A review of pesticides sorption in biochar from maize, rice, and wheat residues: current status and challenges for soil application

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ABSTRACT

The use of pesticides has been increasing in recent years for maintaining traditional agricultural practices. However, these chemicals are associated with several environmental impacts, demanding urgent remediation techniques. Biochar is a carbonaceous material produced by pyrolysis that has the potential for pesticide sorption and remediation. In this context, this interdisciplinary review systematically assessed the state of the knowledge of crop residues to produce biochar for pesticide sorption. We focused on maize, rice, and wheat residues since these are the three most-produced grains worldwide. Besides, we evaluated different biochar handling, storage, and soil dispersion techniques to ease its implementation in agriculture. In general, pyrolysis temperature influences biochar characteristics and its potential for pesticide sorption. Furthermore, biochar amended soils had greater pesticide sorption capacity, limiting potential leaching and runoff. Most studies showed that the feedstock and specific surface area influence the biochar sorption properties, among other factors. Also, biochar reduces pesticides' bioavailability, decreasing their toxicity to soil organisms and improving soil fertility and crop yields. Nonetheless, the retrieved papers assessed only 21 pesticides, mainly consisting of lab-scale batch experiments. Therefore, there is still a gap in studies evaluating biochar aging, its potential desorption, pesticide co-contaminations, the associated microbiological processes, and field applications. Determining flow properties for biochars of different sizes and pellets is vital for reliable handling equipment design, and performing techno-economic assessment under different farm contexts is encouraged. Ultimately, coupling biochar production with residue management could address this challenge on sustainable agricultural systems.

KEYWORDS: Biochar amendment, Biochar handling, Crop residues, Contamination, Soil remediation, Waste management.

1. Introduction

Synthetic chemicals used in conventional agriculture have increased production by controlling pests, weeds, and diseases. Pesticides target living species, as they are biologically active substances with a structure capable of imitating specific molecules (Das, 2013; Rani et al., 2021). Over the past decade, pesticide use surpassed 4 million tons per year worldwide (FAO, 2020). However, pesticides' extensive use has drastically affected the soil, water, and air quality, causing undesirable impacts (e.g., toxicity, carcinogenicity, and mutagenicity) on non-target organisms, including humans (Khalid et al., 2020; Rani et al., 2021; Varjani et al., 2019). In agricultural systems, pesticide contamination can negatively affect soil quality and crop production, jeopardizing ecosystem services, nutrient cycling, enzyme activity, soil biota, and biodiversity (Liu et al., 2018; Yu et al., 2019). Pesticides can also reach the surface and groundwater through diffuse pollution (e.g., run-off and leaching) (Damalas and Eleftherohorinos, 2011; Khalid et al., 2020).

In this scenario, research trends focused on different approaches to mitigate pesticide risks in soil and water, including chemical remediation, containment or immobilization, and bioremediation (Ganie et al., 2021; Morillo and Villaverde, 2017; Rani et al., 2021; Saleh et al., 2020). However, biochar stands out as a cost-effective and environment-friendly alternative for remediation due to its sorption potential (Kwon et al., 2020; Lehmann and Joseph, 2015; Liu et al., 2018; Varjani et al., 2019). This carbon-enriched product results from the thermal decomposition of biomass or organic material, including crop residues (Ali et al., 2019; N. Liu et al., 2015), animal manure (N. Liu et al., 2015; Ren et al., 2018), woody materials (You et al., 2020; Zhu et al., 2020), and biosolids (Ali et al., 2019; Regkouzas and Diamadopoulos, 2019). The pyrolysis process generally occurs at high temperatures (between 350 and 1200 °C) and in an oxygen-limited environment (Lehmann and Joseph, 2015). Biochar application contributes to the immobilization of organic and inorganic pollutants due to its large pore structure (micro and mesoporous), rich surface functional groups (e.g., carbonyl, hydroxyl, phenolic hydroxyl, and carboxyl), large specific surface area (SSA), high pH, and high cation exchange capacity (CEC) (Beesley et al., 2011; Liu et al., 2018; Waqas et al., 2020; Yu et al., 2019). Several studies have demonstrated the potential sorption of various pesticides (e.g., atrazine, fipronil, diuron, 1,3-D, and 2,4-D) onto biochar solutions (Y. Liu et al., 2015; Regkouzas and Diamadopoulos, 2019; Zhu et al., 2020), and soils amended with biochar (Ren et al., 2018; Wu et al., 2019; Yavari et al., 2020; You et al., 2020).

Biochar amendments on agricultural soils can reduce pesticide mobility, transport, and bioavailability or microbial uptake (Yu et al., 2019). Moreover, it can stimulate soil microbiota while enhancing pesticide degradation (Varjani et al., 2019; Waqas et al., 2020), increase nutrient content and water-holding capacity, ameliorate acidic soils and aeration properties, improving soil fertility and crop yields (Khalid et al., 2020; Liu et al., 2018; Palansooriya et al., 2019). Thus, biochar amendments minimize the environmental risks of pesticides in soil and water.

Millions of tons of agricultural waste are produced globally every year from various crop cultivation and processing (Duque-Acevedo et al., 2020). Thus, crop residues are potential low-cost feedstocks for biochar production and an alternative for agricultural waste management. This approach has sustainable and economic benefits by converting wastes into value-added products. Cereals are the most important staple foods for humans and animals worldwide (FAO, 2015), with maize, rice, and wheat figuring among the leading global productions (FAO, 2019); hence, biochar production from these crop residues is of great interest.

With increasing publications on biochar, some review articles summarized the aspects of biochar production and applications (Khalid et al., 2020; Kwon et al., 2020; Li et al., 2019; Liu et al., 2018; Palansooriya et al., 2019; Varjani et al., 2019; Waqas et al., 2020; Wei et al., 2018; Yaashikaa et al., 2019). However, these reviews focused mainly on biochar's physicochemical properties, its influence on soil fertility, removing metals on laboratory experiments or using biochar in aqueous solutions with pesticides. Despite this, few papers highlighted recent trends and implications of using biochar from crop residues on pesticide-contaminated soils (Khalid, 2019; Varjani et al., 2019). Therefore, given the potential of crop residues-based biochar for amendment of pesticides-contaminated agricultural soils, it would be of great interest to have: i) an up-to-date systematic review on biochar amendment in soils, showing current state-of-knowledge and future challenges and perspectives for its advancement; ii) a discussion and comparison regarding biochar studies from different crop residues as feedstocks, focusing on the most produced ones (i.e., maize, rice, and wheat); iii) an interdisciplinary review that highlights and proposes solutions for typical biochar field application challenges, such as equipment for proper transport, storage, and handling, besides methods for dispersion in farm soils.

In this scenario, this research's general objective was to systematically review the current knowledge about crop residues as feedstocks to biochar production for pesticide sorption. The specific aims were to i) gather research data on agricultural residues (i.e., maize, rice, and wheat crops) and pesticide use; ii) provide an overview of the main properties of crop residues-based biochar and their effects on the sorption of pesticides in the soil; iii) conclude the potential of biochar amendments to improve the pesticide sorption capacity; iv) investigate some options for biochar handling, storage, and dispersion in soil applied to agriculture; v) establish limiting factors, uncertainties, and gaps in current research while proposing future approaches.

2. Systematic review

The systematic review (Figure 1) performed in this study followed PRISMA guidelines (Moher et al., 2009), and used the databases from Web of Science, ScienceDirect, SpringerLink, Taylor & Francis, and Scopus. The research gathered papers published between January 1st, 2009, and January 17th, 2021. The adopted string was "biochar AND (adsorption OR sorption) AND (water OR soil) AND (pesticide OR herbicide OR insecticide OR fungicide)", considering only documents in English.

From the selected databases, we identified a total of 2746 papers and 2385 after removing duplicates. The first step consisted of retrieving the following information on these papers: title, first author, publication year, database(s), author(s) country(ies), keywords, environmental matrix, biochar feedstock, and pesticide. The results were then screened on Microsoft Excel®. There has been an increasing number of papers published recently, as shown in Figure 1. Most articles per year were observed in 2020 (n = 749), and 68 documents from 2021 were available by January 17th.

Figure 1 - Systematic review summary: search process and selection of the studies focused on maize, rice, and wheat residues biochar for pesticide sorption.

The second step consisted of narrowing papers relevant to this study aim, which means biochar associated with pesticide sorption. Thus, non-experimental papers (e.g., review and simulations) were excluded, as well as research focusing on other sorbents (e.g., activated carbon and ash) and chemicals besides pesticides (e.g., pharmaceuticals and polychlorinated biphenyls). After, 310 papers were selected, which represents approximately 13% from the first step. A word map was created from the bibliometric extension on the Microsoft Word® to observe the most publishing countries and used keywords (Figure 2). China is the country that published the most (n = 145), followed by the USA (n = 65), and India (n = 29). Furthermore, the main used keywords were biochar (n = 207), sorption (n = 102), and soil (n = 82).

By focusing on agricultural crop residues among different retrieved feedstocks, papers were reduced to 143. The papers were lastly screened to studies that i) focused on sorption; ii) focused on soil application or experimental research; iii) the biochar was produced from the pyrolysis, and iv) used rice, maize, wheat residues for biochar production as these are the most produced grains worldwide as detailed in Section 3 (FAO, 2019). A total of 32 papers were studied (Table 1), and the Supplementary Material presents full information regarding the biochar production, feedstock type, pyrolysis conditions, and whether pre- or post-treatment were considered. Biochar characterization is also reported: pH, CEC, SSA, particle sizes (PS), pore volume (PV), % ash, % C, % N, % H, and % of other elements. Other processes besides sorption are described (e.g., electrochemical and bioremediation) when evidenced by the authors. This paper reviewed the recovered studies (especially in Section 5), and the efficiency of pesticide sorption and soil characterization were gathered to compare and discuss the selected biochars.

Table 1 - Systematic review summary: studies from the final selection on pesticide sorption into crop residue biochars.

Crop Feedstock		Pyrolysis	pH	CEC ($cmol_c\ kg^{-1}$)	SSA ($m^2\ g^{-1}$)	Studied pesticides	References
Maize	corn cob	450 °C 4 h	n.a.	n.a.	1.5 - 356.0	atrazine	Ouyang (2016a)
	stalk	200 - 850 °C n.a.	9.4	n.a.	13.2 - 386.0	2,4-D, atrazine, flubendiamide	Clay (2016); Ouyang (2016a); Das and Mukherjee (2020); Tao (2020)
	straw	300 - 850 °C 4 - 8 h	6.8 - 10.6	459.0 - 468.0	1.7 - 196.0	1,3-D, atrazine, carbaryl, clothianidin, imidacloprid, oxyfluorfen, thiacloprid, topramezone	Graber (2011), Ouyang (2016b), Qin (2019), Ren (2016), Uwamungu (2019), Wu (2019), Zhang (2018, 2020)
Rice	hull	500 - 600 °C 3 - 4 h	6.7 - 9.6	n.a.	10.7 - 95.7	acetochlor, fomesafen, oxyfluorfen	Khorram (2015, 2017, 2018); Li (2018); Wu (2019)
	husk	300 - 700 °C 1 - 3 h	6.0 - 9.2	5.0 - 70.7	2.00 - 202.1	atrazine, diuron, imazapic, imazapyr, oxytetracycline	Aldana (2020); Yavari (2016, 2017a, 2017b, 2020)
	straw	300 - 700 °C 1 - 4 h	7.2 - 11.1	45.3 and 86.5	8.0 - 188.0	2,4-D, acetochlor, atrazine, carbaryl, fomesafen, pyrazosulfuron-ethyl	Lü (2012); Manna, Singh (2015); Ren (2016); Khorram (2018); Zhao (2019); Manna (2019)
Wheat	midds	550 °C n.a.	8.9	n.a.	24.7	1,3-D	Wang (2016)
	straw	250 - 600 °C 1 - 6 h	5.4 - 10.6	22.0 - 92.0	2.7 - 62.6	atrazine, chlorpyrifos, hexachlorobenzene, MCPA, pyrazosulfuron-ethyl, simazine	Song (2012, 2016); Tatarkova (2013); Manna and Singh (2015); Manna and Singh (2019); Wang (2016); Cheng (2017); Humera Aziz (2018); Ren (2018)

Notes: n.a. = not available

The recovered papers are further discussed in the following sections. First, primary crop residues to be used as feedstock for biochar production are presented (Section 3). Then, the pesticides from the retrieved papers are discussed, considering their primary characteristics influencing biochar sorption (Section 4). Next, the main factors that govern pesticide sorption are assessed based on the recovered studies, considering biochar properties and soil applications (Section 5.1). Besides, we focused on the studies addressing maize, rice, and wheat residues biochar (Section 5.2, 5.3, and 5.4, respectively). Further discussions are also provided for the retrieved studies with some key aspects, gaps, and uncertainties (Section 6). Next, we reviewed equipment and techniques for biochar transport, storage, and dispersion (Section 7), considering the lack of field studies to optimize soil application. Finally, a synthesis of the systematic review is presented, highlighting the advantages, limitations, and perspectives of pesticide sorption with residue-based biochar (Section 8).

3. Crop residues as feedstock for biochar production

Crop production generates large amounts of residues throughout its harvesting, including stalks, husks, and straws (Duque-Acevedo et al., 2020). Although residues are widely studied as feedstock for bioethanol (Kim and Dale, 2004), they could be used as soil amendments for reducing soil degradation (Lal, 2008). Therefore, the most appropriate crop residue uses should enhance, maintain, and sustain soil properties, increasing the soil organic carbon and minimizing soil pollution (Lal, 2005). Thus, residue management is crucial for achieving sustainable agricultural systems, recovering soil properties while contributing to carbon sequestration (Ding et al., 2017; Song et al., 2019).

The largest cereal crops worldwide are maize, wheat, and rice (FAO, 2020) (Figure SM1). Maize (*Zea mays* L.) is an annual plant production, and the USA, China, and Brazil are the biggest world producers; China and India are the major rice (*Oryza sativa* L.) producers; and wheat (*Triticum* spp.) cultivation is more prominent in China, India, and Russia (FAO, 2019). As of 2001, cereals corresponded to 74 % of the world's annual residue production, considering the estimated maize, rice, and wheat residue production of 609, 890, and 875 million Mg, respectively (Lal, 2005). This proportion indicates that maize, rice, and wheat produced 1148, 1133, and 1148 million Mg residues in 2019, respectively (FAO, 2020). In terms of nitrogen, these three crops correspond to 75 % of the world's current residue production, considering 9.36, 9.24, and 9.43 million Mg for maize, rice, and wheat, respectively (FAO, 2019). Maize residues (e.g., stalks) are commonly used for cattle livestock and tillage due to their high nutrient content (Villamil et al., 2015). On the other hand, rice straw has a high silica content, and it is not recommended for feeding animals (Agbagla-Dohnani et al., 2003). Rice hulls and straws can increase crop yields when incorporated into the soil (Sistani et al., 1998). Moreover, corn stover is a potential feedstock for bioethanol production (Kadam and McMillan, 2003), while corn cobs are not feasible for energy production (Erickson et al., 2011). Wheat straw and midds can be included in cattle feed and energy sources (Nguyen et al., 2013; ZoBell et al., 2005).

4. Studied pesticides uses and environmental concern

Pesticides are widely applied to agricultural production, among other chemicals (i.e., fertilizers and pharmaceuticals) (L. Zhang et al., 2018). For instance, the commercial product consists of a combination of the active ingredient and other substances. Although the manufacturers' recommended dose varies according to each target species and crop, overdoses are mostly the cause of severe environmental effects (Meena et al., 2020). Asia and the Americas have a total pesticide use per area of cropland (3.67 and 3.52 kg ha^{-1}, respectively) higher than the world's average (2.63 kg ha^{-1}) (FAO, 2020). Moreover, China, the USA, and Brazil are the leading pesticide consumers worldwide (FAO, 2020).

Understanding the pesticides' fate in the environment is essential. After application, these contaminants may leach and runoff and then reach aquatic habitats (Wang et al., 2019). These processes depend on the local climate conditions (Lammoglia et al., 2018), soil type (Vryzas, 2018), and landscape features (Rouzies et al., 2019). Additionally, spray drift and accidental spills may increase their soil and water concentrations (Jemec et al., 2007). The soil type is crucial for pesticide's environmental behavior, and higher Koc (organic carbon-water partition coefficient) values indicate that pesticides are expected to have low mobility. In addition, the soil granulometry, pH, CEC, and carbon content can contribute to pesticide mobility (Lunagariya et al., 2020). Nonetheless, organic matter and clay particles increase some pesticides' sorption in soil (Sadegh-Zadeh et al., 2017; Spark and Swift, 2002). Although soil microbiota influences pesticide fate, biodegradation is not relevant when contaminants are not bioavailable (Scow and Johnson, 1996). Our research identified 21 pesticides in the final selection (Table 2), and information was presented concerning their density, solubility, log Kow (n-octanol-water partition coefficient), Koc, and half-life (Kim et al., 2021; USEPA, 2021).

242 Table 2. Summary of pesticides characteristics (adapted from Kim et al. 2021, and USEPA 2021)

Group	Pesticide	Density 20-25 °C (g cm^{-3})	Solubility 20-25 °C (mg L^{-1})	log Kow	Koc	Soil half-live (days)
Fungicide	hexachlorobenzene	1.21-2.04	0.0047	5.73	3.6-5.5	970-2100
	oxytetracycline	1.63	313	-0.90	195-93,317	>180
Herbicide	2,4-D	1.42	540-677	2.81	20-136	1.6-32.3
	acetochlor	1.11	223	4.14	98.5-335	7-203
	atrazine	1.23	33	2.61	26-1,164	1.4-108
	diuron	1.48	37.4-42	2.68	55.3-962	330
	fomesafen	1.28	50	2.90	34-1,200	21-360
	imazapic	0.24	220	0.39	3	31-410
	imazapyr	0.34	11,300	0.22	8.81	17.7-63.1
	MCPA	1.56	270,000	3.25	50-62	7-41
	oxyfluorfen	1.49	0.116	4.73	8,900	12
	pyrazosulfuron-ethyl	1.44	14.5	1.74	284.2	16–27
	simazine	1.30	6.2	2.18	78-3,559	27-102
	topramezone	1.13	510	1.44	140	>125
Insecticide	carbaryl	1.23	110	2.36	230-390	10
	chlorpyrifos	1.40	1.12-1.4	4.96	995-31,000	4-139
	clothianidin	1.61	327	0.70	60	148-1,155
	flubendiamide	1.66	0.0299	4.20	1,076-3,318	210-770
	imidacloprid	1.54	610	0.57	156-800	34-190
	thiacloprid	1.46	185	1.26	1,100	0.6-3.8
Nematicide	1,3-D	1.22	2,000-2,180	2.03	20-42	2-54

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Most of the pesticides from the selected studies are herbicides (12 out of 21). Atrazine was the most studied pesticide on the retrieved papers (n = 80 after step 2, and n = 9 in the final selection) and the only pesticide on the top 10 keywords after step 2 (Figure 1). Atrazine has high to slight mobility in soil (Koc from 26 to 1164) and a half-life of more than 1,000 days (Kim et al., 2021). This herbicide modifies the growth, enzymatic processes, and photosynthesis in grassy and broadleaf plants (Singh et al., 2018). In addition, the potential atrazine sorption was investigated for several agricultural residues, including cassava waste (Deng et al., 2017; Li et al., 2018), peanut husk (Saha et al., 2017), sawdust (Gao et al., 2019), and sugarcane tops (Huang et al., 2018). Although glyphosate was one of the most studied pesticides after step 2 (n = 15), several studies investigated the sorption on wood biochar (Hall et al., 2018; Junqueira et al., 2020). However, no paper in the final selection reported glyphosate sorption on biochar from our studied residues (i.e., maize, rice, and wheat).

Nonetheless, the sorption of other herbicides was studied for maize, rice, and wheat residues-based biochar. The herbicide 2,4-dichlorophenoxyacetic acid (2,4-D) is a synthetic auxin that targets broadleaf species, and it has high soil mobility (Koc from 20 to 136) and low persistence (1.6 to 32.3 days) (Gan et al., 2003). Acetochlor has high to moderate mobility in soil (Koc of 98.5 to 335), while diuron sorption is strongly influenced by organic matter presence (Kim et al., 2021; Spurlock and Biggar, 1994). Fomesafen mobility depends on the soil type, with a wide range of Koc values (from 34 to 1200) (Kim et al., 2021). Imazapic and imazapyr are very mobile imidazolinone herbicides (Koc of 3 and 8.81, respectively), as the herbicide 2-methyl-4-chlorophenoxyacetic acid (MCPA) has high mobility (Koc from 50 to 62) and half-life from 7 to 41 days (Kim et al., 2021). Pyrazosulfuron-ethyl has half-life values from 16 to 27 days in soils, and it is moderately sorbed in soils (Manna and Singh, 2015). Simazine has high to slight mobility (Koc from 78 to 3,559) with higher sorption under low pH, and topramezone has high mobility (Koc of 140) and low biodegradation potential (Kim et al., 2021).

Insecticides corresponded to 6 out of 21 pesticides from the selected studies. Carbaryl is a carbamate insecticide weakly sorbed and readily biodegradable in soil (half-life of 10 days) (Ahmad et al., 2004). Chlorpyrifos has low to no mobility in various soils (Koc of 995 to 31,000), characterizing a strong sorption potential (Racke, 1993). Clothianidin has high soil mobility (Koc of 60) and persistence (half-life 148 to 1,155 days), a challenge for sorption techniques (Kim et al., 2021). Flubendiamide has slight to low soil mobility (Koc of 1,076 to 3,318), and the half-life ranges from 210 to 770 days (Kim et al., 2021). For imidacloprid soil sorption, organic matter is more relevant than clay content and CEC (Liu et al., 2006). Thiacloprid has low mobility in soil (Koc of 1,100), and it is readily biodegradable (half-life of 0.6 to 3.8 days) (Kim et al. 2020).

Two fungicides were found in the selected studies, hexachlorobenzene (HCB) and oxytetracycline (OTC). HCB is expected to be immobile on soils (Koc 3.6 to 5.5), it is considered a persistent organic pollutant (half-life from 970 to 2,100 days), and sorption might reduce its volatilization (Barber et al., 2005). OTC is an antimicrobial drug, also applied for fungi control, and its sorption depends mostly on soil texture, CEC, and iron oxide content (Jones et al., 2005). Although we did not include “nematicide” in our keywords, one study was found with 1,3-Dichloropropene (1,3-D). This pesticide is commonly applied with chloropicrin as an alternative to methyl bromide to control soilborne diseases and nematodes (Santos et al., 2006).

Residual pesticides can remain for long periods in the environment or agricultural origin products, posing a risk to human health (Kim et al., 2017) and establishing the maximum acceptable intake. Although these limits are less restrictive than those proposed for fauna and flora protection, the legislation is usually guided by human health protection. For this purpose, human exposure pathways are assessed and analyzed, including direct contact (e.g., dermal), ingestion (e.g., drinking water, food, and soil), and inhalation (e.g., soil particles and air).

However, most environmental agencies do not determine the maximum dose through all significant exposures, and some limits are still inefficient for health protection (Li and A. Jennings, 2017). Also, pesticides might cause harmful effects to the biota even within limits established by legislation and environmental agencies (Brovini et al., 2021).

Overall, pesticide pollution endangers the environment, considering adverse effects on water quality, biodiversity, and human health, as highlighted by Tang et al. (2021). These authors identified high-risk areas worldwide, and 34 % of them were in high-biodiversity regions, 5 % in areas with water scarcity, and 19 % located in low and lower-middle-income nations. Also, China was considered the top country susceptible to high pesticide pollution risk, emphasizing the Huang He watershed. Since China is the leading country on studies of biochar application for pesticide sorption, researchers and the government should perform these alternatives in priority areas. Also, pesticides can cause effects on several non-target species (de Figueirêdo et al., 2020; Sanches et al., 2017; Triques et al., 2021), and the ecotoxicological assessment of the pesticides' impacts on representative species is a pathway to understanding their biota damages. Moreover, the ecological risk of their presence in soil and water endangers the proper ecosystem functioning and services (Schäfer et al., 2012; Schiesari and Grillitsch, 2011).

5. Biochar for pesticide-contaminated soils remediation

Remediation techniques are applied to remove, reduce, degrade, or retain contaminants, considering the ecological risks of pesticides in soils. The most appropriate method relies on the environmental characterization of the area, financial resources, predicted execution time, sustainability considerations, and remediation goals according to the future land use (Fernández Rodríguez et al., 2014; Hou and Al-Tabbaa, 2014). Pesticide sorption processes stand out among containment or immobilization technologies by limiting the contaminant potential infiltration and leaching by applying carbonaceous materials as sorbents (Morillo and Villaverde, 2017).

Although biochar and activated carbon are carbon-rich solids with a similar porous structure, the former has lower production and energy costs (Dai et al., 2019; Lehmann and Joseph, 2015). Thus, biochar has been evaluated as an alternative to the commercial activated carbon for contaminants sorption (Dai et al., 2019; Yaashikaa et al., 2019). The production of both sorbents is through pyrolysis, but activated carbon can also be produced by chemical or steam activation (Kazemi Shariat Panahi et al., 2020). Regarding the source material, activated carbon can come from biomass or any carbonaceous substance (e.g., coal), although biochar is made exclusively from biomass. Biochar as soil amendment aims to favor the contaminated or degraded soil's physical, chemical, and biological properties (Kazemi Shariat Panahi et al., 2020). Biochar's sorption capacity is not always as high as activated carbon (Liu et al., 2018), so the use of engineered biochars resulting from activation and modification processes may be relevant in some cases.

5.1. Primary factors for pesticide sorption on biochar

The critical factors determining the biochar sorption efficiency are the feedstock, pyrolysis temperature, solution pH, dosage of biochar, competition with co-existed ions and other contaminants, the aging process, and modification/activation (Abbas et al., 2018). Higher pyrolysis temperature increases the biochar's SSA and micropores, improving the organic contaminants sorption (Abbas et al., 2018); this variation is related to how volatile compounds are released during carbonization (Yu et al., 2019). The pyrolysis temperature also significantly affects the functional chemistry of biochars, as plant-based feedstocks (e.g., crop residues) undergo dehydration and depolymerization of lignin and cellulose in high temperatures.

On the other hand, poultry manure and sewage sludge biochar do not contain lignocellulosic compounds and do not suffer depolymerization (Ahmad et al., 2014). Pyrolysis residence time also increases SSA (Yu et al., 2019) and the ratio of O/C and H/C (Khalid et al., 2020). For maize straw biochar, Zhang et al. (2011) indicate that increasing the pyrolysis temperature (100 to 600 °C) improves the C content (47.46 to 84.29 %), reducing the H and O contents (6.23 to 2.60 %, 45.95 to 11.95 %, respectively). Thereby, O/C and H/C ratios in biochars decrease with high pyrolysis temperature, indicating the dehydration and deoxygenation of feedstock (Ahmad et al., 2014). Aromatic structures are usually on lower H/C ratios, indicating biochar stability and resistance to degradation (Varjani et al., 2019). It is worth noting that the functional group abundance on the biochar surface reduces as the pyrolysis temperature increases (Khalid et al., 2020).

In general, the variation in the pyrolysis temperature also causes different influences in the sorption efficiency. Liu et al. (2018) exemplified that biochar produced at high temperatures has more active sites (i.e., greater SSA), although reducing functional groups can decrease the pesticide sorption capacity. Thus, it is necessary to have balanced and holistic knowledge so that biochar with the desirable characteristics is produced and applied to the soil. Additionally, Biswas et al. (2017) compared pyrolysis behaviors (from 300 to 450 °C) of corn cob, rice husks, rice straw, and wheat straw biochars. The optimal temperature associated with the maximum bio-oil yield for corn cob and rice husks is 450 ºC, while 400 °C is better for rice and wheat straws. Among these biochars, rice husk presented the highest organic carbon conversion (56.62 %).

Crop residues are rich in minerals and, consequently, biochars have high mineral ash content and high pH (Khalid et al., 2020). Despite biochar from higher pyrolysis temperature having higher pH values, the pH_{PZC} and solution pH also influences sorption capacity, mainly if the pesticide is ionizable (Khalid et al., 2020; Liu et al., 2018). Biochar has a variable charge, and high pH values increase the OH dissociation from the functional groups (e.g., carboxyl and hydroxyl) in particles' surface (Ahmad et al., 2014; Yu et al., 2019). Thus, the net negative charge increases, and there is an electrostatic attraction between negative charges and cationic species (Yaashikaa et al., 2019). Herath et al. (2016) reported the optimum pH at 4.0 for maximum glyphosate sorption (82 %) in steam-activated biochar produced from rice husk, while higher solution pH decreased the sorption capacity to 56 % (pH 10). Considering the pH_{PZC} (at pH 4.0), the glyphosate dissociates, and the biochar surface charges positively ($pH < pH_{PZC} = 6.65$). Therefore, in acidic conditions, a strong electrostatic interaction is favored between the anionic glyphosate species (negatively charged) and the surface of the positively charged activated biochar.

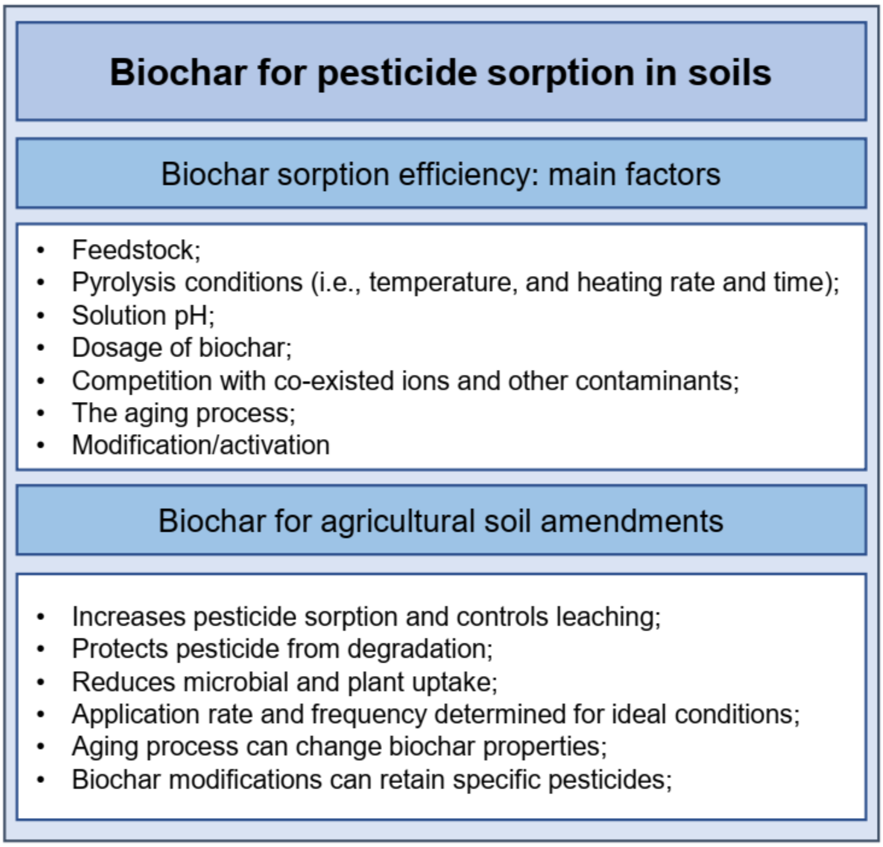
It is essential to verify the biochar application rate and frequency to achieve ideal soil conditions for pesticide remediation (Liu et al., 2018). Different dosages can increase or decrease the pH and modify the soil electrical conductivity (EC) in varied proportions (Palansooriya et al., 2019). The efficiency of pesticide sorption in biochar-amended soils also involves competition, as the soil is a complex system with different organic and inorganic contaminants coexisting. The biochar interaction with inorganic and organic particles in the soil and other pollutants might be competitive and lead to pores blockage, decreasing the sorption capacity of targeted pesticides (Liu et al., 2018).

Biochar aging is a crucial factor that interferes with biochar properties and soil interactions. After application to the soil, synergistic changes of physical, chemical, and biological aging occur, and, especially in highly aromatic biochars, microbial metabolism is favored. As a result, the outer portions of the biochar particles are more altered and protect their interior from the action of the microorganisms. As biochar is a carbon-rich organic material and has relative stability and resistance to degradation, the labile carbon fraction is first degraded; hence, aged biochars become less susceptible to degradation than fresh biochars (Lehmann and Joseph, 2015). Ren et al. (2018) observed that wheat straw biochar’s surface area and chemical composition changed with time after addition to soil. Consequently, aged biochars may have different sorption performance than fresh biochars. Gámiz et al. (2019) indicated improved sorption of aged biochar for removing herbicides (e.g., imazamox, picloram, and terbuthylazine) than fresh biochar. However, Liu et al. (2018) showed that biochar aging generally reduces its sorption potential. Therefore, the effects of aging on the fate of pesticides in biochar-amended soils still need further research.

Biochar modified for particular soils’ needs might enhance the pesticide’s sorption (Kazemi Shariat Panahi et al., 2020; Yu et al., 2019). This process occurs due to the increasing porosity, micropore volume, SSA, and functional groups, eliminating potentially harmful elements (Liu et al., 2018; Wei et al., 2018). Biochar modification methods include chemical reagents, iron ions, metal oxide, and functional nanoparticles (Wei et al., 2018; Yaashikaa et al., 2019). Each engineered biochar can be prepared by pretreating feedstock before pyrolysis or post-treating onto untreated biochar (Liu et al., 2018). The chemical modification involves adding bases and acids to the biochar, and generally, acid activation changes surface properties (e.g., functional groups, charges, porosity, and SSA) (Wei et al., 2018). For example, feedstocks treated with nitric acid can incorporate carboxylic groups (Yaashikaa et al., 2019). The primary activation (usually using NaOH or KOH) induces the basicity and increases the O content on the surface (Wei et al., 2018). Biochar modification also includes the physical activation using steam (Yaashikaa et al., 2019) and the impregnation of functional nanomaterials (e.g., chitosan, carbon nanotubes, ZnS nanocrystals, and graphene oxide). This process improves the SSA, porosity, and thermal stability, creating a newly engineered compound used as an alternative and innovative sorbent (Kazemi Shariat Panahi et al., 2020; Wei et al., 2018). Moreover, modifying biochar for soil amendment must consider the costs of alteration methods and potential risks of environmental pollution by the added elements (Liu et al., 2018).

In synthesis, several critical factors determine amending agricultural soils for pesticide sorption (Figure 2). First, crop management should address biochar production residues, which depend on the feedstock type and pyrolysis conditions (e.g., temperature, heating rate, and time). The biochar characteristics related to pesticide sorption involve ash content, pH and pH_{PZC}, CEC, functional groups, elemental ratios, porosity, and SSA. In agricultural soils, biochar amendments contribute to pesticide sorption, leaching control, protecting the pesticide from degradation, and avoiding microbial uptake. Moreover, the potential effects of the aging process are not yet fully documented.

Figure 2 – Key aspects of biochar application for pesticide sorption on agricultural soils.



Biochar for pesticide sorption in soils

Biochar sorption efficiency: main factors

- Feedstock;
- Pyrolysis conditions (i.e., temperature, and heating rate and time);
- Solution pH;
- Dosage of biochar;
- Competition with co-existed ions and other contaminants;
- The aging process;
- Modification/activation

Biochar for agricultural soil amendments

- Increases pesticide sorption and controls leaching;
- Protects pesticide from degradation;
- Reduces microbial and plant uptake;
- Application rate and frequency determined for ideal conditions;
- Aging process can change biochar properties;
- Biochar modifications can retain specific pesticides;

5.2. Biochar from maize crop residues

Twelve studies from the final selection evaluated 24 different maize residues biochars for pesticide sorption (Table 1). Among these biochars, 15 used straw, 7 used stalk, and 2 used corn cob as feedstock; 1 biochar was produced with pre-and post-treatment, 1 biochar with only pre-treatment, 1 biochar with post-treatment, and the others were not mentioned. All the studies were conducted on a laboratory scale using spiked soils, and most of them involved agricultural soils. Also, pyrolysis temperatures ranged from 200 to 850 °C. Several studies stated that biochar-amended soils were more effective in the pesticide sorption compared to the biochar-free soil for atrazine (Clay et al., 2016; Ouyang et al., 2016a, 2016b; Qin et al., 2019; Tao et al., 2020), 2,4-D (Clay et al., 2016), carbaryl (Ren et al., 2016) and thiacloprid (P. Zhang et al., 2018). For instance, Clay et al. (2016) reported an increase from 4.5 to 6-fold on the sorption efficiency for atrazine after soil amendment with 10 % of maize stalk biochar.

The pesticide sorption on biochar amended soil depends on both pesticides and biochar properties, besides soil characteristics. In our review, biochars from the same feedstock (e.g., maize crop residues) presented a significant variation in their properties: pH values varied from 6.8 to 10.6; the SSA was between 1.5 and 386 m^2 g^{-1}, and ash content ranged from 3.01 to 32 %. Also, biochar properties are strongly influenced by the feedstock material characteristics and pyrolysis conditions. For instance, maize straw biochar had the largest SSA (44.966 m^2 g^{-1}), total pore volume (0.0345 cm^3 g^{-1}), and ash content (9.03 %) than biochar from corn cob (1.506 m^2 g^{-1}, 0.0032 cm^3 g^{-1} and 3.01 %, respectively). Consequently, this was probably one of the factors that favored the better sorption performance of maize straw biochar (when the initial concentration of atrazine solution was 1 mg L^{-1}, the removal rate was 27.02 and 76.65 % for soil mixed with 5 % of corn cob and straw biochars, respectively) (Ouyang et al., 2016b).

Several studies confirmed the temperature interference on the maize straw biochars SSA among the pyrolysis conditions, improving from 6.71 to 265 m^2 g^{-1}, as the pyrolysis temperature increased from 350 to 700 °C. Similarly, the pH increased from 7.9 to 10.6. Consequently, the highest carbaryl sorption affinity was evidenced for the biochar produced at the highest temperature (700 °C) and with the highest rate of addition to the soil (5 %), with a sorption affinity (K_f, Freundlich isotherm) of 83.2 (mg kg^{-1}) (mg L^{-1})$^{-n}$ (Ren et al., 2016). Accordingly, Tao et al. (2020) evaluated maize stalk biochar, and batch sorption experiments revealed an improvement in maximum sorption capacity from 21.96 to 35.88 mg g^{-1}, respectively, by increasing pyrolysis temperature from 250 to 850 °C. In the same way, biochar application increased the K_f of imidacloprid, and clothianidin (Zhang et al., 2020) into maize straw biochar-amended soil with charring temperature (300 - 700 °C).

Besides, Zhang et al. (2020) reported that the amendment with low-pyrolyzing temperature biochar (300 °C) benefited the imidacloprid and clothianidin biodegradation due to the supply of organic carbon and available nitrogen for microorganisms, although inhibiting the chemical degradation. On the other hand, the high-pyrolyzing temperature biochars (500 to 700 °C) favored chemical degradation, inhibiting biodegradation. For thiacloprid, the observations were similar (P. Zhang et al., 2018). Biochar particle size range influences the sorption efficiency of pesticides, as observed by Clay et al. (2016). Atrazine and 2,4-D sorption increased significantly with the reduction of the biochar particle size. For 2,4-D, K_f was risen from 190 (for biochar mean size of 2 to 4 mm) to 398 $\mu mol^{1-1/n}$ $L^{1/n}$ kg^{-1} (for size below 2 mm); while for atrazine, the increase in K_f was more prominent from 209 to 912 $\mu mol^{1-1/n}$ $L^{1/n}$ kg^{-1} in the same biochar size range (Clay et al., 2016).

Some studies use biochar modification or pre- and post-treatment to develop biochars with enhanced pesticide removal capacity from the soil. The maize straw biomass pretreatment with ammonium dihydrogen phosphate (ADP) increased the atrazine removal from soil amended due to the increase in biochar SSA (44.966 for 356.010 m^2 g^{-1}) and total pore volume (0.0345 for 0.221 cm^3 g^{-1}) (Ouyang et al., 2016b). Clay et al. (2016) evaluated the influence of post-process handling. The first biochar sample was cooled to room temperature, while a second sample was immersed in water immediately after pyrolysis to prevent slow combustion. The atrazine sorption data for water-cooled biochar showed a K_f of 151 $\mu mol^{1-1/n}$ $L^{1/n}$ kg^{-1}, a lower value than the results for air-dried biochar (209 to 912 $\mu mol^{1-1/n}$ $L^{1/n}$ kg^{-1}).

The biochar addition alters soil properties. For example, Zhang et al. (2020) observed that a typical Chinese soil pH increased from 4.4 to 6.8 after a 2 % application of maize straw biochar (500 °C). Also, pH, EC, available nutrients, organic carbon, hydrogen contents, and SSA of the soil were improved by adding biochar from maize crop residues. The dissolved organic carbon increased upon the addition of biochars pyrolyzed at 300 °C, while the biochars produced at 700 °C decreased their concentrations (P. Zhang et al., 2018). Pesticide sorption capacities are expected to vary on soils with different properties. Clay et al. (2016) pointed out that a 1 % addition of maize stover biochar increased atrazine sorption affinity for the fine loamy sand by about 45 % and for the silty clay loam by 25 %. The biochar-amended soil constituents become heavily dependent on each other and with specific behaviors for each environmental condition. At the initial atrazine solution of 1 mg L^{-1}, the soil amended with corn cob- and stalk-based biochar (0.5 and 1.0 % addition rate) had better performance than the pure biochar. On the contrary, at 20 mg L^{-1}, the pure biochar derived from maize stalk had a better removal rate than the biochar-amended soil (Ouyang et al., 2016b).

Previous literature showed that the maize biochar application rate in the soil is fundamental for optimizing pesticide sorption. Among the 12 included articles (Table 1), 11 studies involved maximum doses of 5 %, and one study evaluated doses up to 10 %. Overall, it generated significant improvements in the pesticide sorption capacity. The atrazine's removal rate in column experiments increased from 38.7 to 58.3 % by increasing the application rate of the maize straw-derived biochar from 0.5 to 1.0 % (Ouyang et al., 2016a). However, some studies indicated that high application rates could result in negative impacts. Clay et al. (2016) reported that 1 % addition of maize stalk biochar to two different soil types (silty clay loam and fine loamy sand) did not affect the pH or EC. Adding 10 % of biochar has already increased the EC, especially in the sandy soil (less buffering capacity). However, large and frequent applications must be associated with monitoring EC to avoid saline conditions and, consequently, losses in agricultural productivity.

Graber et al. (2011) investigated the interaction of 1,3-D in a solid-liquid-gaseous system of a biochar-amended soil. The addition of 1 % of maize straw biochar (500 °C) promoted strong 1,3-D sorption with solid particles, causing substantial reductions in the 1,3-D concentrations in the gaseous phase. Still, there were also reductions in the aqueous phase, precisely the active portion for nematode control. Thus, there was adequate control of the nematodes in the studied system. However, the authors emphasized that biochars with greater sorption capacities (e.g., those with higher pyrolysis temperatures or large doses) should be used cautiously. Otherwise, depending on sorption conditions, it can negatively impact pest control and agronomic systems.

Overall, the pesticide sorption onto the soils amended with maize residue biochars was accurately described by the Freundlich model, such as for atrazine (Clay et al., 2016; Ouyang et al., 2016b), 2,4-D (Clay et al., 2016), flubendiamide (Das and Mukherjee, 2020), 1,3-D (Graber et al., 2011), carbaryl (Ren et al., 2016), thiacloprid (P. Zhang et al., 2018), imidacloprid, and clothianidin (Zhang et al., 2020). For instance, the isothermal sorption fitted well with the Freundlich model ($R^2 > 0.96$) on soil amended with different biochar additions from corn cob and stalk (Ouyang et al., 2016b). Ren et al. (2016) also reported experimental data adjustments ($R^2 > 0.98$) of carbaryl sorption to maize straw biochar-amended soil. It suggests that the pesticide sorption occurred predominantly on the heterogeneous surfaces of the particles in these studies. On the other hand, the Langmuir model better described the topramezone’s sorption process, which means the monolayer sorption played a dominating role

(Uwamungu et al., 2019). Tao et al. (2020) reported that the Freundlich model is better suited to fit the atrazine sorption onto biochar produced from maize stalk at 250 °C, while the Langmuir model matched well with the biochars made at 550 and 850 °C. The kinetic experiments results showed that pesticide sorption was faster in the first phase by the larger number of active sorption sites. Thus, the sorption equilibrium was reached after 8 to 12 h, when 0.5 g of soil and 0.02 g of biochar were added with topramezone (Uwamungu et al., 2019), and 10 h for atrazine mixed with 15 mg of biochar (Tao et al., 2020).

In addition to increasing sorption efficiency, Das and Mukherjee (2020) pointed out that the biochar addition in soil reduced the desorption process. A considerable portion of the flubendiamide sorbed in the soil matrix remained retained during the desorption test. The biochar addition to the soil reduces diffuse pollution from leaching, as simulated by Ouyang et al. (2016a) in rainfall-leaching experiments with different soil column configurations. The lowest leaching atrazine contents appeared in the smaller rainfall intensities and in the columns where biochar was applied to the soil. The soil with a biochar and gravel combination provided the highest efficiency of atrazine control (on average 87.85 %) when the biochar addition rate was 3 %.

Previous studies have highlighted that biochar application in the soil could affect pesticide biodegradation. For example, the biochar amendment in the soil at 5 % decreased the half-life values of flubendiamide from 165.3 and 178.6 to 103.5 and 117.4 days, respectively (Das and Mukherjee, 2020). For carbaryl, the decrease with 5 % biochar addition was 34.6 to 27.7 (350 °C) and 33 days (700 °C) (Ren et al., 2016). For imidacloprid, the decrease with 2 % biochar addition was 86.7 to 73.0 (300 °C), 77.6 (500 °C), and 80.6 days (700 °C) (Zhang et al., 2020). Conversely, for clothianidin, these authors reported an increase in half-life with 2 % addition from 52.4 to 93.0 (300 °C), 72.0 (500 °C), and 62.8 days (700 °C). Thus, the degradation rate increased with biochar addition on soil, occurring via biotic and abiotic processes.

Most researchers investigate pesticide sorption individually, despite the complexity of actual contamination and the need for combinations of treatments. Tao et al. (2020) evaluated the combined application between biochar and co-cultured functional microorganisms. The results showed a 49 % higher potential to degrade 100 mg L^{-1} atrazine within 24 h than pure degrading bacteria DNS32 and increase the soil's total and available phosphorus content. Qin et al. (2019) assessed the maize straw biochar and sepiolite to remediate the combined pesticide and metal pollution. While biochar targeted atrazine, cadmium was mostly immobilized by sepiolite; thus, the authors concluded that combined application was efficient for immobilizing both contaminants.

5.3. Biochar from rice crop residues

Table 1 shows 15 articles that assessed 25 biochars produced from rice crop residues, most from rice straw (n = 13). Rice husk and rice hull were also used. Pyrolysis temperature varied from 300 to 700 °C, and just 3 of the 25 biochars passed for some treatment after pyrolysis. The most studied pesticides were imazapic (n = 4), imazapyr (n = 3) e fomesafen (n = 3). Although all biochars were made from rice crop residues, they have a variety of characteristics. For instance, pH varied in the range of 6.0 to 11.1, and SSA went from 1.99 to 202.11 m^2 g^{-1}. Ash content was between 9 and 50.3 %. All these variations are related to the fact that, besides feedstock, pyrolysis conditions are also determinants for biochar properties.

In general, for rice-derived biochar, higher pyrolysis temperatures resulted in materials with higher pH, ash content, SSA, and porosity, but with lower CEC (Lü et al., 2012; Manna and Singh, 2015; Ren et al., 2016; Yavari et al., 2016; Zhao et al., 2019). Apart from temperature, other pyrolysis conditions influence biochar characteristics, and consequently, its sorption capacity. Yavari et al. (2017) studied the influence of temperature (from 300 to 700 °C), heating rate (3 to 10 °C min^{-1}), and residence time (1 to 3 h) in rice husk biochar characteristics. The maximum organic carbon content was found in the biochar with the highest pyrolysis temperature and the slowest heating rate. CEC was negatively correlated with temperature and heating rate, while the SSA was positively correlated with temperature and residence time.

Overall, rice residues-derived biochar application in the soil can improve pesticide sorption capacity (Aldana et al., 2020; Khorram et al., 2015; Lü et al., 2012; Manna and Singh, 2015; Ren et al., 2016; Wu et al., 2019). This improvement happens even with small biochar doses, as the maximum amount used was 5 % (w/w) (Table 1). Khorram et al. (2015) investigated the sorption of fomesafen in soils amended with 0.5, 1, and 2 % rice hull biochar produced at 600 °C. Biochar-amended soils enhanced fomesafen sorption, as K_f increased from 0.69 to 14.44 $mg^{1–1/nf}$ $L^{1/nf}$ $kg^{–1}$ in the soil with 2 % biochar. Similarly, for carbaryl sorption, Ren et al. (2016) showed an increase of K_f from 15.5 to 125.9 mg kg^{-1} (mg $L^{-1})^{-n}$ after applying rice biochar (700 °C) at 5 %. In this case, the authors compared biochars produced at two different temperatures and showed that biochars made at higher temperatures had the most satisfactory results. Several studies have also examined the biochar effects in the leaching of pesticides, and it has been demonstrated that biochar helps retain the substances at the top layer. For example, Khorram et al. (2018) assessed the leaching of fomesafen in rice biochar-amended soil in columns, and the retention increased from 13.45 to 76 % with 2 % (w/w) biochar-amended soil; the pesticide was retained in the top 5 cm of the columns.

Manna and Singh (2015) also reported the temperature effects for pyrazosulfuron-ethyl, as biochars from higher temperatures achieved higher specific surface and porosity. In this research, the control soil (sandy loam) had 5.3 to 8.6 % of pesticide sorption, whereas biochar produced at 400 °C had 7.5 to 50.4 %, and 600 °C biochar sorption was 55.9 to 91.8 %. However, Yavari et al. (2017b) reported different effects for imazapic and imazapyr sorption by soils with 1 % of rice husk biochar at different pyrolysis conditions. In this case, sorption capacities for both herbicides were higher for the biochar produced at the lowest temperature (300 °C) and a slow heating rate (3 °C min^{-1}).

Few studies addressed biochars after treatments. Yavari et al. (2020) produced a rice husk biochar (pyrolysis at 300 °C, 3 h) and modified this material by mixing it with a chitosan solution diluted in acid acetic for 30 min, and by dripping NaOH solution into it. After 12 h, deionized water washed the modified biochar. The comparative analysis of biochar sorption performance before and after treatment is indicative of the changes resulting from the action of chitosan. The authors reported that chitosan-modified biochars had remarkably higher moisture content, pH, and CEC than non-modified biochars. Chitosan-modified biochar also showed a higher sorption capacity of imazapic and imazapyr. The value of K_f for imazapic varied from 1.744 in the pure soil to 3.090 in the biochar amended soil with 1 % biochar and to 4.391 for chitosan-modified biochar amended soil. However, it would also be relevant to test only chitosan to validate its effects in the modified biochar.

Finally, most researchers also investigated the pesticides' sorption individually. A recent study by Aldana et al. (2020) examined the sorption of atrazine, diuron, and OTC on mixtures of tropical soils and rice biochar at 1, 2.5, and 5%. Higher doses increased the sorption of all compounds, and atrazine was the only substance detected in the equilibrium solution, even in the mixture with 5 % biochar. According to these authors, diuron was sorbed first and competed with atrazine for the sorption sites. Besides, soil dissolved organic matter might cover sorption sites from biochar. Despite sorption, the degradation of the pesticides by biochar amended-soils has also been addressed, and it depends on the pesticide's type. Manna and Singh (2019) showed that applying 400 and 600 °C rice straw biochar in sandy loam soil at a biochar dose of 0.02 and 0.05 g kg^{-1} increased pyrazosulfuron-ethyl persistence under flooded and non-flooded conditions. An increasing amount of biochar decreased pyrazosulfuron-ethyl degradation. Conversely, for carbaryl, Ren et al. (2016) reported that biochars as soil amendments promoted chemical degradation and affected the pesticide's microbial degradation.

5.4. Biochar from wheat crop residues

Table 1 shows 13 different biochars produced from wheat crop residues. Most of them are derived from wheat straw, and only one from wheat midds. The pyrolysis temperature in these studies ranged from 250 to 600 °C. Among the materials (Table 1), only one was submitted to treatment before pyrolysis (Tatarková et al., 2013). The straw was carbonized in a sand bath at 200 °C for 24 h, and the residue was pyrolyzed at 300 °C. These papers studied a variety of 7 pesticides, and the most studied were pyrazosulfuron-ethyl and HCB.

As the previous feedstocks, various characteristics of wheat residue biochars changed in different pyrolysis conditions. For instance, the pH varied between 5.4 and 10.6, CEC was in the range of 22 and 68.7 $cmol_c$ kg^{-1}, and SSA ranged from 2.7 to 62.6 m^2 g^{-1}. In general, the studies showed that increasing pyrolysis temperatures increases pH, SSA, and porosity (Cheng et al., 2017; Manna and Singh, 2015). However, regarding the effect of pyrolysis temperature on CEC, there were contrasting results. For example, Cheng et al. (2017) studied wheat straw biochar produced at four peak temperatures (250, 350, 450, and 550 °C) and found that CEC decreased (from 68.7 to 22.0 $cmol_c$ kg^{-1}) with higher temperatures. Conversely, Manna and Singh (2015) showed that increasing pyrolysis temperature for wheat straw biochar did not significantly affect CEC (62.0 and 62.6 $cmol_c$ kg^{-1} for the 400 and 600 °C biochars, respectively).

Studies regarding wheat residue biochar provide evidence that the application of this material in soils can improve the sorption of pesticides (Cheng et al., 2017; Humera Aziz et al., 2018; Manna and Singh, 2015; Tatarková et al., 2013). Tatarková et al. (2013) used a wheat straw biochar produced at 300 °C (pH of 10.6 and SSA of was 4.59 m^2 g^{-1}). They demonstrated that 1 % biochar amended soil had 2.53 times higher MCPA sorption capacity than the non-amended soil. Furthermore, the quantity of MCPA leached in soil columns alone was 56 %, while 35 % leached in columns with 1 % wheat straw biochar. Humera Aziz et al. (2018) demonstrated that the application of wheat straw biochar prepared at 500°C (CEC of 85 $cmol_c$ kg^{-1}, total organic carbon of 43.80 % and SSA of 4.83 m^2 g^{-1}) at 0.25 and 0.5 % in sandy clay loam soil (pH of 7.44, CEC of 5.2 $cmol_c$ kg^{-1} and total organic carbon of 0.87 %) from Pakistan increased chlorpyrifos sorption. The data was adjusted by Freundlich isotherm, and K_f rose from 4.34 to 218.83 L kg^{-1} after the mixture with 0.5 % biochar. Manna and Singh (2015) reported a similar effect for pyrazosulfuron-ethyl sorption by adding 0.1, 0.2, and 0.5 % wheat straw biochar in sandy loam soil from India. Increasing the pyrolysis temperature from 400 to 600 °C did not significantly increase the organic carbon and CEC, but it doubled the SSA (10.15 and 20.38 m^2 g^{-1}, respectively) and improved the sorption capacity of the biochar. Manna and Singh (2019) also demonstrated that amendment with these same biochars influences pesticide leaching because of its strong sorption. They reported that the application of wheat straw biochar made at 400 and 600 °C at 5 % in the soil led to a decrease in the pyrazosulfuron-ethyl loss by 9 e 39 %, respectively.

In general, the Freundlich isotherm adjusted pesticide sorption data (Humera Aziz et al., 2018; Manna and Singh, 2015; Tatarková et al., 2013). Manna and Singh (2015) discussed the effect of biochar on the mean value (standard deviations were not provided) of the Freundlich exponent 1/n, as nonlinearity in pyrazosulfuron-ethyl sorption increased with higher biochar doses. The 1/n values were higher than 1 in the pure soil, suggesting nonlinear sorption isotherms (S-type). On the other hand, 1/n becomes less than 1 in soils amended with 0.2 and 0.5 % biochar, reflecting an L-type adsorption isotherm. It indicates that the adsorbate molecules did not suffer intense competition from the water molecule at low concentrations, but sorption sites become limited as the concentration increases. Unlike these results, Tatarková et al. (2013) showed that the Freundlich exponent values for MCPA sorption were close to 1 for non-amended soil, biochar-amended soil, and biochar, indicating constant MCPA partitioning between sorbent and solution for all the materials within the concentration range (0.5 to 22 mg L^{-1}). The use of classifications with numerical ranges should always be done with caution. Statistical analysis and presentation of standard deviations of results, especially close to class boundaries, may be of interest to reduce uncertainties and increase the reliability of data interpretations.

Although several studies involve biochar effects on pesticide sorption, questions have been raised about their impact on other processes, including degradation, volatilization, and plant uptake (Cheng et al., 2017; Manna and Singh, 2019; Wang et al., 2016). Recent evidence suggested that the adding wheat straw biochar improves the pesticide persistence in soil due to the strong affinity between pesticide and biochar particles. Some studies sustain this hypothesis, such as Cheng et al. (2017) for simazine and Manna and Singh (2019) for pyrazosulfuron-ethyl. Moreover, in the study of Tatarková et al. (2013), the half-life of MCPA increased from 5.2 days for the non-amended soil to 21.5 days for the amended soil. On the other hand, the dissipation would increase in biochar amended soils because of the microbial activity stimulation by biochar nutrients. Song et al. (2012) carried out incubation tests with HCB and reported that in the first 2 weeks, faster HCB dissipation occurred in the 0.1 and 0.5 % biochar-amended treatments compared to control. Nevertheless, a significant decrease in HCB dissipation was noted in the biochar-amended soils after 4 weeks.

6. Key aspects, gaps, and uncertainties

6.1. Pesticide bioavailability and ecotoxicity

Regarding the pesticide uptake by plants, Khorram et al. (2017) showed that rice biochar amendment could effectively suppress the undesirable inhibitory effect of fomesafen on corn growth. Song et al. (2012) tested the bioaccumulation of HCB in earthworms; their primary concern was that strong sorption of contaminants would result in accumulation by the mesofauna of ingestion of biochar particles. However, concentrations of HCB in earthworms decreased with increasing biochar application rate. After that, in another study, Song et al. (2016) investigated a biochar-plant tandem remediation scheme for HCB, adding 1 and 2 % of wheat biochar in soil and using ryegrass as the growing plant. Biochar amendment immobilized HCB in soils, and the uptake of HCB by ryegrass root was reduced by 93.05 % by 1 % biochar amendment compared to that of unamended soil. Unfortunately, no selected study presented ecotoxicological assessments of pesticide biochar sorption, despite two studies identified in the previous steps. For instance, Bielská et al. (2018) indicated reducing bioavailability and bioaccessibility of hydrophobic organic compounds by increasing 5 % the dose of biochar from mixed wood shavings and rice husks. However, this study identified biochar-induced toxicity by the highest amount (10 %) to the springtail *Folsomia candida*, which could be associated with pH-related effects or food sorption.

Although most studies focused on the remediation of isolated pesticides, these contaminants may have increased ecological risks in combination (Belden and Brain, 2018). Additionally, some pesticide transformation products can be more toxic than the parental compound (Sinclair and Boxall, 2003), a challenge for pesticide management and environmental remediation (Levine and Borgert, 2018). Nonetheless, in a co-contamination, hydrophobic organic compounds (including pyrene and DDE) in the mixture did not show competitive sorption to biochar (Bielská et al., 2018), which is an advantage considering multiple soil contaminants.

Biochar selection should allow pollution control while maintaining pesticide efficiency. For instance, Lü et al. (2012) incorporated 2,4-D and acetochlor into the studied rice straw biochar (i.e., pyrolyzed at 350 °C, with 31 % ash, 20.6 m^2 g^{-1} of SSA, and H/C ratio of 0.342) as a sorptive carrier for retaining these herbicides. Doses of 0.5 and 1 % of biochar in soil decreased the acetochlor release rate, indicating the capacity to regulate herbicides' behavior. Besides, Graber et al. (2011) suggested that higher SSA wood-derived biochar could negatively impact herbicide efficacy in terms of phytoavailability. Thus, depending on the biochar characteristics and strength of sorption capacity, pesticide concentrations in the aqueous solution decrease and are not enough to promote pest control. This should be considered when planning the application.

6.2. Microbiological processes associated with biochar sorption

Most of the retrieved studies did not discuss microbial activity and its interactions with pesticides and biochar. On the contrary, some studies sterilized soils before biochar application to avoid microbial interferences. Still, pesticides can affect the soil microbiota and inhibit biodegradation. For example, Zhang et al. (2018) indicated that thiacloprid shifted the soil microbiota, and the biodegradation depended on soil pH, dissolved organic matter, and nutrients (e.g., N and P). Nonetheless, biochar addition generally enhanced microbial activity and multiplication, leading to more significant pesticide degradation, as shown by Das and

Mukherjee (2020). These authors considered that maize stalk biochar was a readily available source of energy for the microbiota.

With a combined application approach of biochar in soil together with a degrading bacteria (i.e., *Acinetobacter lwoffii* DNS32), Tao et al. (2020) showed a 49 % greater capacity to degrade 100 mg L^{-1} of atrazine in 1 day compared to experiments using only adding the bacteria to the soil. In this scenario, microbial degradation could also increase pesticide dissipation, as observed by Wu et al. (2019) for oxyfluorfen and maize straw and rice hull biochars. Accordingly, Song et al. (2016) showed that wheat straw biochar stimulated microbial activity for dissipating hexachlorobenzene, mainly when associated with plant roots. Wu et al. (2019) also found that a rice hull biochar pyrolyzed at 500 °C (with 50.34 % ash, SSA of 95.67 m^2 g^{-1}, and pH of 6.96) could improve oxyfluorfen degradation. The sorbent provided a suitable environment for microorganisms and stimulated soil microbial activity. Wang et al. (2016) showed that wheat midds biochar (i.e., pyrolyzed at 550 °C, with pH of 8.86, SSA of 24.73 m^2 g^{-1}, and pH of 8.82) alters 1,3-D degradation rates primarily through abiotic processes. They indicated a 130 % increase in the half-life for pesticide dissipation in soil with 1 % biochar, while 60 % higher in sterilized soils than control.

Furthermore, the biochar effect in the biodegradation of pesticides may vary with pyrolysis temperatures. For example, Ren et al. (2016) studied carbaryl degradation in soils amended with rice and maize biochars under sterile and unsterile conditions. There was an increase in the biotic removal rate of carbaryl for soils amended with biochars produced at low temperatures (350 °C). However, the addition of biochar from high temperatures (700 °C) decreased biodegradation rates. The authors assumed that this difference is because of easily degradable compounds in the low-temperatures biochars. Also, these biochars did not affect the soil pH, which favors microbial communities. Zhang et al. (2020) observed similar behavior as a function of pyrolysis temperature for biodegradation of imidacloprid and clothianidin in soil amended with maize straw biochar.

6.3. The effects of the aging process on biochar sorption

Ren et al. (2018) identified changes in wheat straw biochar properties (1 % dose) and its atrazine sorption capacity by aging in field soil (0.5, 1, 1.3, and 2 years). They reported that the SSA of the fresh biochar amended soil increased from 10.7 to 59.1 $m^2 g^{-1}$ after 0.5 years and then decreased with aging time, reaching 8.33 $m^2 g^{-1}$ after 2 years in the soil. According to the authors, this behavior is related to the initial exposure of micropores due to the dissipation of labile fraction from the biochar surface just after the application of biochar (increasing SSA), and then the adhesion of soil organic matter and minerals to the surface of the biochar (decreasing SSA). Another study (Khorram et al., 2017) investigated the aging process on fomesafen sorption-desorption and indicated that the rice husk biochar was still effective after 6 months compared to the unamended soil. However, for 0.5 % of biochar, the total leaching rate of fomesafen increased from 67.5 % in freshly amended soil to 78.1 % in the soil aged 6 months. So, the aging process generally reduces the sorption capacity of rice biochars, suggesting a need for reapplication.

Similarly, the decrease of sorption because of the aging effect was also reported for oxyfluorfen (Wu et al., 2019). In this case, to simulate the aging process, they used an artificial method (H_2O_2 treatment). The soil's capacity to absorb oxyfluorfen increased linearly with added biochar, but the sorption capacity of biochar-amended soil decreased with aging. According to these authors, over time, changes might occur on physical or chemical properties in biochar surface or blocked sorption sites by acid, minerals, oxides, and native pollutants in soil. However, after 6 months of aging, the sorption capacity was still more significant than measured for the unamended soils. Thus, desorption could result from pH changes, reintroducing the pesticide to the soil (Liu et al., 2018), and the long-term biochar application and aging effects still need further research.

As feedstock, different crop residues result in biochars with various properties and, consequently, different pesticide sorption capacities. Some researchers in our final selection compared biochars made of varying crop residues at the same conditions. For example, Ren et al. (2016) studied rice straw and maize straw biochars pyrolyzed at 350 °C. The authors reported that a 5 % rice straw biochar-amended soil showed higher sorption of carbaryl than a 5 % maize straw biochar-amended soil. Some of the factors that contributed to these results were the higher SSA, ash content, and H/C ratio of the rice straw biochar (9.01 m^2 g^{-1}, 29.1 %, and 0.725, respectively) when compared with the properties of the maize straw biochar (6.71 m^2 g^{-1}, 15.4 % and 0.685 respectively). Wu et al. (2019) also reported a higher sorption capacity for oxyfluorfen by biochar derived from rice hull at 500 °C than maize straw biochar at 300 °C. Rice biochar also seems to be more effective than wheat biochar. Manna and Singh (2015) compared the effect of these two materials on pyrazosulfuron-ethyl sorption in sandy loam soil. Rice-derived biochar produced at 600 °C showed higher pH, O, C, and porosity than the wheat biochar made at the same conditions. As a result, rice biochar sorbed 55.9 to 91.8 % of the herbicide, while wheat biochar sorbed 6.9 to 86.0 %. Then, Manna and Singh (2019) reported that rice biochar also had a more considerable effect on herbicide degradation. Under non-flooded conditions, the application of 0.05 g kg^{-1} of rice biochar produced at 600 °C resulted in a 6-fold increase in the half-life of pyrazosulfuron-ethyl.

6.4. Potential pesticide desorption

In addition to sorption, studying pesticide desorption is also essential to understand the strength of the bond between pesticide and biochar components, the reversibility of the reaction, and pesticides' availability. However, only a few papers present discussed desorption results (10 out of 32), including the pesticides fomesafen, 2,4-D, pyrazosulfuron-ethyl, acetochlor, imazapic, imazapyr, flubendiamide, HCB, and MCPA. Only one study tested desorption with maize residues biochar (total of 12). In addition, the retrieved studies from this review lack the ecotoxicological analysis regarding the desorption process. In general, the Freundlich equation satisfactorily fitted the desorption isotherms. These authors compared materials using the percentage of desorbed pesticide, the desorption coefficient (K_f), and the hysteresis coefficient (H), indicating the reaction potential reversibility.

Most of the retrieved papers showed a decrease in desorption due to the addition of biochar in soils. For instance, Khorram et al. (2017) studied the sorption of fomesafen in mixtures of soil with rice straw biochar and showed that the desorption (K_f) varied from 0.42 $mg^{1-1/n}\ L^{1/n}\ kg^{-1}$ in the unamended soil to 21.24 $mg^{1-1/n}\ L^{1/n}\ kg^{-1}$ for the mixture with 2 % biochar. In addition, the value of H also decreased (from 0.76 in the unamended soil to 0.50 with 2 % biochar), indicating less desorption. Similar results were found by Manna e Singh (2015) for pyrazosulfuron-ethyl, Khorram et al. (2018) for fomesafen, Yavari et al. (2016; 2019) for imazapic e imazapyr (all of them using rice straw biochar), Das and Mukherjee (2020) for flubendiamide (with maize stalk biochar), and Song et al. (2016) for HCB (using wheat straw biochar). Therefore, they suggest that the bond between pesticides and biochar particles is more robust than between pesticides and unamended soil particles.

On the contrary, some researchers pointed out that the increase of sorption capacity from the same dose is not always proportional to the decrease in desorption. For instance, Tatarkova et al. (2013) concluded that the bonds between wheat straw biochar and MCPA might be weak.

Despite decreased desorbed MCPA (from 64.2 % for the unamended soil to 55.1 % with 1 % biochar), these differences are less significant than the sorption results. Khorram et al. (2015) presented similar results for fomesafen in rice biochar as the increase of desorption K_f with increasing biochar dose; the value of H was between 0.41 to 0.71 in the unamended soils and between 0.95 to 0.99 in soils with 2 % biochar.

Furthermore, there is no consensus regarding the effect of different pyrolysis temperatures on desorption for various pesticides. For example, Yavari et al. (2016) studied soil with 1 % rice biochar and found more desorption of imazapic and imazapyr for mixtures using biochar produced at higher temperatures. On the contrary, Lu et al. (2012) studied the desorption of acetochlor and 2,4-D in pure rice biochar and pointed out that there was more reversibility for biochars produced at lower temperatures.

7. Biochar transport, storage, and applicability

Most studies on pesticide-contaminated soils consist of lab-scale batch experiments, and there is a gap on full-scale or *in situ* technologies (Morillo and Villaverde, 2017). For instance, only two papers reported results on pilot-scale experiments and biochar field application in the final paper selection. Among several challenges related to the utilization of biochar, easing handling and storage steps are critical for actual biochar implementation in the agriculture business. Therefore, this section describes some options for appropriate: i) transport of biochar produced in pyrolysis plants to the farm; ii) storage of biochar in the farm; and iii) dispersion of biochar in the soil.

Significant aspects impacting the transport of biochar from pyrolysis plants to farms are the distance between these two businesses, the size of the agricultural company, and its demand for biochar. In general, farms’ demand for biochar could be fulfilled by packing powders in big bags and distributing them to regional cooperative or logistic centers via road transport. However, it might be feasible for farms with attached pyrolysis units to implement connected transport and biochar storage systems. This initiative decreases human intervention in the process, hence increasing overall farms' yield.

From the reactor unit, pneumatic conveying lines could transfer biochar to storage vessels or silos, which means that the bulk material is transported through a pipeline with an airstream. Biochar is fluidized with low gas flow rates due to its low particle density and particle size; hence, pneumatic transport is an appealing economic way to handle such material. Some authors measured the basic flow energy and permeability of biochar originated from lignin residues (Toloue Farrokh et al., 2018) and birch tree chips (Toloue Farrokh et al., 2020), and concluded that these powders (mean diameter from 52 to 73 µm, and bulk density from 574 to 737 kg m^{-3}) might flow easily and with lower tendency to cause blockage of pipes during pneumatic conveying operations.

Other relevant advantages of pneumatic conveying systems are that it requires very little maintenance, and powders can be either conveyed in dilute or dense mode to prevent the breakage of particles; the system's design is flexible as pipelines can be adjusted to the farm layout; it is a dust-free system since the flow of biochar occurs inside of tubes; and the solids flow rate can be monitored from simple pressure measurements as well as controlled with non-mechanical valves, which are inexpensive and are resistant to wear and seizure (Geldart and Jones, 1991; Massaro Sousa et al., 2020; Smolders and Baeyens, 1995).

Although there is limited information on the actual conveying of biochar, pneumatic transport is a consolidated research field. For example, the efficient design of transport pipelines might be performed using flow diagrams based on dimensionless numbers (e.g., Reynolds and Archimedes) that account for different powder and air properties and pipeline dimensions

(Kalman, 2020; Kalman and Rawat, 2020). Moreover, practical experience and research literature on the conveying of pulverized coal are vast, which is helpful information to handle biochar given the similarities between these two powders in terms of bulk density and particle-size distribution. Papers reporting experimental tests in various scale units and numerical simulations with different approaches are addressed in detail elsewhere (Chinnayya et al., 2009; Cong et al., 2011; Jin et al., 2019; Lu et al., 2011; Zhou et al., 2020, 2018).

Silos are appealing equipment to meet process storage demand that also provides complete isolation from the external environment, minimizing biochar loss due to humidity degradation, pests' contamination, or dust. Jenike's method is often used to design cylindrical or wedge-shaped silo hoppers aiming at appropriate mass- or funnel-flow discharge of bulk solids with different properties (Enstad, 1975; Massaro Sousa et al., 2021; Oginni and Fasina, 2018). However, to the best of our knowledge, the flow properties of biochar required for the design of silos have not been fully assessed in the literature, which is of great interest for future studies.

Despite this, successful design and operation of silo hoppers with pulverized coals are reported for both gravity-driven and air-assisted discharge of powders (Guo et al., 2015; Lu et al., 2015, 2012). Depending on samples' particle-size distribution and moisture content, minimum hopper inclination for mass-flow discharge ranges from 11 to 22°, whereas the outlet diameter must be higher than 0.3 m (Chen et al., 2012; Y. Liu et al., 2015). Biochar generally presents better flowability classification than pulverized coal under consolidated conditions (Toloue Farrokh et al., 2020, 2018), thus using steeper silos with cone angles of 10° and outlet diameter higher than 0.3 m might be sufficient to handle most biochar powders. However, measuring bulk and flow properties is highly encouraged to optimize the silo design and prevent flow issues, significantly whether the silo wall material or the biochar particle size and moisture content deviate from the ones shown in the previous studies.

In principle, biochar can be dispersed in soil with equivalent techniques for spreading fertilizers and pH correctors. However, these methods should be optimized considering farm particularities, business size, terrain conditions (e.g., slopes and soil wettability), local climate, and duration of rainy seasons, among other aspects. Dust emissions can be reduced, for example, with wet soil applications (Li et al., 2018). Moreover, using pelletized biochar might be an alternative to prevent excessive biochar loss by wind action or water leaching. While some papers reported the successful biochars densification for solid fuel applications (Bazargan et al., 2014; Hu et al., 2016; Ranzi et al., 2018), future studies should consider pellet properties for field applicability. Some relevant factors include pellet resistance when in contact with different environmental conditions, total contact area for pesticide sorption, and optimal pellet size to perform an economic and homogeneous distribution of biochar in soil.

In general, adding biochar to the soil can result in several benefits, including improvements in carbon sequestration, greenhouse gas mitigation, soil fertility, plant growth, and crop yields (Ding et al., 2016; Hussain et al., 2017), solid advantages for agricultural areas. Besides, plant growth stimulation could improve ecological restoration and ecosystem services (Rey Benayas et al., 2009). The productivity increases due to more significant water holding capacity and lower infiltration, which could also be an alternative for degraded or arid soils (Diatta et al., 2020). The feedstock for biochar production is varied, including crop residues, wood biomass, leaves, animal manure, solid waste, sewage, and industrial sludge (Ahmad et al., 2014; Lehmann and Joseph, 2015). The alternative for applying crop residues to biochar production could concatenate agricultural waste management and environmental remediation techniques. Finally, note that the best selection of units and methods for handling biochars is intrinsically related to the regional technology development, farm business size, and field particularities; hence, performing techno-economic assessment under different farm contexts is encouraged to clarify this point.

8. Final considerations

The increase in crop production had led to a demand for residue management, which could be coupled with biochar production. Biochar has a potential for pesticide sorption in agricultural soils in this scenario, and studies have increased in the last few years. Particularly maize, rice, and wheat residues are appropriate feedstocks for biochar production and contaminated soil amendment. In this review, we highlighted some advantages of these applications, such as:

- Biochar amendments improved soil quality, restored soil properties, and contributed to carbon sequestration.
- Biochar amendments have the potential sorption of pesticides, reducing their soil mobility and bioavailability.
- Moreover, studies have shown several benefits from biochar application, including the potential to ameliorate soil quality and properties (e.g., organic matter). Thus, biochar could promote soil restoration and ecosystem services maintenance.
- Agricultural cooperatives can manage biochar production and logistics, and this could benefit mini-farms as a low-cost amendment.
- Multiple feedstocks for biochar production could be used in rotation systems, as residue management in the long-term could improve carbon sequestration in agriculture.

On the other hand, these applications still need further research and development, mainly due to some limitations and gaps, including:

- Most research focused on batch experiments in lab-scale, highlighting a need for field application research and study of other contaminants. Also, there is a need to study the long-term effects of biochar application and its potential desorption.
- Retrieved studies were mainly for a few pesticides (only 21 different active substances). Therefore, biochar sorption should be evaluated for different pesticides and co-

contaminations since they behave differently depending on their chemical characteristics.

- Studies should consider the entire biochar life cycle. Monitoring all steps is essential to ensure the biochar production meets the proposed goals for its application. Also, this approach can avoid the risks of biochar containing contaminants (e.g., PAHs).
- Future studies should evaluate the influence of biochar particle size on remediation dynamics, especially *in situ*. Micro- and nano-particles can show more significant horizontal movement (runoff) and vertical movement. Thus, once they have absorbed pesticides, they can be transported to greater distances.
- There is still limited knowledge about the aging process of biochar. A more systematic understanding of the complexity of physical and chemical changes is needed, and also the influence of different soil types and climate changes (e.g., wet/dry and freezing/melting cycles).
- Biochar can reduce pesticide bioavailability and, consequently, its biodegradation. Nonetheless, the microbiological processes still need investigation.
- Ecological risk assessment is still a gap regarding research on biochar applications. Thus, bioassays are encouraged since several bioindicators are sensitive to pesticides, besides the potential to assess desorption.
- Characterizing biochar bulk and flow properties is fundamental for designing solids feeders, transport, and storage equipment. In addition, pelletized biochar’s flow, mechanical, and structural properties should be assessed to achieve cost-effective dispersion of this material in farm soils.
- No studies showed an economic analysis of biochar applications. Therefore, performing process techno-economic analysis under different farm contexts is encouraged.

- Restoration methods must be feasible, technically achievable, and socially acceptable. In addition, governments should provide financial incentives for environmental remediation in rural areas.

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No potential conflict of interest was reported by the authors.

Author Contributions

Conceptualization: A.P.O., J.Z.L., J.P.M., L.M.S.; Methodology: A.P.O., J.Z.L., J.P.M.; Formal analysis: A.P.O., J.Z.L., J.P.M., L.M.S.; Investigation: A.P.O., J.Z.L., J.P.M., L.M.S.; Data curation: A.P.O., J.Z.L., J.P.M.; Writing - Original Draft: A.P.O., J.Z.L., J.P.M., L.M.S.; Writing – Review & Editing: V.G.S.R., E.L.G.E.; Visualization: A.P.O., J.Z.L., J.P.M., L.M.S.; Supervision: A.P.O.; Project administration: A.P.O.; Funding Acquisition: V.G.S.R., E.L.G.E.

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