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# Effect of Biochar Amendments on the Sorption and Desorption Herbicides in Agricultural Soil

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## Abstract

Improved understanding of herbicide destinations, effects, and environmental risks through worldwide studies is crucial to minimizing impacts to nontarget organisms, especially in tropical regions rich in biodiversity. In recent years, there has been widespread international concern about the toxic effects of herbicides on humans, faunas, and native floras. Therefore, the adoption of agricultural practices that minimize the environmental effects of herbicides has been frequently studied, for example, the addition of biochar in agricultural soils. Biochar can be defined as the by-product of a thermal process conducted under low oxygen or oxygen-free conditions (pyrolysis) to convert plant biomass to biofuels, where biochar is the solid product of pyrolysis. The addition of biochar to the soil can easily potentiate the herbicide retention process, which, in addition to contributing positively to the reduction of chemical contaminants in the environment, may exert negative effects on herbicide behavior and the efficacy of these products on weed control. Thus, this chapter will present the general characteristics of biochar, as well as the impact of this material on sorption-desorption of herbicides in the soil.

**Keywords:** bioavailability, black carbon, contaminated soils, pyrolysis, retention process

## 1. Introduction

Improved understanding of herbicide fate, effects, and environmental risks through worldwide studies is crucial to minimize impacts to nontarget organisms, especially in tropical regions rich in biodiversity [1]. In recent years, according to Yavari et al. [2], there has been widespread international concern about the toxic effects of herbicides on humans, faunas, and native floras. Therefore, the adoption of agricultural practices that minimize the environmental effects of herbicides has been frequently studied, for example, the addition of biochar (charcoal or black carbon) to agricultural soils.

Biochar can be defined as the by-product of a thermal process conducted under low oxygen or oxygen-free conditions (pyrolysis) to convert plant biomass to biofuels [3, 4], where the biochar is the solid product of pyrolysis [5]. Pyrolysis

or carbonization is a process that involves the application of heat to the biomass in order to concentrate the heat and collect the by-products. It is an interesting alternative, mainly for the treatment of residues, in general of the biomass, aiming its direct application in the soil or composing the compost. The main difference between pyrolysis and incineration is that by pyrolysis it is possible to recover condensable gases (pyroligneous or bio-oil) and those that do not condense, but with high combustion power providing additional energy for the processing unit. Added to this, its contribution is notable for the fact that it minimizes the emissions of greenhouse gases (GHGs) inherent in current agriculture.

Initially, biochar, described as “Terra-Preta de Índio” by Sombroek [6], found in Amazonian soils, and formed by the anthropogenic addition of ceramics and artifacts, has pyrogenic carbon molecules that undergo partial carbonization and are more stable than other forms [7, 8]. Studies of the material provided the basis for agricultural use because of its properties and its benefits to the soil. Since then, biochar has been used to mitigate agronomic problems [9]. Biochar has also been studied as an alternative in the remediation of chemical contaminants in the soil; its use has implicated in the behavior and efficacy of herbicides in the control of weeds and in the environmental impact of these products.

In addition to being found in nature, biochar can also be produced artificially, as previously described and the factors related to the pyrolytic process, such as temperature, heating rate, and pressure, can alter the recovery amounts of each final product, the values of energy of the bio-oils and the physicochemical properties of biochar [10], as well as the types of materials used in the firing can present different answers regarding these characteristics.

Biochar has been used in agricultural fields with positive effects on the soil microbiota [11], changes in soil properties, increasing surface area, pH, C/N ratio [12], nutrient cycling in the soil, increase of available water in the soil for the plants, soil organic matter (SOM) construction, reduction of soil bulk density, C sequestration, and reduction of herbicide transport to surface and subsurface waters [13]. This carbonaceous material can also stabilize heavy metals and decrease their release at levels toxic to the soil [2], being an important alternative in soils with water deficit and nutrient deficiency. However, biochar production by pyrolysis with an incomplete combustion process can be considered as a producer of pollution, containing inorganic molecules, heavy metals, and others that can be harmful to the environment [14].

The use of biochar in agricultural soils as fertilizer and soil conditioner has been more exploited; however, little is known of the effect of this material on soil contaminated with herbicides and also its effect on weed control. The fate and environmental behavior of herbicides as well as their effectiveness when applied directly to the soil, such as preemergent herbicides with residual action, are strongly influenced by the retention binding with soil colloidal particles and the organic carbon (OC) content [15]. Therefore, the addition of biochar to the soil can easily potentiate the herbicide retention process, which, in addition to contributing positively to the reduction of chemical contaminants in the environment, may exert negative effects on herbicide behavior and the effectiveness of these products in weed control. Thus, this chapter will present the general characteristics of biochar, as well as the impact of this material on sorption-desorption of herbicides in the soil.

## **2. General characteristics of biochar**

In an approach on the issue, Brito [16] presents several factors that can act on the nature and yields of pyrolysis products. These factors are as follows:

- a. Factors related to the nature of the raw material: elemental composition, density, grain size, mineral content, composition of the three main polymers (cellulose, hemicelluloses, and lignin), calorific value, and mechanical strength.
- b. Process factors: final temperature, pressure, residence time in the heating zone, heating rate, thermal fluxes and the heat transfer coefficients resulting from the heating rate, chemical or thermal pretreatments in the biomass.

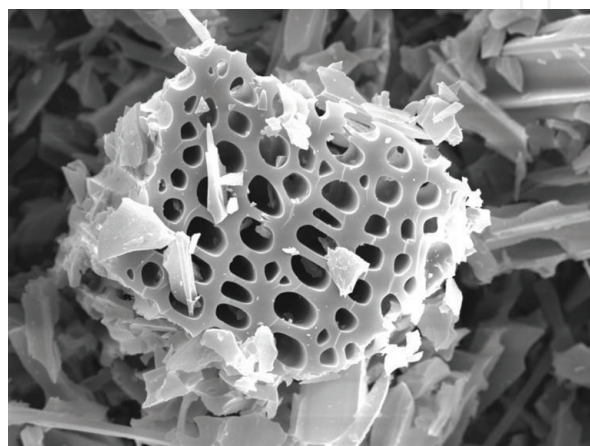
However, here are described the aspects related to the use and efficiency of biochar in the soil, aiming to increase the properties of the set.

## 2.1 Surface area and porosity

In general, the action of heat on biomass via pyrolysis ( $>500^{\circ}\text{C}$ ) results in a more graphitized (aromatic) material—biochar, with greater specific surface area and reduced abundance of surface functional groups. In contrast, lower pyrolysis temperatures ( $<400^{\circ}\text{C}$ ) produce biochars with low specific surface area, which implies partitioning and specific interactions with functional groups on the surface of the biochar [17]. Porosity is another property affected. Higher temperatures result in a more porous biochar when compared to those obtained under lower pyrolysis temperatures [17, 18]. According to the authors, the increase in porosity is accompanied by an increase in the proportion of micropores that contribute significantly to the sorption power of these carbonaceous materials. For example, **Figure 1** shows an image of scanning electron microscope (SEM) of the biochar derived of *Eucalyptus* spp. The biochar exhibits a rough and irregular surface that is characteristic of the material.

In addition, it is well known that desorption is affected by the extent of herbicide absorption in the biochar, controlling its bioavailability in agricultural soils. In general, higher pyrolysis temperatures lead to higher hysteretic desorption processes [17]. One of the intrinsic properties of biochar is its sorption capacity. It may influence other properties, such as mechanical resistance. In India, Japan, and some European countries, its high sorption capacity has been used to capture radioactive elements in the soil, such as Radon (Rn), for example [18].

According to Andrade and Della Lucia [19], this sorption is related to the high porosity of biochar, given by the difference between its actual specific mass and its apparent specific mass. The authors also stated that the porosity of the biochar is linked to the final temperature of the applied pyrolysis, but also add to the existence of the effects of the density of the raw material that gave rise to it.



**Figure 1.**  
Scanning electron microscope (SEM) image of biochar derived of *Eucalyptus* spp. Magnification is  $1000\times$ .



According to Maia et al. [8], the chemical composition of the biomass is highly variable according to the botanical species and the biomass part (leaves, branches, wood, bagasse, residues from the extraction of vegetable oil, among others) and thus significantly influences the products obtained after pyrolysis. Added to this, they provide anatomically distinct biochar (porosity, grain size, among others).

Yu et al. [20] observed higher sorption of diuron in the biochar produced at 850°C than in another produced at 450°C. According to Sharma et al. [21], the elevation of the pyrolysis temperature in the biochar production can raise the retention potential of organic contaminants when applied to the soil; however, the pyrolysis at 400°C decreased the surface area of the biochar particle. Chen et al. [22] indicated that at the temperature of 700°C, the biochar presents half of the specific surface area. The temperature of the process determines the type of carbon present in the biochar, with the reaction time being less decisive [23].

Thus, porosity constitutes one of the most relevant characteristics for biochar aiming at its application in agricultural soils. Yu et al. [20] studied the sorption capacity of herbicidal agents in soils with and without the incorporation of biochar produced from different species and pyrolysis temperatures. The results obtained by the authors showed better results for the soils that received the biochar obtained at the highest temperature, regardless of the biomass used.

## 2.2 Apparent specific mass and true density

The density of feedstock is of great importance in obtaining the biochar, since for the same mass, one desires good yields in conversion of the biochar, provided that the density of the feedstock is high. In practical terms, the higher the density of the source material, the higher the density of the biochar after the pyrolysis. Some studies report that the increase in density is associated with the increase of the lignin content, which implies higher yield in biochar. According to Pétroff and Doat [24], lignin is rich in carbon and thus favors conversion.

[illegible]

## 2.3 pH

The addition of biochar to the soil, in granulometry similar to the fractions that make up the sand, silt, and clay, can alter the limits of consistency, improve water retention capacity, increase pH, and contribute to soil structure improvement [17]. This fact is attributed to the great presence of positive charges at the ends of the carbon chains of the biochar. The subsidized hypothesis for this is that the higher the pyrolysis temperature, the higher the fixed carbon content, and consequently the greater the presence of positive charges in the structure obtained from the biochar.

Clay and Malo [26] found that the biochars of corn and *Panicum virgatum*, produced at high temperatures ( $>650^{\circ}\text{C}$ ), regardless of processing time, were very alkaline ( $\text{pH} > 9$ ). In processes with lower temperatures ( $<550^{\circ}\text{C}$ ), the materials had  $\text{pH} < 5$ .

However, Yang et al. [27] considered the pyrolysis temperature more relevant in the production of biochar for the treatment efficiency of contaminated soils than the material used. In studies comparing the pyrolysis temperature of the wood biochar of *Pinus radiata*, the herbicide terbutylazine was more sorbed in the biochar obtained at  $700^{\circ}\text{C}$  than those obtained at  $350^{\circ}\text{C}$  [28]. In contrast, Li et al. [29], studying the leaching of 2,4-D and acetochlor, found a reduction in leaching and amplification in herbicide efficacy with biochars produced at low-temperature ( $350^{\circ}\text{C}$ ) pyrolysis.

In practice, the biochars obtained by higher pyrolysis temperatures have a higher capacity to raise the pH of the soils that were initially incorporated.

## 2.4 Relationship C:N and H:C and minerals

The biochar obtained from the pyrolysis biomass generally presents low content of nitrogen and hydrogen, which results in a high C:N and H:C ratio [30]. Oxygen is the second most abundant element of the material and its content is inversely related to the final pyrolysis temperature applied. There are also ashes, which come from the mineral elements mainly from bark. In the ashes, potassium, calcium, phosphorus, and sodium predominate. The composition of the ashes is strongly related to the chemistry of the soils where the original biomass was developed. These properties give the biochar a great capacity of persistence in the soil. In studies of dating of biochar fragments (coal) found in soils, it is common to observe samples with thousands of years [31]. Some studies also suggest the positive effect of the coals on physical water properties of soils, increasing their retention capacity and humidity [32]. In general, the pyrolysis gives rise to the C:N and H:C ratio in relation to the raw material that gave rise to the biochar.

## 2.5 Chemical composition immediately

The immediate chemical composition is formed by the contents of volatile materials, ashes, and fixed carbon. The denominated fraction of volatile material is emitted during the heating of the biochar constituted of molecules of  $\text{CO}$ ,  $\text{CO}_2$ , and hydrocarbons. Another amount of carbon remains relatively intact, and as it is not eliminated along with the volatile material, it is called the fixed carbon. In practice, the content of volatile material and fixed carbon is determined by heating the biochar at a temperature of around  $900^{\circ}\text{C}$ . Ash is the residue of mineral oxides obtained by the complete combustion of the biochar. The oxidized residue obtained is calculated as the biochar ash content.

Biomass, when subjected to the action of heat, at high temperatures undergoes a process of transformation, in which all its components are extensively modified [33]. Better biochar immediate properties of biochar—higher fixed carbon content and lower volatile and ash content—are associated with high lignin feedstocks for certain pyrolysis conditions. Each temperature range generates a different product, and the final temperature has a great influence on the final characteristics of the biochar.

Singh et al. [34] indicated a difference in the values of the total carbon fixed in biochars of different materials, so that this content was higher in those coming from eucalyptus wood and eucalypt leaves when compared to cattle manure. The higher carbon content influences the sorption capacity of the herbicides. Cabrera et al. [35] verified the effect of different biochars on sorption of bentazone so that

the sorption increased according to the organic carbon contents dissolved by the materials. For aminocyclopyrachlor, Cabrera et al. [35] found higher sorption in biochars that contained larger surface area and humification index. Exemplifying the hypothesis that each herbicide interacts with the biochar properties govern its behavior in the environment.

In conclusion, the properties of biochar are attributed to the conditions of pyrolysis, temperature, and time, as well as the raw material used [23]. In Brazil, due to the high availability of wood and its derivatives, besides the agricultural base residues, these materials are the basis of the biomass used as a raw material for conversion into biochar. These materials contain a high proportion of cellulose, hemicelluloses, and lignin, the main compositions being converted into carbon matrix in the formation of the biochar, so that these aggregates and their proportional abundance determine the properties of the biochar produced [2].

### 3. Impact of biochar on herbicides retention processes in the soil

The environmental performance and herbicide efficacy applied to the soil are strongly influenced by the retention with the soil particles, mainly the OC content [15], which can be potentiated with the addition of biochar. The herbicide-soil interaction is directly related to the physical-chemical properties of the products and the soil, in addition to the environmental conditions. The impacts of biochar on sorption and desorption of herbicides are presented in **Table 1**, according to the surveys of recent years on this subject.

#### 3.1 Sorption herbicides

According to Khorram et al. [14], sorption is the first process that occurs after the addition of the herbicide in the soil. Thus, retention is an important factor that directly affects other processes, such as herbicide transport via leaching, surface runoff, and volatilization, as well as bioavailability and impacts on nontarget organisms [36]. High OC content, higher surface area, and more porous structures result in higher herbicide sorption capacities [23]. In soils amended with biochar, sorption of herbicides can be increased, reducing the risks of contamination and exposure in the ecosystem and human health [37]. Martin et al. [38] found an increase in the Freundlich sorption coefficient ( $K_f$ ) of atrazine using chicken litter biochar at the dose of  $10 \text{ t ha}^{-1}$ , when compared to soil without biochar. Tatarková et al. [39] indicated that sorption of MCPA (4-chloro-2-methylphenoxyacetic acid) by biochar without soil and by soil amended with biochar ( $1.0\% \text{ m m}^{-1}$ ) was 82 and 2.53 times higher than in unamended soil, respectively. For one of the most used herbicides in the world, atrazine, a study demonstrated an increase in the  $K_f$  value of 5 for sandy soil and 4.3 times for clayey soil with the 1% amended of wheat biochar [40]. Xu et al. [41] reported increased sorption and  $K_f$  values of 1.5 and 3 times in soil, when there was amended soil in 0.1 and 0.5% with rice straw biochar.

The pyrolysis temperature, as previously reported, alters the properties of the biochar, thus altering its relationship with herbicide retention. Using the wheat straw biochar, with a firing temperature of  $300^\circ\text{C}$ , Spokas et al. [42] reported the high sorption capacity of the sawdust biochar ( $5\% \text{ m m}^{-1}$ ) in sandy soil for atrazine and acetochlor, attributed to the high OC content (69%) and specific surface area ( $1.6 \text{ m}^2 \text{ g}^{-1}$ ) of biochar. Hall et al. [43] in glyphosate study obtained higher values of sorption of the herbicide according to the increase in the temperature of burning of the materials, where the highest retention was reported in biochar produced at  $900^\circ\text{C}$ .

Feedstock	Herbicide	Retention of herbicide	Effect	Source
Wheat ash (1%)	Diuron	Sorption	Increased sorption (fourfold) in amended soils	Yang and Sheng [48]
Biochar derived from wheat (0.05, 0.5, and 1%)	Diuron	Sorption	Increased sorption (7- to 80-fold) with 1% of biochar	Yang et al. [49]
Biochar derived from <i>Eucalyptus</i> spp. (450°C) at 0.1, 0.5, 1.0, 2.0, and 5.0% application rate	Diuron	Sorption	Increased sorption (7- to 80-fold) with 1% of biochar	Yu et al. [20]
Biochar derived from <i>Eucalyptus</i> spp. (50°C) at 0.1, 0.2, 0.5, 0.8, and 1.0%	Diuron	Sorption	Increased sorption (5- to 125-fold) in amended soils	Yu et al. [20]
Biochar derived from sawdust	Atrazine and acetochlor	Sorption	Increase of 1.5-fold the $K_d$ for acetochlor. Sorption of atrazine was also increased	Spokas et al. [42]
Sewage of dairy products, 200°C for 4 h, 350°C for 4 h	Atrazine	Sorption	Increase of the sorption in the biochar 200°C in amended soil	Cao et al. [50]
Biochar derived from charcoal (350°C)	Terbuthylazine	Sorption	Increased sorption (2.7-fold) in amended soils	Wang et al. [28]
Biochar derived from sawdust (700°C)	Terbuthylazine	Sorption	Increased sorption (63-fold) in amended soils	Wang et al. [28]
Hardwood sawing (500°C), hardwood (540°C), and wooden pallets (>500°C) at 2%	MCPA and fluometuron	Sorption	Sorption increased by 240–5200%	Cabrera et al. [51]
Biochar produced from chicken bed and wheat straw (400°C)	Fluridone and norflurazon	Sorption	Sorption increased by 24- and 36-fold, respectively	Sun et al. [52]
Paper mill slurry (500°C) at 1–5% and chicken bed (500°C) at 1%	Diuron and atrazine	Sorption	Increase of sorption of diuron in 220–448% and atrazine in 270–515%	Martin et al. [38]



Feedstock	Herbicide	Retention of herbicide	Effect	Source
<i>Eucalyptus</i> sp. (0.1–1%)	Isoproturon	Sorption	Sorption and hysteresis increased	Sopeña et al. [45]
Pallets of wood (>500°C), macadamia nuts (850°C), and hardwood (540°C) at 10%	Aminocyclopyrachlor and bentazone	Sorption	Increased sorption of 18–240% for aminocyclopyrachlor and 13–35% for bentazone	Cabrera et al. [35]
Beechwood (550°C) at 1.5%	Imazamox	Sorption	Increased sorption of <5%	Dechene et al. [53]
Biochar produced from sugarcane bagasse, soybean meal, wood chips, among others	MCPA, nicosulfuron, terbuthylazine, and indaziflam	Sorption	Increased sorption for all herbicides	Trigo et al. [54]
Biochar derived from corn silage (750°C) at 0.5%	Isoproturon	Sorption	The amount of bioavailable herbicide was reduced 10- to 2283-fold in treatment with biochar	Eibisch et al. [55]
Biochar of wood pallets (650°C), wood chips (500°C), and corn bran (490°C)	Aminocyclopyrachlor, picloram, metsulfuron-methyl, oxyfluorfen, and alachlor	Sorption	Aminocyclopyrachlor, metsulfuron-methyl, and picloram showed relatively low sorption; alachlor intermediate sorption and oxyfluorfen heavily sorbed	Hall et al. [56]
Biochar of pecan, cherry, and apple flakes (350, 500, 700, and 900°C) and wooden pallets (350, 500, and 700°C)	Glyphosate	Sorption	Sorption increased according to the pyrolysis temperature (higher at 900°C), depending on concentration	Hall et al. [43]
Biochar derived from sawdust (700°C)	Terbuthylazine	Desorption	Reduced desorption	Wang et al. [28]
Sawing of hardwood (500°C), hardwood (540°C), and wooden pallets (>500°C) at 2%	MCPA and fluometuron	Desorption	Reduced desorption in 85- to 3000-fold	Cabrera et al. [51]
<i>Eucalyptus</i> sp. (0.1–1%)	Isoproturon	Desorption	Reduced desorption in amended soils	Sopeña et al. [45]

Source: Adapted from Beesley et al. [57], Mesa and Spokas [23], and Khorram et al. [14].

**Table 1.**  
Summary of recently selected studies using biochars and their influence on retention process of herbicides.

Another important feature affected by the pyrolysis temperature is the chemical composition of the biochar surface, so that the types of molecules present directly influence the retention of the herbicides. Sun et al. [44], analyzing the composition of wood and grass biochars under different thermal treatments (200–600°C), found the presence of cellulose, hemicellulose, and lignin groups (more present in wood biochar). At temperatures between 400 and 600°C, the noncarbonized aromatic carbon signals from the remaining lignin were identified and disappeared at temperatures above 500°C. The aliphatic carbon appeared between temperatures of 300 and 600°C, but above 600°C, was not pronounced. These variations interfere with the sorption capacity of the biochars, which in this experiment were exemplified by the sorption of fluridone in portions of aromatic biochar and values of sorption coefficient normalized as a function of the OC content ( $K_{oc}$ ) higher than in the others, which were present in low temperatures.

Biochars that contain high specific surface area contribute to the increase of soil sorption of herbicides, as shown by Cabrera et al. [35], where they found almost complete sorption for aminocyclopyrachlor and bentazone in soils amended with biochar from wooden pallets (500°C). Sopeña et al. [45] indicated that biochar of *Eucalyptus dunni* with high specific surface area, sorption of isoproturon was five times higher than in unamended soils with biochar. When using wood of *Pinus radiata* as raw material for the production of biochar (350 and 700°C), Wang et al. [28] found increased terbuthylazine sorption in areas that had increased OC content of the soil and specific surface area with the addition of biochar. The total volume of pores in the soil indicates the greater or lesser specific surface area for the sorption of a herbicide. Biochar increases this amount of pores in the soil, as identified by Sandhu and Kumar [46]. The total pore volume is also related to the pyrolysis temperature, which, according to Wei et al. [47], is reduced at temperatures higher than 500°C for rice bark biochar, but there is increase in specific surface area (greater amount of micropores). In this same study, the pyrolyzed biochar at 750°C with a smaller pore diameter (9.23 nm) provided stronger sorption capacity for metolachlor due to intraparticle diffusion mechanisms and pore filling.

Besides the effect that the physical properties exert under the sorption of the different herbicides, the chemical properties also demonstrate strong influence in this process. The pH variation confers different sorption behaviors of ionic and nonionic molecules to the biochar as adsorbent in the soil. Sun et al. [44] observed that for norflurazon, the pH change had no effect on the sorption of this, because the nonionic molecules of the herbicide bind to the sorption sites and remain unaffected. For fluridone, sorption in both biochars (wood and grass) decreased with the pH increase because it ionizes at pH values lower than 4 (acid ionization constant— $pK_a = 1.7$ ); however, in regions in which the pH remained higher (pH 4–14), there was no ionization, and that with the increase of the proton concentration, there was the conversion of negative ionic functions to neutral sorption sites that fluridone probably binds.

Yang et al. [58] observed a decrease in sorption of diuron with increasing pH in the wheat biochar due to the alteration of the surface charge properties by deprotonation of the functional groups over the pH range. The study also evaluated pH variation in bromoxynil sorption, as well as Sheng et al. [59], both of which verified sorption of the herbicide in soil amended with wheat biochar was higher at low pH than at high pH. This fact can be justified because its  $pK_a$  is 4.06, and at  $pH < 4.06$ , this herbicide is in its molecular form, and already at  $pH > 4.06$ , it will be in the anionic form, which leads to the repulsion of loads on the soil and lower sorption of the product. In the case of ametryn, when in soil without biochar, the sorption of the herbicide occurred at lower pH and, when in addition to the biochar, the higher sorption occurred at higher pH, showing the increase of the affinity of the herbicide with the biochar due to protonation [60].

### 3.2 Desorption herbicides

The herbicide sorbed by the soil particles usually returns to the soil solution, that is, it is desorbed to be available again to the transport by absorption and degradation; however, this process in soils with biochar was less studied when compared to the sorption process [23].

In contrast to sorption, desorption decreases when biochar is added to the soil and the herbicide eventually returns to the soil solution, and sorption can often become irreversible. Irreversible sorption of herbicides was reported by Yu et al. [61], Wang et al. [28], and Sopeña et al. [45], which included sorption of the herbicides in the specific surface area, trapped in micropores, and partitioned into condensed structures of the biochar particles. In a study with wheat straw at 1% ( $\text{m m}^{-1}$ ), Tatarková et al. [39] found the reduction of MCPA sorption from 64.2% in unamended soil to 55.1% in biochar amended soil. For Loganathan et al. [41], the amount of atrazine remaining in sandy and clayey soils amended with biochar was higher than in unamended soils. Cabrera et al. [35] found the almost negligible desorption for aminocyclopyrachlor in biochar amended soil from wood pallets ( $>500^{\circ}\text{C}$ ). Wang et al. [28] also reported slower and lower desorption rates for terbutylazine in soil amended with sawdust biochar produced at  $700^{\circ}\text{C}$ , followed by biochar produced at  $350^{\circ}\text{C}$ . On the other hand, Khorram et al. [4] have reported easier desorption of fomesafen molecules weakly bound to rice bark biochar because the specific surface areas of the material are relatively low.

The reduction in herbicide desorption and consequently the lower concentration of these in the soil solution is more evident in altered soil with biochar in relation to the soil amended with the material. In this sense, there is, in general, a lower leaching potential of the herbicides and lower bioavailabilities of these, both for the degradation and the control of weeds.

## 4. Effect of biochar aged on herbicide sorption in soil

Another important factor in the properties of biochar is the action of time, which can alter the interaction of biochar with herbicides. Some physical processes such as breaking of the structure of biochar by the action of the climate can increase the specific surface area of the biochars [62] and the sorptive capacity of these materials. Kumari et al. [63] obtained higher specific surface area and cation exchange capacity (CEC) in soils amended with wood biochar ( $500^{\circ}\text{C}$ ) after 7–19 months, resulting in increased sorption of glyphosate in all soils of the study. Trigo et al. [64] observed an increase in the sorption of metolachlor in soils amended with distinct biochars over the years (macadamia: fresh = 2.4 times, 1 year = 2.5 times, 4 years = 1.9 times, wood: fresh = 2 times, and 5 years = 14 times). Martin et al. [38] evaluated sorption of atrazine and diuron in soil aged with biochar ( $10 \text{ t ha}^{-1}$ ) for 32 months. In this study, with fresh soil amended with biochar, there was an increase of twofold to fivefold in sorption of the herbicides in relation to the soil without biochar. With 5 years of aging, the biochar presented, in experiment with biochar of residues of the production of mushrooms and rice husk (70%) and peels of cotton seeds (30%) ( $400^{\circ}\text{C}$ ), increases in specific surface area of 98–114.3% according to Dong et al. [65]. However, the average pore diameter decreased and the surface was more propitious for material leaching. Structurally, there was no difference in fresh material.

On the other hand, in some studies, the aging of the biochar particles in the soil resulted in the reduction in the sorption capacity of the herbicides by reducing the specific surface area and the porosity of the biochar as the material aging, blocking

the pores and the sorption sites, especially for high molecular weight molecules [66]. Martin et al. [66], in the same experiment mentioned previously, obtained for the diuron 47–68% reduction in the sorption capacity in relation to the control soil, which may be due to the clogging of the pores of the soil particles over time. Cao et al. [67], when aging rice husk biochar (500°C for 30 minutes) in soil, for a period of 13 months, found reduction in carbon and nitrogen content, reduction in pH values close to neutralized, and reduction in porosity and specific surface area of the biochar.

The degradation of the biochar particles throughout the weathering process alters their mass and their effect on herbicide remediation. Dong et al. [65] found a loss of biochar mass of ~40% over 5 years, regardless of the amount applied (30, 60, or 90 t ha<sup>-1</sup>). Other authors have also observed loss of mass over time [68, 69]. Aging of the biochar can also entail structural changes in the material. Trigo et al. [54], analyzing the surface of aged biochars for 1 and 2 years, found clay minerals adhered by the addition of biochar to the soil, carboxylic acids covering the structure, and the elimination of fatty acids throughout the incubation periods, thus altering the types of possible connections to be made with this surface and the herbicide retention capacity. In the same study, after 2 years of incubation, the specific surface area on the biochar particles was even larger and the pores filled with mineral material. During the incubation period, there was a reduction in the OC content, from 80.4 mg L<sup>-1</sup> of fresh biochar to 31.6 mg L<sup>-1</sup> of biochar with 1 year of incubation, which may be due to natural elimination or degradation. However, these structural and chemical changes that alter the sorptive capacity of the biochar vary according to the nature of each material, as well as the pyrolysis temperature and the conditions and time at which the material will be incubated in the soil.

## 5. Conclusion

The application of biochar in the remediation of soil contaminant herbicides is an interesting management alternative due to high sorption and low desorption with these chemicals. Although the use is well explored worldwide, there is still a need for further research because of contradictory results regarding the benefits of using biochar and its effects on production, plant protection, and environmental contaminants. In addition to verifying the different interactions of the biochar and its properties in agricultural soils, it is worth emphasizing the importance of the possibility of using different materials in the production of biochars derived from different agricultural and industrial activities, which can promote the rational use of resources and destine them to agricultural production and minimization of the environmental impacts caused by these activities.

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