wet/dry and freeze/melt phases) all require a more complete overview.

- Assess the environmental risks of biochar applications.
- Studies on biochar implementation in agricultural fields related to biochar transport to the farm, the storage facilities and dispersion in the soil.
- Development of rehabilitation strategies that are required to be financially sustainable, practically possible, and culturally allowable.
- Perform the technical–economic analysis of biochar applications under long field experiments.

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