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A Review of Pesticides Sorption in Biochar from Maize, Rice, and Wheat Residues: current status and challenges for soil application

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1 **A review of pesticides sorption in biochar from maize, rice, and wheat residues:**

2 **current status and challenges for soil application**

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23 ABSTRACT

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3 24 The use of pesticides has been increasing in recent years for maintaining traditional agricultural
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5 25 practices. However, these chemicals are associated with several environmental impacts,
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8 26 demanding urgent remediation techniques. Biochar is a carbonaceous material produced by
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10 27 pyrolysis that has the potential for pesticide sorption and remediation. In this context, this
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13 28 interdisciplinary review systematically assessed the state of the knowledge of crop residues to
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15 29 produce biochar for pesticide sorption. We focused on maize, rice, and wheat residues since
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18 30 these are the three most-produced grains worldwide. Besides, we evaluated different biochar
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20 31 handling, storage, and soil dispersion techniques to ease its implementation in agriculture. In
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22 32 general, pyrolysis temperature influences biochar characteristics and its potential for pesticide
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25 33 sorption. Furthermore, biochar amended soils had greater pesticide sorption capacity, limiting
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27 34 potential leaching and runoff. Most studies showed that the feedstock and specific surface area
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30 35 influence the biochar sorption properties, among other factors. Also, biochar reduces
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32 36 pesticides' bioavailability, decreasing their toxicity to soil organisms and improving soil
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35 37 fertility and crop yields. Nonetheless, the retrieved papers assessed only 21 pesticides, mainly
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37 38 consisting of lab-scale batch experiments. Therefore, there is still a gap in studies evaluating
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40 39 biochar aging, its potential desorption, pesticide co-contaminations, the associated
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42 40 microbiological processes, and field applications. Determining flow properties for biochars of
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44 41 different sizes and pellets is vital for reliable handling equipment design, and performing
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46 42 techno-economic assessment under different farm contexts is encouraged. Ultimately, coupling
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49 43 biochar production with residue management could address this challenge on sustainable
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52 44 agricultural systems.

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55 45 **KEYWORDS:** Biochar amendment, Biochar handling, Crop residues, Contamination, Soil
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57 46 remediation, Waste management.
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47 1. Introduction

48 Synthetic chemicals used in conventional agriculture have increased production by controlling
49 pests, weeds, and diseases. Pesticides target living species, as they are biologically active
50 substances with a structure capable of imitating specific molecules (Das, 2013; Rani et al.,
51 2021). Over the past decade, pesticide use surpassed 4 million tons per year worldwide (FAO,
52 2020). However, pesticides' extensive use has drastically affected the soil, water, and air
53 quality, causing undesirable impacts (e.g., toxicity, carcinogenicity, and mutagenicity) on non-
54 target organisms, including humans (Khalid et al., 2020; Rani et al., 2021; Varjani et al., 2019).
55 In agricultural systems, pesticide contamination can negatively affect soil quality and crop
56 production, jeopardizing ecosystem services, nutrient cycling, enzyme activity, soil biota, and
57 biodiversity (Liu et al., 2018; Yu et al., 2019). Pesticides can also reach the surface and
58 groundwater through diffuse pollution (e.g., run-off and leaching) (Damalas and
59 Eleftherohorinos, 2011; Khalid et al., 2020).

60 In this scenario, research trends focused on different approaches to mitigate pesticide risks in
61 soil and water, including chemical remediation, containment or immobilization, and
62 bioremediation (Ganie et al., 2021; Morillo and Villaverde, 2017; Rani et al., 2021; Saleh et
63 al., 2020). However, biochar stands out as a cost-effective and environment-friendly alternative
64 for remediation due to its sorption potential (Kwon et al., 2020; Lehmann and Joseph, 2015;
65 Liu et al., 2018; Varjani et al., 2019). This carbon-enriched product results from the thermal
66 decomposition of biomass or organic material, including crop residues (Ali et al., 2019; N. Liu
67 et al., 2015), animal manure (N. Liu et al., 2015; Ren et al., 2018), woody materials (You et
68 al., 2020; Zhu et al., 2020), and biosolids (Ali et al., 2019; Regkouzas and Diamadopoulos,
69 2019). The pyrolysis process generally occurs at high temperatures (between 350 and 1200 °C)
70 and in an oxygen-limited environment (Lehmann and Joseph, 2015). Biochar application

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71 contributes to the immobilization of organic and inorganic pollutants due to its large pore
72 structure (micro and mesoporous), rich surface functional groups (e.g., carbonyl, hydroxyl,
73 phenolic hydroxyl, and carboxyl), large specific surface area (SSA), high pH, and high cation
74 exchange capacity (CEC) (Beesley et al., 2011; Liu et al., 2018; Waqas et al., 2020; Yu et al.,
75 2019). Several studies have demonstrated the potential sorption of various pesticides (e.g.,
76 atrazine, fipronil, diuron, 1,3-D, and 2,4-D) onto biochar solutions (Y. Liu et al., 2015;
77 Regkouzas and Diamadopoulou, 2019; Zhu et al., 2020), and soils amended with biochar (Ren
78 et al., 2018; Wu et al., 2019; Yavari et al., 2020; You et al., 2020).

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

86 Millions of tons of agricultural waste are produced globally every year from various crop
87 cultivation and processing (Duque-Acevedo et al., 2020). Thus, crop residues are potential low-
88 cost feedstocks for biochar production and an alternative for agricultural waste management.
89 This approach has sustainable and economic benefits by converting wastes into value-added
90 products. Cereals are the most important staple foods for humans and animals worldwide
91 (FAO, 2015), with maize, rice, and wheat figuring among the leading global productions (FAO,
92 2019); hence, biochar production from these crop residues is of great interest.

93 With increasing publications on biochar, some review articles summarized the aspects of
94 biochar production and applications (Khalid et al., 2020; Kwon et al., 2020; Li et al., 2019; Liu

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95 et al., 2018; Palansooriya et al., 2019; Varjani et al., 2019; Waqas et al., 2020; Wei et al., 2018;
96 Yaashikaa et al., 2019). However, these reviews focused mainly on biochar's physicochemical
97 properties, its influence on soil fertility, removing metals on laboratory experiments or using
98 biochar in aqueous solutions with pesticides. Despite this, few papers highlighted recent trends
99 and implications of using biochar from crop residues on pesticide-contaminated soils (Khalid,
100 2019; Varjani et al., 2019). Therefore, given the potential of crop residues-based biochar for
101 amendment of pesticides-contaminated agricultural soils, it would be of great interest to have:
102 i) an up-to-date systematic review on biochar amendment in soils, showing current state-of-
103 knowledge and future challenges and perspectives for its advancement; ii) a discussion and
104 comparison regarding biochar studies from different crop residues as feedstocks, focusing on
105 the most produced ones (i.e., maize, rice, and wheat); iii) an interdisciplinary review that
106 highlights and proposes solutions for typical biochar field application challenges, such as
107 equipment for proper transport, storage, and handling, besides methods for dispersion in farm
108 soils.

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

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119 2. Systematic review

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3 120 The systematic review (Figure 1) performed in this study followed PRISMA guidelines (Moher
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6 121 et al., 2009), and used the databases from Web of Science, ScienceDirect, SpringerLink, Taylor
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8 122 & Francis, and Scopus. The research gathered papers published between January 1st, 2009, and
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10 123 January 17th, 2021. The adopted string was “biochar AND (adsorption OR sorption) AND
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12 124 (water OR soil) AND (pesticide OR herbicide OR insecticide OR fungicide)”, considering only
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15 125 documents in English.

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18 126 From the selected databases, we identified a total of 2746 papers and 2385 after removing
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21 127 duplicates. The first step consisted of retrieving the following information on these papers: title,
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23 128 first author, publication year, database(s), author(s) country(ies), keywords, environmental
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26 129 matrix, biochar feedstock, and pesticide. The results were then screened on Microsoft Excel[®].
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28 130 There has been an increasing number of papers published recently, as shown in Figure 1. Most
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31 131 articles per year were observed in 2020 (n = 749), and 68 documents from 2021 were available
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33 132 by January 17th.

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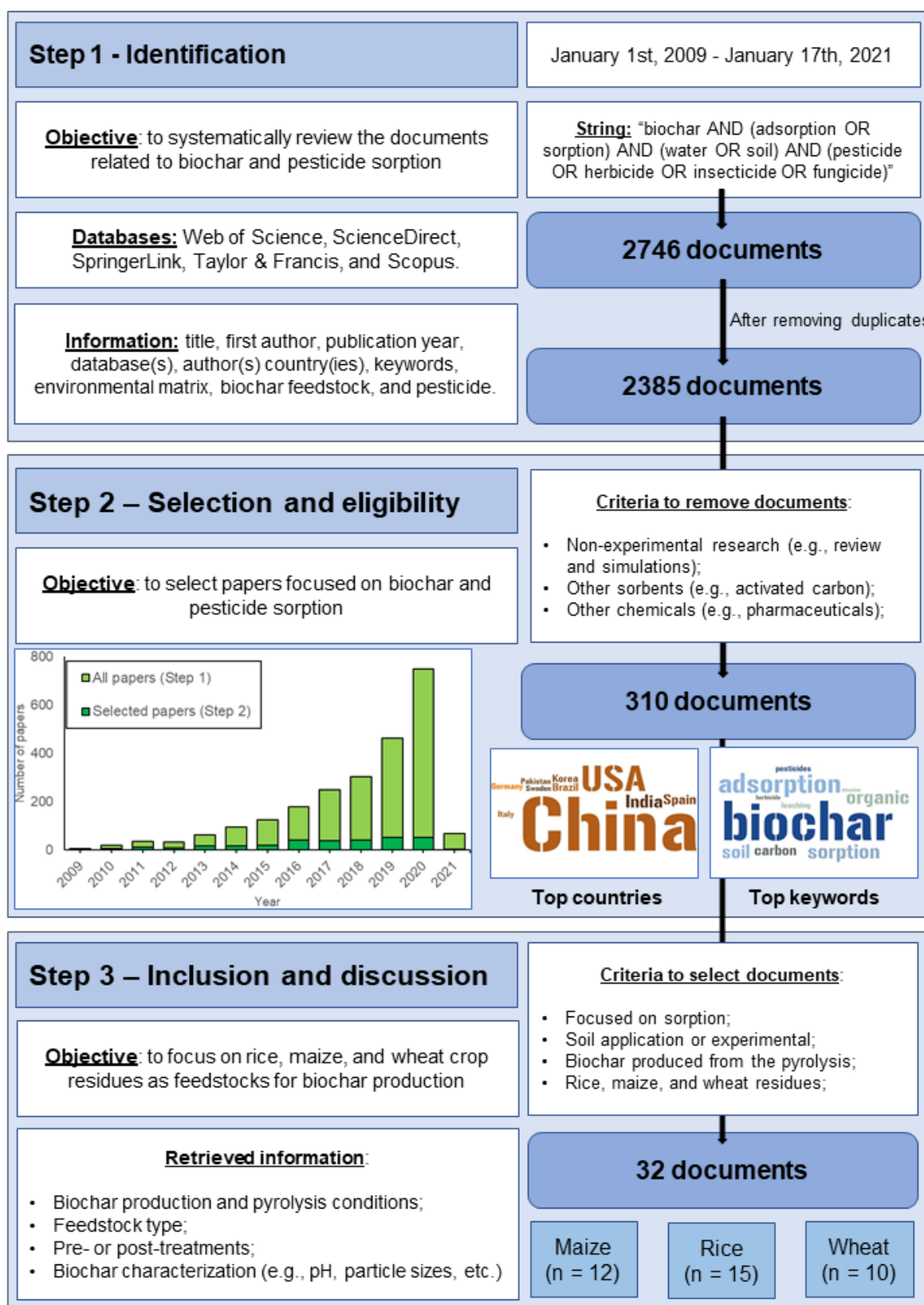
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141 Figure 1 - Systematic review summary: search process and selection of the studies focused on maize, rice, and
 142 wheat residues biochar for pesticide sorption.



144 The second step consisted of narrowing papers relevant to this study aim, which means biochar
1 associated with pesticide sorption. Thus, non-experimental papers (e.g., review and
2 145 simulations) were excluded, as well as research focusing on other sorbents (e.g., activated
3 146 carbon and ash) and chemicals besides pesticides (e.g., pharmaceuticals and polychlorinated
4 147 biphenyls). After, 310 papers were selected, which represents approximately 13% from the first
5 148 step. A word map was created from the bibliometric extension on the Microsoft Word® to
6 149 observe the most publishing countries and used keywords (Figure 2). China is the country that
7 150 published the most (n = 145), followed by the USA (n = 65), and India (n = 29). Furthermore,
8 151 the main used keywords were biochar (n = 207), sorption (n = 102), and soil (n = 82).
9 152

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

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168 Table 1 - Systematic review summary: studies from the final selection on pesticide sorption into crop residue
 169 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	mids	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)

170 Notes: n.a. = not available

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

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185 **3. Crop residues as feedstock for biochar production**

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

194 The largest cereal crops worldwide are maize, wheat, and rice (FAO, 2020) (Figure SM1).

195 Maize (*Zea mays* L.) is an annual plant production, and the USA, China, and Brazil are the

196 biggest world producers; China and India are the major rice (*Oryza sativa* L.) producers; and
197 wheat (*Triticum* spp.) cultivation is more prominent in China, India, and Russia (FAO, 2019).
198 As of 2001, cereals corresponded to 74 % of the world's annual residue production, considering
199 the estimated maize, rice, and wheat residue production of 609, 890, and 875 million Mg,
200 respectively (Lal, 2005). This proportion indicates that maize, rice, and wheat produced 1148,
201 1133, and 1148 million Mg residues in 2019, respectively (FAO, 2020). In terms of nitrogen,
202 these three crops correspond to 75 % of the world's current residue production, considering
203 9.36, 9.24, and 9.43 million Mg for maize, rice, and wheat, respectively (FAO, 2019). Maize
204 residues (e.g., stalks) are commonly used for cattle livestock and tillage due to their high
205 nutrient content (Villamil et al., 2015). On the other hand, rice straw has a high silica content,
206 and it is not recommended for feeding animals (Agbagla-Dohnani et al., 2003). Rice hulls and
207 straws can increase crop yields when incorporated into the soil (Sistani et al., 1998). Moreover,
208 corn stover is a potential feedstock for bioethanol production (Kadam and McMillan, 2003),
209 while corn cobs are not feasible for energy production (Erickson et al., 2011). Wheat straw and
210 midds can be included in cattle feed and energy sources (Nguyen et al., 2013; ZoBell et al.,
211 2005).

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213 **4. Studied pesticides uses and environmental concern**

214 Pesticides are widely applied to agricultural production, among other chemicals (i.e., fertilizers
215 and pharmaceuticals) (L. Zhang et al., 2018). For instance, the commercial product consists of
216 a combination of the active ingredient and other substances. Although the manufacturers'
217 recommended dose varies according to each target species and crop, overdoses are mostly the
218 cause of severe environmental effects (Meena et al., 2020). Asia and the Americas have a total
219 pesticide use per area of cropland (3.67 and 3.52 kg ha⁻¹, respectively) higher than the world's

220 average (2.63 kg ha⁻¹) (FAO, 2020). Moreover, China, the USA, and Brazil are the leading
221 pesticide consumers worldwide (FAO, 2020).

222 Understanding the pesticides' fate in the environment is essential. After application, these
223 contaminants may leach and runoff and then reach aquatic habitats (Wang et al., 2019). These
224 processes depend on the local climate conditions (Lammoglia et al., 2018), soil type (Vryzas,
225 2018), and landscape features (Rouzies et al., 2019). Additionally, spray drift and accidental
226 spills may increase their soil and water concentrations (Jemec et al., 2007). The soil type is
227 crucial for pesticide's environmental behavior, and higher Koc (organic carbon-water partition
228 coefficient) values indicate that pesticides are expected to have low mobility. In addition, the
229 soil granulometry, pH, CEC, and carbon content can contribute to pesticide mobility
230 (Lunagariya et al., 2020). Nonetheless, organic matter and clay particles increase some
231 pesticides' sorption in soil (Sadegh-Zadeh et al., 2017; Spark and Swift, 2002). Although soil
232 microbiota influences pesticide fate, biodegradation is not relevant when contaminants are not
233 bioavailable (Scow and Johnson, 1996). Our research identified 21 pesticides in the final
234 selection (Table 2), and information was presented concerning their density, solubility, log Kow
235 (n-octanol-water partition coefficient), Koc, and half-life (Kim et al., 2021; USEPA, 2021).

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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
Insecticide	simazine	1.30	6.2	2.18	78-3,559	27-102
	topramezone	1.13	510	1.44	140	>125
	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
Nematicide	imidacloprid	1.54	610	0.57	156-800	34-190
	thiacloprid	1.46	185	1.26	1,100	0.6-3.8
	1,3-D	1.22	2,000-2,180	2.03	20-42	2-54

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

256 Nonetheless, the sorption of other herbicides was studied for maize, rice, and wheat residues-
257 based biochar. The herbicide 2,4-dichlorophenoxyacetic acid (2,4-D) is a synthetic auxin that
258 targets broadleaf species, and it has high soil mobility (Koc from 20 to 136) and low persistence
259 (1.6 to 32.3 days) (Gan et al., 2003). Acetochlor has high to moderate mobility in soil (Koc of
260 98.5 to 335), while diuron sorption is strongly influenced by organic matter presence (Kim et
261 al., 2021; Spurlock and Biggar, 1994). Fomesafen mobility depends on the soil type, with a
262 wide range of Koc values (from 34 to 1200) (Kim et al., 2021). Imazapic and imazapyr are very
263 mobile imidazolinone herbicides (Koc of 3 and 8.81, respectively), as the herbicide 2-methyl-
264 4-chlorophenoxyacetic acid (MCPA) has high mobility (Koc from 50 to 62) and half-life from
265 7 to 41 days (Kim et al., 2021). Pyrazosulfuron-ethyl has half-life values from 16 to 27 days in
266 soils, and it is moderately sorbed in soils (Manna and Singh, 2015). Simazine has high to slight
267 mobility (Koc from 78 to 3,559) with higher sorption under low pH, and topramezone has high
268 mobility (Koc of 140) and low biodegradation potential (Kim et al., 2021).

269 Insecticides corresponded to 6 out of 21 pesticides from the selected studies. Carbaryl is a
270 carbamate insecticide weakly sorbed and readily biodegradable in soil (half-life of 10 days)
271 (Ahmad et al., 2004). Chlorpyrifos has low to no mobility in various soils (Koc of 995 to
272 31,000), characterizing a strong sorption potential (Racke, 1993). Clothianidin has high soil
273 mobility (Koc of 60) and persistence (half-life 148 to 1,155 days), a challenge for sorption
274 techniques (Kim et al., 2021). Flubendiamide has slight to low soil mobility (Koc of 1,076 to
275 3,318), and the half-life ranges from 210 to 770 days (Kim et al., 2021). For imidacloprid soil
276 sorption, organic matter is more relevant than clay content and CEC (Liu et al., 2006).
277 Thiacloprid has low mobility in soil (Koc of 1,100), and it is readily biodegradable (half-life of
278 0.6 to 3.8 days) (Kim et al. 2020).

279 Two fungicides were found in the selected studies, hexachlorobenzene (HCB) and
280 oxytetracycline (OTC). HCB is expected to be immobile on soils (Koc 3.6 to 5.5), it is
281 considered a persistent organic pollutant (half-life from 970 to 2,100 days), and sorption might
282 reduce its volatilization (Barber et al., 2005). OTC is an antimicrobial drug, also applied for
283 fungi control, and its sorption depends mostly on soil texture, CEC, and iron oxide content
284 (Jones et al., 2005). Although we did not include “nematicide” in our keywords, one study was
285 found with 1,3-Dichloropropene (1,3-D). This pesticide is commonly applied with chloropicrin
286 as an alternative to methyl bromide to control soilborne diseases and nematodes (Santos et al.,
287 2006).

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

294 However, most environmental agencies do not determine the maximum dose through all
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3 295 significant exposures, and some limits are still inefficient for health protection (Li and A.
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5 296 Jennings, 2017). Also, pesticides might cause harmful effects to the biota even within limits
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7 297 established by legislation and environmental agencies (Brovini et al., 2021).
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10 298 Overall, pesticide pollution endangers the environment, considering adverse effects on water
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12 299 quality, biodiversity, and human health, as highlighted by Tang et al. (2021). These authors
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14 300 identified high-risk areas worldwide, and 34 % of them were in high-biodiversity regions, 5 %
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16 301 in areas with water scarcity, and 19 % located in low and lower-middle-income nations. Also,
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18 302 China was considered the top country susceptible to high pesticide pollution risk, emphasizing
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20 303 the Huang He watershed. Since China is the leading country on studies of biochar application
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22 304 for pesticide sorption, researchers and the government should perform these alternatives in
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24 305 priority areas. Also, pesticides can cause effects on several non-target species (de Figueirêdo et
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26 306 al., 2020; Sanches et al., 2017; Triques et al., 2021), and the ecotoxicological assessment of the
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28 307 pesticides' impacts on representative species is a pathway to understanding their biota damages.
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30 308 Moreover, the ecological risk of their presence in soil and water endangers the proper ecosystem
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32 309 functioning and services (Schäfer et al., 2012; Schiesari and Grillitsch, 2011).
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42 43 311 **5. Biochar for pesticide-contaminated soils remediation**

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46 312 Remediation techniques are applied to remove, reduce, degrade, or retain contaminants,
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48 313 considering the ecological risks of pesticides in soils. The most appropriate method relies on
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50 314 the environmental characterization of the area, financial resources, predicted execution time,
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52 315 sustainability considerations, and remediation goals according to the future land use (Fernández
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54 316 Rodríguez et al., 2014; Hou and Al-Tabbaa, 2014). Pesticide sorption processes stand out
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56 317 among containment or immobilization technologies by limiting the contaminant potential
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1 318 infiltration and leaching by applying carbonaceous materials as sorbents (Morillo and
2 319 Villaverde, 2017).
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5 320 Although biochar and activated carbon are carbon-rich solids with a similar porous structure,
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7 321 the former has lower production and energy costs (Dai et al., 2019; Lehmann and Joseph, 2015).
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10 322 Thus, biochar has been evaluated as an alternative to the commercial activated carbon for
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12 323 contaminants sorption (Dai et al., 2019; Yaashikaa et al., 2019). The production of both sorbents
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15 324 is through pyrolysis, but activated carbon can also be produced by chemical or steam activation
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17 325 (Kazemi Shariat Panahi et al., 2020). Regarding the source material, activated carbon can come
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20 326 from biomass or any carbonaceous substance (e.g., coal), although biochar is made exclusively
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22 327 from biomass. Biochar as soil amendment aims to favor the contaminated or degraded soil's
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25 328 physical, chemical, and biological properties (Kazemi Shariat Panahi et al., 2020). Biochar's
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27 329 sorption capacity is not always as high as activated carbon (Liu et al., 2018), so the use of
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30 330 engineered biochars resulting from activation and modification processes may be relevant in
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32 331 some cases.
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39 333 *5.1. Primary factors for pesticide sorption on biochar* 40 41

42 334 The critical factors determining the biochar sorption efficiency are the feedstock, pyrolysis
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44 335 temperature, solution pH, dosage of biochar, competition with co-existed ions and other
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47 336 contaminants, the aging process, and modification/activation (Abbas et al., 2018). Higher
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49 337 pyrolysis temperature increases the biochar's SSA and micropores, improving the organic
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52 338 contaminants sorption (Abbas et al., 2018); this variation is related to how volatile compounds
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54 339 are released during carbonization (Yu et al., 2019). The pyrolysis temperature also significantly
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57 340 affects the functional chemistry of biochars, as plant-based feedstocks (e.g., crop residues)
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59 341 undergo dehydration and depolymerization of lignin and cellulose in high temperatures.
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342 On the other hand, poultry manure and sewage sludge biochar do not contain lignocellulosic
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2 343 compounds and do not suffer depolymerization (Ahmad et al., 2014). Pyrolysis residence time
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5 344 also increases SSA (Yu et al., 2019) and the ratio of O/C and H/C (Khalid et al., 2020). For
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7 345 maize straw biochar, Zhang et al. (2011) indicate that increasing the pyrolysis temperature (100
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9 346 to 600 °C) improves the C content (47.46 to 84.29 %), reducing the H and O contents (6.23 to
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11 347 2.60 %, 45.95 to 11.95 %, respectively). Thereby, O/C and H/C ratios in biochars decrease with
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13 348 high pyrolysis temperature, indicating the dehydration and deoxygenation of feedstock (Ahmad
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15 349 et al., 2014). Aromatic structures are usually on lower H/C ratios, indicating biochar stability
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17 350 and resistance to degradation (Varjani et al., 2019). It is worth noting that the functional group
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19 351 abundance on the biochar surface reduces as the pyrolysis temperature increases (Khalid et al.,
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21 352 2020).

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27 353 In general, the variation in the pyrolysis temperature also causes different influences in the
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29 354 sorption efficiency. Liu et al. (2018) exemplified that biochar produced at high temperatures
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31 355 has more active sites (i.e., greater SSA), although reducing functional groups can decrease the
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33 356 pesticide sorption capacity. Thus, it is necessary to have balanced and holistic knowledge so
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35 357 that biochar with the desirable characteristics is produced and applied to the soil. Additionally,
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37 358 Biswas et al. (2017) compared pyrolysis behaviors (from 300 to 450 °C) of corn cob, rice husks,
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39 359 rice straw, and wheat straw biochars. The optimal temperature associated with the maximum
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41 360 bio-oil yield for corn cob and rice husks is 450 °C, while 400 °C is better for rice and wheat
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43 361 straws. Among these biochars, rice husk presented the highest organic carbon conversion (56.62
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45 362 %).

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52 363 Crop residues are rich in minerals and, consequently, biochars have high mineral ash content
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54 364 and high pH (Khalid et al., 2020). Despite biochar from higher pyrolysis temperature having
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56 365 higher pH values, the pH_{PZC} and solution pH also influences sorption capacity, mainly if the
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58 366 pesticide is ionizable (Khalid et al., 2020; Liu et al., 2018). Biochar has a variable charge, and
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367 high pH values increase the OH dissociation from the functional groups (e.g., carboxyl and
368 hydroxyl) in particles' surface (Ahmad et al., 2014; Yu et al., 2019). Thus, the net negative
369 charge increases, and there is an electrostatic attraction between negative charges and cationic
370 species (Yaashikaa et al., 2019). Herath et al. (2016) reported the optimum pH at 4.0 for
371 maximum glyphosate sorption (82 %) in steam-activated biochar produced from rice husk,
372 while higher solution pH decreased the sorption capacity to 56 % (pH 10). Considering the
373 pH_{PZC} (at pH 4.0), the glyphosate dissociates, and the biochar surface charges positively (pH <
374 $pH_{PZC} = 6.65$). Therefore, in acidic conditions, a strong electrostatic interaction is favored
375 between the anionic glyphosate species (negatively charged) and the surface of the positively
376 charged activated biochar.

377 It is essential to verify the biochar application rate and frequency to achieve ideal soil conditions
378 for pesticide remediation (Liu et al., 2018). Different dosages can increase or decrease the pH
379 and modify the soil electrical conductivity (EC) in varied proportions (Palansooriya et al.,
380 2019). The efficiency of pesticide sorption in biochar-amended soils also involves competition,
381 as the soil is a complex system with different organic and inorganic contaminants coexisting.
382 The biochar interaction with inorganic and organic particles in the soil and other pollutants
383 might be competitive and lead to pores blockage, decreasing the sorption capacity of targeted
384 pesticides (Liu et al., 2018).

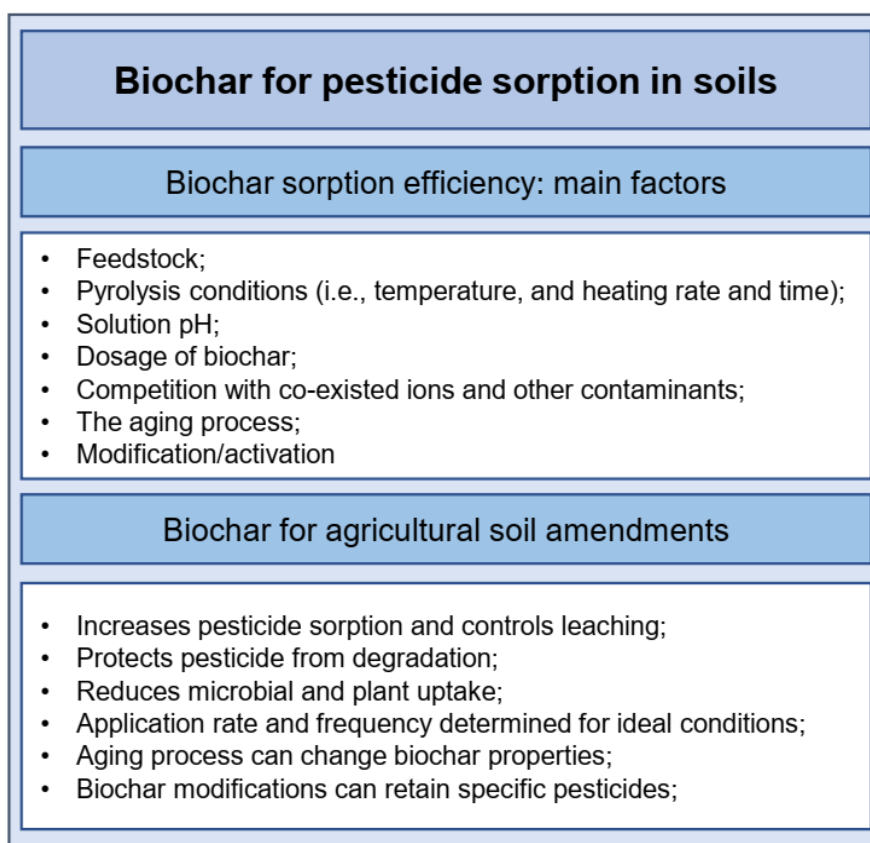
385 Biochar aging is a crucial factor that interferes with biochar properties and soil interactions.
386 After application to the soil, synergistic changes of physical, chemical, and biological aging
387 occur, and, especially in highly aromatic biochars, microbial metabolism is favored. As a result,
388 the outer portions of the biochar particles are more altered and protect their interior from the
389 action of the microorganisms. As biochar is a carbon-rich organic material and has relative
390 stability and resistance to degradation, the labile carbon fraction is first degraded; hence, aged
391 biochars become less susceptible to degradation than fresh biochars (Lehmann and Joseph,

392 2015). Ren et al. (2018) observed that wheat straw biochar's surface area and chemical
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2 393 composition changed with time after addition to soil. Consequently, aged biochars may have
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5 394 different sorption performance than fresh biochars. Gámiz et al. (2019) indicated improved
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7 395 sorption of aged biochar for removing herbicides (e.g., imazamox, picloram, and
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9 396 terbuthylazine) than fresh biochar. However, Liu et al. (2018) showed that biochar aging
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11 397 generally reduces its sorption potential. Therefore, the effects of aging on the fate of pesticides
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13 398 in biochar-amended soils still need further research.
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18 399 Biochar modified for particular soils' needs might enhance the pesticide's sorption (Kazemi
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20 400 Shariat Panahi et al., 2020; Yu et al., 2019). This process occurs due to the increasing porosity,
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22 401 micropore volume, SSA, and functional groups, eliminating potentially harmful elements (Liu
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24 402 et al., 2018; Wei et al., 2018). Biochar modification methods include chemical reagents, iron
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26 403 ions, metal oxide, and functional nanoparticles (Wei et al., 2018; Yaashikaa et al., 2019). Each
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28 404 engineered biochar can be prepared by pretreating feedstock before pyrolysis or post-treating
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30 405 onto untreated biochar (Liu et al., 2018). The chemical modification involves adding bases and
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32 406 acids to the biochar, and generally, acid activation changes surface properties (e.g., functional
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34 407 groups, charges, porosity, and SSA) (Wei et al., 2018). For example, feedstocks treated with
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36 408 nitric acid can incorporate carboxylic groups (Yaashikaa et al., 2019). The primary activation
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38 409 (usually using NaOH or KOH) induces the basicity and increases the O content on the surface
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40 410 (Wei et al., 2018). Biochar modification also includes the physical activation using steam
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42 411 (Yaashikaa et al., 2019) and the impregnation of functional nanomaterials (e.g., chitosan,
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44 412 carbon nanotubes, ZnS nanocrystals, and graphene oxide). This process improves the SSA,
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46 413 porosity, and thermal stability, creating a newly engineered compound used as an alternative
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48 414 and innovative sorbent (Kazemi Shariat Panahi et al., 2020; Wei et al., 2018). Moreover,
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50 415 modifying biochar for soil amendment must consider the costs of alteration methods and
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52 416 potential risks of environmental pollution by the added elements (Liu et al., 2018).
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417 In synthesis, several critical factors determine amending agricultural soils for pesticide sorption
 418 (Figure 2). First, crop management should address biochar production residues, which depend
 419 on the feedstock type and pyrolysis conditions (e.g., temperature, heating rate, and time). The
 420 biochar characteristics related to pesticide sorption involve ash content, pH and pH_{PZC} , CEC,
 421 functional groups, elemental ratios, porosity, and SSA. In agricultural soils, biochar
 422 amendments contribute to pesticide sorption, leaching control, protecting the pesticide from
 423 degradation, and avoiding microbial uptake. Moreover, the potential effects of the aging process
 424 are not yet fully documented.

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



427 5.2. Biochar from maize crop residues

428 Twelve studies from the final selection evaluated 24 different maize residues biochars for
 429 pesticide sorption (Table 1). Among these biochars, 15 used straw, 7 used stalk, and 2 used

1 430 corn cob as feedstock; 1 biochar was produced with pre-and post-treatment, 1 biochar with
2 431 only pre-treatment, 1 biochar with post-treatment, and the others were not mentioned. All the
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4 432 studies were conducted on a laboratory scale using spiked soils, and most of them involved
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6 433 agricultural soils. Also, pyrolysis temperatures ranged from 200 to 850 °C. Several studies
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8 434 stated that biochar-amended soils were more effective in the pesticide sorption compared to the
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10 435 biochar-free soil for atrazine (Clay et al., 2016; Ouyang et al., 2016a, 2016b; Qin et al., 2019;
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12 436 Tao et al., 2020), 2,4-D (Clay et al., 2016), carbaryl (Ren et al., 2016) and thiacloprid (P. Zhang
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14 437 et al., 2018). For instance, Clay et al. (2016) reported an increase from 4.5 to 6-fold on the
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16 438 sorption efficiency for atrazine after soil amendment with 10 % of maize stalk biochar.
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23 439 The pesticide sorption on biochar amended soil depends on both pesticides and biochar
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25 440 properties, besides soil characteristics. In our review, biochars from the same feedstock (e.g.,
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27 441 maize crop residues) presented a significant variation in their properties: pH values varied from
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29 442 6.8 to 10.6; the SSA was between 1.5 and 386 m² g⁻¹, and ash content ranged from 3.01 to 32
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31 443 %. Also, biochar properties are strongly influenced by the feedstock material characteristics
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33 444 and pyrolysis conditions. For instance, maize straw biochar had the largest SSA (44.966 m² g⁻¹
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35 445 ¹), total pore volume (0.0345 cm³ g⁻¹), and ash content (9.03 %) than biochar from corn cob
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37 446 (1.506 m² g⁻¹, 0.0032 cm³ g⁻¹ and 3.01 %, respectively). Consequently, this was probably one
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39 447 of the factors that favored the better sorption performance of maize straw biochar (when the
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41 448 initial concentration of atrazine solution was 1 mg L⁻¹, the removal rate was 27.02 and 76.65
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43 449 % for soil mixed with 5 % of corn cob and straw biochars, respectively) (Ouyang et al., 2016b).
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50 450 Several studies confirmed the temperature interference on the maize straw biochars SSA
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52 451 among the pyrolysis conditions, improving from 6.71 to 265 m² g⁻¹, as the pyrolysis
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54 452 temperature increased from 350 to 700 °C. Similarly, the pH increased from 7.9 to 10.6.
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56 453 Consequently, the highest carbaryl sorption affinity was evidenced for the biochar produced at
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1 454 the highest temperature (700 °C) and with the highest rate of addition to the soil (5 %), with a
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3 455 sorption affinity (K_f , Freundlich isotherm) of $83.2 \text{ (mg kg}^{-1}) \text{ (mg L}^{-1})^{-n}$ (Ren et al., 2016).
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5 456 Accordingly, Tao et al. (2020) evaluated maize stalk biochar, and batch sorption experiments
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7 457 revealed an improvement in maximum sorption capacity from 21.96 to 35.88 mg g^{-1} ,
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9
10 458 respectively, by increasing pyrolysis temperature from 250 to 850 °C. In the same way, biochar
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12 459 application increased the K_f of imidacloprid, and clothianidin (Zhang et al., 2020) into maize
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14 460 straw biochar-amended soil with charring temperature (300 - 700 °C).
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18 461 Besides, Zhang et al. (2020) reported that the amendment with low-pyrolyzing temperature
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20 462 biochar (300 °C) benefited the imidacloprid and clothianidin biodegradation due to the supply
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23 463 of organic carbon and available nitrogen for microorganisms, although inhibiting the chemical
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25 464 degradation. On the other hand, the high-pyrolyzing temperature biochars (500 to 700 °C)
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28 465 favored chemical degradation, inhibiting biodegradation. For thiacloprid, the observations
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30 466 were similar (P. Zhang et al., 2018). Biochar particle size range influences the sorption
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33 467 efficiency of pesticides, as observed by Clay et al. (2016). Atrazine and 2,4-D sorption
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35 468 increased significantly with the reduction of the biochar particle size. For 2,4-D, K_f was risen
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38 469 from 190 (for biochar mean size of 2 to 4 mm) to $398 \mu\text{mol}^{1-1/n} \text{ L}^{1/n} \text{ kg}^{-1}$ (for size below 2 mm);
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40 470 while for atrazine, the increase in K_f was more prominent from 209 to $912 \mu\text{mol}^{1-1/n} \text{ L}^{1/n} \text{ kg}^{-1}$
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42 471 in the same biochar size range (Clay et al., 2016).
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46 472 Some studies use biochar modification or pre- and post-treatment to develop biochars with
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48 473 enhanced pesticide removal capacity from the soil. The maize straw biomass pretreatment with
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51 474 ammonium dihydrogen phosphate (ADP) increased the atrazine removal from soil amended
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53 475 due to the increase in biochar SSA (44.966 for $356.010 \text{ m}^2 \text{ g}^{-1}$) and total pore volume (0.0345
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55 476 for $0.221 \text{ cm}^3 \text{ g}^{-1}$) (Ouyang et al., 2016b). Clay et al. (2016) evaluated the influence of post-
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58 477 process handling. The first biochar sample was cooled to room temperature, while a second
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1 478 sample was immersed in water immediately after pyrolysis to prevent slow combustion. The
2 479 atrazine sorption data for water-cooled biochar showed a K_f of $151 \mu\text{mol}^{1-1/n} \text{L}^{1/n} \text{kg}^{-1}$, a lower
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4 480 value than the results for air-dried biochar (209 to $912 \mu\text{mol}^{1-1/n} \text{L}^{1/n} \text{kg}^{-1}$).
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8 481 The biochar addition alters soil properties. For example, Zhang et al. (2020) observed that a
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10 482 typical Chinese soil pH increased from 4.4 to 6.8 after a 2 % application of maize straw biochar
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12 483 (500 °C). Also, pH, EC, available nutrients, organic carbon, hydrogen contents, and SSA of
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14 484 the soil were improved by adding biochar from maize crop residues. The dissolved organic
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16 485 carbon increased upon the addition of biochars pyrolyzed at 300 °C, while the biochars
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18 486 produced at 700 °C decreased their concentrations (P. Zhang et al., 2018). Pesticide sorption
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20 487 capacities are expected to vary on soils with different properties. Clay et al. (2016) pointed out
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22 488 that a 1 % addition of maize stover biochar increased atrazine sorption affinity for the fine
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24 489 loamy sand by about 45 % and for the silty clay loam by 25 %. The biochar-amended soil
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26 490 constituents become heavily dependent on each other and with specific behaviors for each
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28 491 environmental condition. At the initial atrazine solution of 1 mg L^{-1} , the soil amended with
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30 492 corn cob- and stalk-based biochar (0.5 and 1.0 % addition rate) had better performance than
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32 493 the pure biochar. On the contrary, at 20 mg L^{-1} , the pure biochar derived from maize stalk had
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34 494 a better removal rate than the biochar-amended soil (Ouyang et al., 2016b).
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43 495 Previous literature showed that the maize biochar application rate in the soil is fundamental for
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45 496 optimizing pesticide sorption. Among the 12 included articles (Table 1), 11 studies involved
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47 497 maximum doses of 5 %, and one study evaluated doses up to 10 %. Overall, it generated
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49 498 significant improvements in the pesticide sorption capacity. The atrazine's removal rate in
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51 499 column experiments increased from 38.7 to 58.3 % by increasing the application rate of the
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53 500 maize straw-derived biochar from 0.5 to 1.0 % (Ouyang et al., 2016a). However, some studies
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55 501 indicated that high application rates could result in negative impacts. Clay et al. (2016) reported
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1 502 that 1 % addition of maize stalk biochar to two different soil types (silty clay loam and fine
2 503 loamy sand) did not affect the pH or EC. Adding 10 % of biochar has already increased the
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4 504 EC, especially in the sandy soil (less buffering capacity). However, large and frequent
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7 505 applications must be associated with monitoring EC to avoid saline conditions and,
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9 506 consequently, losses in agricultural productivity.

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13 507 Graber et al. (2011) investigated the interaction of 1,3-D in a solid-liquid-gaseous system of a
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15 508 biochar-amended soil. The addition of 1 % of maize straw biochar (500 °C) promoted strong
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18 509 1,3-D sorption with solid particles, causing substantial reductions in the 1,3-D concentrations
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20 510 in the gaseous phase. Still, there were also reductions in the aqueous phase, precisely the active
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22 511 portion for nematode control. Thus, there was adequate control of the nematodes in the studied
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24 512 system. However, the authors emphasized that biochars with greater sorption capacities (e.g.,
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26 513 those with higher pyrolysis temperatures or large doses) should be used cautiously. Otherwise,
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29 514 depending on sorption conditions, it can negatively impact pest control and agronomic systems.

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33 515 Overall, the pesticide sorption onto the soils amended with maize residue biochars was
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35 516 accurately described by the Freundlich model, such as for atrazine (Clay et al., 2016; Ouyang
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37 517 et al., 2016b), 2,4-D (Clay et al., 2016), flubendiamide (Das and Mukherjee, 2020), 1,3-D
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39 518 (Graber et al., 2011), carbaryl (Ren et al., 2016), thiacloprid (P. Zhang et al., 2018),
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41 519 imidacloprid, and clothianidin (Zhang et al., 2020). For instance, the isothermal sorption fitted
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43 520 well with the Freundlich model ($R^2 > 0.96$) on soil amended with different biochar additions
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45 521 from corn cob and stalk (Ouyang et al., 2016b). Ren et al. (2016) also reported experimental
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47 522 data adjustments ($R^2 > 0.98$) of carbaryl sorption to maize straw biochar-amended soil. It
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49 523 suggests that the pesticide sorption occurred predominantly on the heterogeneous surfaces of
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51 524 the particles in these studies. On the other hand, the Langmuir model better described the
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53 525 topramezone's sorption process, which means the monolayer sorption played a dominating role
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526 (Uwamungu et al., 2019). Tao et al. (2020) reported that the Freundlich model is better suited
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2 527 to fit the atrazine sorption onto biochar produced from maize stalk at 250 °C, while the
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4 528 Langmuir model matched well with the biochars made at 550 and 850 °C. The kinetic
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7 529 experiments results showed that pesticide sorption was faster in the first phase by the larger
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10 530 number of active sorption sites. Thus, the sorption equilibrium was reached after 8 to 12 h,
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12 531 when 0.5 g of soil and 0.02 g of biochar were added with topramezone (Uwamungu et al.,
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14 532 2019), and 10 h for atrazine mixed with 15 mg of biochar (Tao et al., 2020).

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18 533 In addition to increasing sorption efficiency, Das and Mukherjee (2020) pointed out that the
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20 534 biochar addition in soil reduced the desorption process. A considerable portion of the
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22 535 flubendiamide sorbed in the soil matrix remained retained during the desorption test. The
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24 536 biochar addition to the soil reduces diffuse pollution from leaching, as simulated by Ouyang et
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27 537 al. (2016a) in rainfall-leaching experiments with different soil column configurations. The
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30 538 lowest leaching atrazine contents appeared in the smaller rainfall intensities and in the columns
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32 539 where biochar was applied to the soil. The soil with a biochar and gravel combination provided
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35 540 the highest efficiency of atrazine control (on average 87.85 %) when the biochar addition rate
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37 541 was 3 %.

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41 542 Previous studies have highlighted that biochar application in the soil could affect pesticide
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43 543 biodegradation. For example, the biochar amendment in the soil at 5 % decreased the half-life
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45 544 values of flubendiamide from 165.3 and 178.6 to 103.5 and 117.4 days, respectively (Das and
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48 545 Mukherjee, 2020). For carbaryl, the decrease with 5 % biochar addition was 34.6 to 27.7 (350
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50 546 °C) and 33 days (700 °C) (Ren et al., 2016). For imidacloprid, the decrease with 2 % biochar
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53 547 addition was 86.7 to 73.0 (300 °C), 77.6 (500 °C), and 80.6 days (700 °C) (Zhang et al., 2020).
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55 548 Conversely, for clothianidin, these authors reported an increase in half-life with 2 % addition
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1 549 from 52.4 to 93.0 (300 °C), 72.0 (500 °C), and 62.8 days (700 °C). Thus, the degradation rate
2 550 increased with biochar addition on soil, occurring via biotic and abiotic processes.
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5 551 Most researchers investigate pesticide sorption individually, despite the complexity of actual
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7 552 contamination and the need for combinations of treatments. Tao et al. (2020) evaluated the
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9 553 combined application between biochar and co-cultured functional microorganisms. The results
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11 554 showed a 49 % higher potential to degrade 100 mg L⁻¹ atrazine within 24 h than pure degrading
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13 555 bacteria DNS32 and increase the soil's total and available phosphorus content. Qin et al. (2019)
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15 556 assessed the maize straw biochar and sepiolite to remediate the combined pesticide and metal
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17 557 pollution. While biochar targeted atrazine, cadmium was mostly immobilized by sepiolite;
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19 558 thus, the authors concluded that combined application was efficient for immobilizing both
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21 559 contaminants.
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31 561 *5.3. Biochar from rice crop residues*

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34 562 Table 1 shows 15 articles that assessed 25 biochars produced from rice crop residues, most
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36 563 from rice straw (n = 13). Rice husk and rice hull were also used. Pyrolysis temperature varied
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38 564 from 300 to 700 °C, and just 3 of the 25 biochars passed for some treatment after pyrolysis. The
39
40 565 most studied pesticides were imazapic (n = 4), imazapyr (n = 3) e fomesafen (n = 3). Although
41
42 566 all biochars were made from rice crop residues, they have a variety of characteristics. For
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44 567 instance, pH varied in the range of 6.0 to 11.1, and SSA went from 1.99 to 202.11 m² g⁻¹. Ash
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46 568 content was between 9 and 50.3 %. All these variations are related to the fact that, besides
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48 569 feedstock, pyrolysis conditions are also determinants for biochar properties.
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55 570 In general, for rice-derived biochar, higher pyrolysis temperatures resulted in materials with
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57 571 higher pH, ash content, SSA, and porosity, but with lower CEC (Lü et al., 2012; Manna and
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59 572 Singh, 2015; Ren et al., 2016; Yavari et al., 2016; Zhao et al., 2019). Apart from temperature,
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573 other pyrolysis conditions influence biochar characteristics, and consequently, its sorption
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2 574 capacity. Yavari et al. (2017) studied the influence of temperature (from 300 to 700 °C), heating
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4 575 rate (3 to 10 °C min⁻¹), and residence time (1 to 3 h) in rice husk biochar characteristics. The
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7 576 maximum organic carbon content was found in the biochar with the highest pyrolysis
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10 577 temperature and the slowest heating rate. CEC was negatively correlated with temperature and
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12 578 heating rate, while the SSA was positively correlated with temperature and residence time.

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15 579 Overall, rice residues-derived biochar application in the soil can improve pesticide sorption
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18 580 capacity (Aldana et al., 2020; Khorram et al., 2015; Lü et al., 2012; Manna and Singh, 2015;
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20
21 581 Ren et al., 2016; Wu et al., 2019). This improvement happens even with small biochar doses,
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23 582 as the maximum amount used was 5 % (w/w) (Table 1). Khorram et al. (2015) investigated the
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25 583 sorption of fomesafen in soils amended with 0.5, 1, and 2 % rice hull biochar produced at 600
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27
28 584 °C. Biochar-amended soils enhanced fomesafen sorption, as K_f increased from 0.69 to 14.44
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30 585 $\text{mg}^{1-1/nf} \text{L}^{1/nf} \text{kg}^{-1}$ in the soil with 2 % biochar. Similarly, for carbaryl sorption, Ren et al. (2016)
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33 586 showed an increase of K_f from 15.5 to 125.9 $\text{mg kg}^{-1} (\text{mg L}^{-1})^{-n}$ after applying rice biochar
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35 587 (700 °C) at 5 %. In this case, the authors compared biochars produced at two different
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38 588 temperatures and showed that biochars made at higher temperatures had the most satisfactory
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40 589 results. Several studies have also examined the biochar effects in the leaching of pesticides,
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43 590 and it has been demonstrated that biochar helps retain the substances at the top layer. For
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45 591 example, Khorram et al. (2018) assessed the leaching of fomesafen in rice biochar-amended
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48 592 soil in columns, and the retention increased from 13.45 to 76 % with 2 % (w/w) biochar-
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50 593 amended soil; the pesticide was retained in the top 5 cm of the columns.

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53 594 Manna and Singh (2015) also reported the temperature effects for pyrazosulfuron-ethyl, as
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56 595 biochars from higher temperatures achieved higher specific surface and porosity. In this
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58 596 research, the control soil (sandy loam) had 5.3 to 8.6 % of pesticide sorption, whereas biochar
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1 597 produced at 400 °C had 7.5 to 50.4 %, and 600 °C biochar sorption was 55.9 to 91.8 %.
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3 598 However, Yavari et al. (2017b) reported different effects for imazapic and imazapyr sorption
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5 599 by soils with 1 % of rice husk biochar at different pyrolysis conditions. In this case, sorption
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7 600 capacities for both herbicides were higher for the biochar produced at the lowest temperature
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10 601 (300 °C) and a slow heating rate (3 °C min⁻¹).

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13 602 Few studies addressed biochars after treatments. Yavari et al. (2020) produced a rice husk
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15 603 biochar (pyrolysis at 300 °C, 3 h) and modified this material by mixing it with a chitosan
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18 604 solution diluted in acid acetic for 30 min, and by dripping NaOH solution into it. After 12 h,
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20 605 deionized water washed the modified biochar. The comparative analysis of biochar sorption
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23 606 performance before and after treatment is indicative of the changes resulting from the action of
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25 607 chitosan. The authors reported that chitosan-modified biochars had remarkably higher moisture
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28 608 content, pH, and CEC than non-modified biochars. Chitosan-modified biochar also showed a
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30 609 higher sorption capacity of imazapic and imazapyr. The value of K_f for imazapic varied from
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33 610 1.744 in the pure soil to 3.090 in the biochar amended soil with 1 % biochar and to 4.391 for
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35 611 chitosan-modified biochar amended soil. However, it would also be relevant to test only
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38 612 chitosan to validate its effects in the modified biochar.

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41 613 Finally, most researchers also investigated the pesticides' sorption individually. A recent study
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43 614 by Aldana et al. (2020) examined the sorption of atrazine, diuron, and OTC on mixtures of
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46 615 tropical soils and rice biochar at 1, 2.5, and 5%. Higher doses increased the sorption of all
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49 616 compounds, and atrazine was the only substance detected in the equilibrium solution, even in
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51 617 the mixture with 5 % biochar. According to these authors, diuron was sorbed first and competed
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53 618 with atrazine for the sorption sites. Besides, soil dissolved organic matter might cover sorption
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56 619 sites from biochar. Despite sorption, the degradation of the pesticides by biochar amended-
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58 620 soils has also been addressed, and it depends on the pesticide's type. Manna and Singh (2019)

621 showed that applying 400 and 600 °C rice straw biochar in sandy loam soil at a biochar dose
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3 622 of 0.02 and 0.05 g kg⁻¹ increased pyrazosulfuron-ethyl persistence under flooded and non-
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5 623 flooded conditions. An increasing amount of biochar decreased pyrazosulfuron-ethyl
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7 624 degradation. Conversely, for carbaryl, Ren et al. (2016) reported that biochars as soil
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10 625 amendments promoted chemical degradation and affected the pesticide's microbial
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12 626 degradation.

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19 628 *5.4. Biochar from wheat crop residues*

22 629 Table 1 shows 13 different biochars produced from wheat crop residues. Most of them are
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25 630 derived from wheat straw, and only one from wheat midds. The pyrolysis temperature in these
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27 631 studies ranged from 250 to 600 °C. Among the materials (Table 1), only one was submitted to
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30 632 treatment before pyrolysis (Tatarková et al., 2013). The straw was carbonized in a sand bath at
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32 633 200 °C for 24 h, and the residue was pyrolyzed at 300 °C. These papers studied a variety of 7
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35 634 pesticides, and the most studied were pyrazosulfuron-ethyl and HCB.

38 635 As the previous feedstocks, various characteristics of wheat residue biochars changed in
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40 636 different pyrolysis conditions. For instance, the pH varied between 5.4 and 10.6, CEC was in
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43 637 the range of 22 and 68.7 cmol_c kg⁻¹, and SSA ranged from 2.7 to 62.6 m² g⁻¹. In general, the
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45 638 studies showed that increasing pyrolysis temperatures increases pH, SSA, and porosity (Cheng
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48 639 et al., 2017; Manna and Singh, 2015). However, regarding the effect of pyrolysis temperature
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50 640 on CEC, there were contrasting results. For example, Cheng et al. (2017) studied wheat straw
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52 641 biochar produced at four peak temperatures (250, 350, 450, and 550 °C) and found that CEC
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55 642 decreased (from 68.7 to 22.0 cmol_c kg⁻¹) with higher temperatures. Conversely, Manna and
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58 643 Singh (2015) showed that increasing pyrolysis temperature for wheat straw biochar did not
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1 644 significantly affect CEC (62.0 and 62.6 $\text{cmol}_c \text{ kg}^{-1}$ for the 400 and 600 °C biochars,
2 645 respectively).

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5 646 Studies regarding wheat residue biochar provide evidence that the application of this material
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8 647 in soils can improve the sorption of pesticides (Cheng et al., 2017; Humera Aziz et al., 2018;
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10 648 Manna and Singh, 2015; Tatarková et al., 2013). Tatarková et al. (2013) used a wheat straw
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12 649 biochar produced at 300 °C (pH of 10.6 and SSA of was 4.59 $\text{m}^2 \text{ g}^{-1}$). They demonstrated that
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15 650 1 % biochar amended soil had 2.53 times higher MCPA sorption capacity than the non-amended
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18 651 soil. Furthermore, the quantity of MCPA leached in soil columns alone was 56 %, while 35 %
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20 652 leached in columns with 1 % wheat straw biochar. Humera Aziz et al. (2018) demonstrated that
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22 653 the application of wheat straw biochar prepared at 500°C (CEC of 85 $\text{cmol}_c \text{ kg}^{-1}$, total organic
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24 654 carbon of 43.80 % and SSA of 4.83 $\text{m}^2 \text{ g}^{-1}$) at 0.25 and 0.5 % in sandy clay loam soil (pH of
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26 655 7.44, CEC of 5.2 $\text{cmol}_c \text{ kg}^{-1}$ and total organic carbon of 0.87 %) from Pakistan increased
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29 656 chlorpyrifos sorption. The data was adjusted by Freundlich isotherm, and K_f rose from 4.34 to
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32 657 218.83 L kg^{-1} after the mixture with 0.5 % biochar. Manna and Singh (2015) reported a similar
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34 658 effect for pyrazosulfuron-ethyl sorption by adding 0.1, 0.2, and 0.5 % wheat straw biochar in
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37 659 sandy loam soil from India. Increasing the pyrolysis temperature from 400 to 600 °C did not
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40 660 significantly increase the organic carbon and CEC, but it doubled the SSA (10.15 and 20.38 m^2
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42 661 g^{-1} , respectively) and improved the sorption capacity of the biochar. Manna and Singh (2019)
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44 662 also demonstrated that amendment with these same biochars influences pesticide leaching
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47 663 because of its strong sorption. They reported that the application of wheat straw biochar made
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50 664 at 400 and 600 °C at 5 % in the soil led to a decrease in the pyrazosulfuron-ethyl loss by 9 e 39
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52 665 %, respectively.

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54
55 666 In general, the Freundlich isotherm adjusted pesticide sorption data (Humera Aziz et al., 2018;
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57 667 Manna and Singh, 2015; Tatarková et al., 2013). Manna and Singh (2015) discussed the effect
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60 668 of biochar on the mean value (standard deviations were not provided) of the Freundlich
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669 exponent $1/n$, as nonlinearity in pyrazosulfuron-ethyl sorption increased with higher biochar
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2 670 doses. The $1/n$ values were higher than 1 in the pure soil, suggesting nonlinear sorption
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4 671 isotherms (S-type). On the other hand, $1/n$ becomes less than 1 in soils amended with 0.2 and
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7 672 0.5 % biochar, reflecting an L-type adsorption isotherm. It indicates that the adsorbate
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10 673 molecules did not suffer intense competition from the water molecule at low concentrations,
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12 674 but sorption sites become limited as the concentration increases. Unlike these results, Tatarková
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14 675 et al. (2013) showed that the Freundlich exponent values for MCPA sorption were close to 1
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16 676 for non-amended soil, biochar-amended soil, and biochar, indicating constant MCPA
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19 677 partitioning between sorbent and solution for all the materials within the concentration range
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22 678 (0.5 to 22 mg L⁻¹). The use of classifications with numerical ranges should always be done with
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24 679 caution. Statistical analysis and presentation of standard deviations of results, especially close
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27 680 to class boundaries, may be of interest to reduce uncertainties and increase the reliability of data
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29 681 interpretations.

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32 682 Although several studies involve biochar effects on pesticide sorption, questions have been
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34 683 raised about their impact on other processes, including degradation, volatilization, and plant
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37 684 uptake (Cheng et al., 2017; Manna and Singh, 2019; Wang et al., 2016). Recent evidence
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40 685 suggested that the adding wheat straw biochar improves the pesticide persistence in soil due to
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42 686 the strong affinity between pesticide and biochar particles. Some studies sustain this hypothesis,
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45 687 such as Cheng et al. (2017) for simazine and Manna and Singh (2019) for pyrazosulfuron-ethyl.
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47 688 Moreover, in the study of Tatarková et al. (2013), the half-life of MCPA increased from 5.2
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49 689 days for the non-amended soil to 21.5 days for the amended soil. On the other hand, the
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52 690 dissipation would increase in biochar amended soils because of the microbial activity
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54 691 stimulation by biochar nutrients. Song et al. (2012) carried out incubation tests with HCB and
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57 692 reported that in the first 2 weeks, faster HCB dissipation occurred in the 0.1 and 0.5 % biochar-

693 amended treatments compared to control. Nevertheless, a significant decrease in HCB
694 dissipation was noted in the biochar-amended soils after 4 weeks.

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696 **6. Key aspects, gaps, and uncertainties**

697 *6.1. Pesticide bioavailability and ecotoxicity*

698 Regarding the pesticide uptake by plants, Khorram et al. (2017) showed that rice biochar
699 amendment could effectively suppress the undesirable inhibitory effect of fomesafen on corn
700 growth. Song et al. (2012) tested the bioaccumulation of HCB in earthworms; their primary
701 concern was that strong sorption of contaminants would result in accumulation by the
702 mesofauna of ingestion of biochar particles. However, concentrations of HCB in earthworms
703 decreased with increasing biochar application rate. After that, in another study, Song et al.
704 (2016) investigated a biochar-plant tandem remediation scheme for HCB, adding 1 and 2 % of
705 wheat biochar in soil and using ryegrass as the growing plant. Biochar amendment immobilized
706 HCB in soils, and the uptake of HCB by ryegrass root was reduced by 93.05 % by 1 % biochar
707 amendment compared to that of unamended soil. Unfortunately, no selected study presented
708 ecotoxicological assessments of pesticide biochar sorption, despite two studies identified in the
709 previous steps. For instance, Bielská et al. (2018) indicated reducing bioavailability and
710 bioaccessibility of hydrophobic organic compounds by increasing 5 % the dose of biochar from
711 mixed wood shavings and rice husks. However, this study identified biochar-induced toxicity
712 by the highest amount (10 %) to the springtail *Folsomia candida*, which could be associated
713 with pH-related effects or food sorption.

714 Although most studies focused on the remediation of isolated pesticides, these contaminants
715 may have increased ecological risks in combination (Belden and Brain, 2018). Additionally,

1 716 some pesticide transformation products can be more toxic than the parental compound (Sinclair
2 717 and Boxall, 2003), a challenge for pesticide management and environmental remediation
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4 718 (Levine and Borgert, 2018). Nonetheless, in a co-contamination, hydrophobic organic
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7 719 compounds (including pyrene and DDE) in the mixture did not show competitive sorption to
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10 720 biochar (Bielská et al., 2018), which is an advantage considering multiple soil contaminants.

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13 721 Biochar selection should allow pollution control while maintaining pesticide efficiency. For
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15 722 instance, Lü et al. (2012) incorporated 2,4-D and acetochlor into the studied rice straw biochar
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18 723 (i.e., pyrolyzed at 350 °C, with 31 % ash, 20.6 m² g⁻¹ of SSA, and H/C ratio of 0.342) as a
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20 724 sorptive carrier for retaining these herbicides. Doses of 0.5 and 1 % of biochar in soil decreased
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22
23 725 the acetochlor release rate, indicating the capacity to regulate herbicides' behavior. Besides,
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25 726 Graber et al. (2011) suggested that higher SSA wood-derived biochar could negatively impact
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28 727 herbicide efficacy in terms of phytoavailability. Thus, depending on the biochar characteristics
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30 728 and strength of sorption capacity, pesticide concentrations in the aqueous solution decrease and
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33 729 are not enough to promote pest control. This should be considered when planning the
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35 730 application.

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41 732 *6.2. Microbiological processes associated with biochar sorption*

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45 733 Most of the retrieved studies did not discuss microbial activity and its interactions with
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47 734 pesticides and biochar. On the contrary, some studies sterilized soils before biochar application
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50 735 to avoid microbial interferences. Still, pesticides can affect the soil microbiota and inhibit
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52 736 biodegradation. For example, Zhang et al. (2018) indicated that thiacloprid shifted the soil
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55 737 microbiota, and the biodegradation depended on soil pH, dissolved organic matter, and nutrients
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57 738 (e.g., N and P). Nonetheless, biochar addition generally enhanced microbial activity and
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59 739 multiplication, leading to more significant pesticide degradation, as shown by Das and
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1 740 Mukherjee (2020). These authors considered that maize stalk biochar was a readily available
2 741 source of energy for the microbiota.
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5 742 With a combined application approach of biochar in soil together with a degrading bacteria
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7 743 (i.e., *Acinetobacter lwoffii* DNS32), Tao et al. (2020) showed a 49 % greater capacity to degrade
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9 744 100 mg L⁻¹ of atrazine in 1 day compared to experiments using only adding the bacteria to the
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11 745 soil. In this scenario, microbial degradation could also increase pesticide dissipation, as
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13 746 observed by Wu et al. (2019) for oxyfluorfen and maize straw and rice hull biochars.
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15 747 Accordingly, Song et al. (2016) showed that wheat straw biochar stimulated microbial activity
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17 748 for dissipating hexachlorobenzene, mainly when associated with plant roots. Wu et al. (2019)
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19 749 also found that a rice hull biochar pyrolyzed at 500 °C (with 50.34 % ash, SSA of 95.67 m² g⁻¹
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21 750 ¹, and pH of 6.96) could improve oxyfluorfen degradation. The sorbent provided a suitable
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23 751 environment for microorganisms and stimulated soil microbial activity. Wang et al. (2016)
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25 752 showed that wheat midds biochar (i.e., pyrolyzed at 550 °C, with pH of 8.86, SSA of 24.73 m²
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27 753 g⁻¹, and pH of 8.82) alters 1,3-D degradation rates primarily through abiotic processes. They
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29 754 indicated a 130 % increase in the half-life for pesticide dissipation in soil with 1 % biochar,
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31 755 while 60 % higher in sterilized soils than control.
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40 756 Furthermore, the biochar effect in the biodegradation of pesticides may vary with pyrolysis
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42 757 temperatures. For example, Ren et al. (2016) studied carbaryl degradation in soils amended
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44 758 with rice and maize biochars under sterile and unsterile conditions. There was an increase in
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46 759 the biotic removal rate of carbaryl for soils amended with biochars produced at low
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48 760 temperatures (350 °C). However, the addition of biochar from high temperatures (700 °C)
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50 761 decreased biodegradation rates. The authors assumed that this difference is because of easily
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52 762 degradable compounds in the low-temperatures biochars. Also, these biochars did not affect the
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54 763 soil pH, which favors microbial communities. Zhang et al. (2020) observed similar behavior as
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764 a function of pyrolysis temperature for biodegradation of imidacloprid and clothianidin in soil
765 amended with maize straw biochar.

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767 *6.3. The effects of the aging process on biochar sorption*

768 Ren et al. (2018) identified changes in wheat straw biochar properties (1 % dose) and its atrazine
769 sorption capacity by aging in field soil (0.5, 1, 1.3, and 2 years). They reported that the SSA of
770 the fresh biochar amended soil increased from 10.7 to 59.1 m² g⁻¹ after 0.5 years and then
771 decreased with aging time, reaching 8.33 m² g⁻¹ after 2 years in the soil. According to the
772 authors, this behavior is related to the initial exposure of micropores due to the dissipation of
773 labile fraction from the biochar surface just after the application of biochar (increasing SSA),
774 and then the adhesion of soil organic matter and minerals to the surface of the biochar
775 (decreasing SSA). Another study (Khorram et al., 2017) investigated the aging process on
776 fomesafen sorption-desorption and indicated that the rice husk biochar was still effective after
777 6 months compared to the unamended soil. However, for 0.5 % of biochar, the total leaching
778 rate of fomesafen increased from 67.5 % in freshly amended soil to 78.1 % in the soil aged 6
779 months. So, the aging process generally reduces the sorption capacity of rice biochars,
780 suggesting a need for reapplication.

781 Similarly, the decrease of sorption because of the aging effect was also reported for oxyfluorfen
782 (Wu et al., 2019). In this case, to simulate the aging process, they used an artificial method
783 (H₂O₂ treatment). The soil's capacity to absorb oxyfluorfen increased linearly with added
784 biochar, but the sorption capacity of biochar-amended soil decreased with aging. According to
785 these authors, over time, changes might occur on physical or chemical properties in biochar
786 surface or blocked sorption sites by acid, minerals, oxides, and native pollutants in soil.
787 However, after 6 months of aging, the sorption capacity was still more significant than

1 788 measured for the unamended soils. Thus, desorption could result from pH changes,
2 789 reintroducing the pesticide to the soil (Liu et al., 2018), and the long-term biochar application
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4 790 and aging effects still need further research.
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8 791 As feedstock, different crop residues result in biochars with various properties and,
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10 792 consequently, different pesticide sorption capacities. Some researchers in our final selection
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12 793 compared biochars made of varying crop residues at the same conditions. For example, Ren et
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14 794 al. (2016) studied rice straw and maize straw biochars pyrolyzed at 350 °C. The authors
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16 795 reported that a 5 % rice straw biochar-amended soil showed higher sorption of carbaryl than a
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18 796 5 % maize straw biochar-amended soil. Some of the factors that contributed to these results
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20 797 were the higher SSA, ash content, and H/C ratio of the rice straw biochar (9.01 m² g⁻¹, 29.1 %,
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22 798 and 0.725, respectively) when compared with the properties of the maize straw biochar (6.71
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24 799 m² g⁻¹, 15.4 % and 0.685 respectively). Wu et al. (2019) also reported a higher sorption capacity
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26 800 for oxyfluorfen by biochar derived from rice hull at 500 °C than maize straw biochar at 300
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28 801 °C. Rice biochar also seems to be more effective than wheat biochar. Manna and Singh (2015)
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30 802 compared the effect of these two materials on pyrazosulfuron-ethyl sorption in sandy loam soil.
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32 803 Rice-derived biochar produced at 600 °C showed higher pH, O, C, and porosity than the wheat
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34 804 biochar made at the same conditions. As a result, rice biochar sorbed 55.9 to 91.8 % of the
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36 805 herbicide, while wheat biochar sorbed 6.9 to 86.0 %. Then, Manna and Singh (2019) reported
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38 806 that rice biochar also had a more considerable effect on herbicide degradation. Under non-
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40 807 flooded conditions, the application of 0.05 g kg⁻¹ of rice biochar produced at 600 °C resulted
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42 808 in a 6-fold increase in the half-life of pyrazosulfuron-ethyl.
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56 810 *6.4. Potential pesticide desorption*

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1 811 In addition to sorption, studying pesticide desorption is also essential to understand the strength
2 812 of the bond between pesticide and biochar components, the reversibility of the reaction, and
3 813 pesticides' availability. However, only a few papers present discussed desorption results (10
4 814 out of 32), including the pesticides fomesafen, 2,4-D, pyrazosulfuron-ethyl, acetochlor,
5 815 imazapic, imazapyr, flubendiamide, HCB, and MCPA. Only one study tested desorption with
6 816 maize residues biochar (total of 12). In addition, the retrieved studies from this review lack the
7 817 ecotoxicological analysis regarding the desorption process. In general, the Freundlich equation
8 818 satisfactorily fitted the desorption isotherms. These authors compared materials using the
9 819 percentage of desorbed pesticide, the desorption coefficient (K_f), and the hysteresis coefficient
10 820 (H), indicating the reaction potential reversibility.

25 821 Most of the retrieved papers showed a decrease in desorption due to the addition of biochar in
26 822 soils. For instance, Khorram et al. (2017) studied the sorption of fomesafen in mixtures of soil
27 823 with rice straw biochar and showed that the desorption (K_f) varied from $0.42 \text{ mg}^{1-1/n} \text{ L}^{1/n} \text{ kg}^{-1}$
28 824 in the unamended soil to $21.24 \text{ mg}^{1-1/n} \text{ L}^{1/n} \text{ kg}^{-1}$ for the mixture with 2 % biochar. In addition,
29 825 the value of H also decreased (from 0.76 in the unamended soil to 0.50 with 2 % biochar),
30 826 indicating less desorption. Similar results were found by Manna e Singh (2015) for
31 827 pyrazosulfuron-ethyl, Khorram et al. (2018) for fomesafen, Yavari et al. (2016; 2019) for
32 828 imazapic e imazapyr (all of them using rice straw biochar), Das and Mukherjee (2020) for
33 829 flubendiamide (with maize stalk biochar), and Song et al. (2016) for HCB (using wheat straw
34 830 biochar). Therefore, they suggest that the bond between pesticides and biochar particles is more
35 831 robust than between pesticides and unamended soil particles.

53 832 On the contrary, some researchers pointed out that the increase of sorption capacity from the
54 833 same dose is not always proportional to the decrease in desorption. For instance, Tatarkova et
55 834 al. (2013) concluded that the bonds between wheat straw biochar and MCPA might be weak.

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

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

846

847 **7. Biochar transport, storage, and applicability**

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

856 Significant aspects impacting the transport of biochar from pyrolysis plants to farms are the
857 distance between these two businesses, the size of the agricultural company, and its demand for
858 biochar. In general, farms' demand for biochar could be fulfilled by packing powders in big

859 bags and distributing them to regional cooperative or logistic centers via road transport.

860 However, it might be feasible for farms with attached pyrolysis units to implement connected

861 transport and biochar storage systems. This initiative decreases human intervention in the

862 process, hence increasing overall farms' yield.

863 From the reactor unit, pneumatic conveying lines could transfer biochar to storage vessels or

864 silos, which means that the bulk material is transported through a pipeline with an airstream.

865 Biochar is fluidized with low gas flow rates due to its low particle density and particle size;

866 hence, pneumatic transport is an appealing economic way to handle such material. Some

867 authors measured the basic flow energy and permeability of biochar originated from lignin

868 residues (Toloue Farrokh et al., 2018) and birch tree chips (Toloue Farrokh et al., 2020), and

869 concluded that these powders (mean diameter from 52 to 73 μm , and bulk density from 574 to

870 737 kg m^{-3}) might flow easily and with lower tendency to cause blockage of pipes during

871 pneumatic conveying operations.

872 Other relevant advantages of pneumatic conveying systems are that it requires very little

873 maintenance, and powders can be either conveyed in dilute or dense mode to prevent the

874 breakage of particles; the system's design is flexible as pipelines can be adjusted to the farm

875 layout; it is a dust-free system since the flow of biochar occurs inside of tubes; and the solids

876 flow rate can be monitored from simple pressure measurements as well as controlled with non-

877 mechanical valves, which are inexpensive and are resistant to wear and seizure (Geldart and

878 Jones, 1991; Massaro Sousa et al., 2020; Smolders and Baeyens, 1995).

879 Although there is limited information on the actual conveying of biochar, pneumatic transport

880 is a consolidated research field. For example, the efficient design of transport pipelines might

881 be performed using flow diagrams based on dimensionless numbers (e.g., Reynolds and

882 Archimedes) that account for different powder and air properties and pipeline dimensions

1 883 (Kalman, 2020; Kalman and Rawat, 2020). Moreover, practical experience and research
2 884 literature on the conveying of pulverized coal are vast, which is helpful information to handle
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4 885 biochar given the similarities between these two powders in terms of bulk density and particle-
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7 886 size distribution. Papers reporting experimental tests in various scale units and numerical
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10 887 simulations with different approaches are addressed in detail elsewhere (Chinnayya et al., 2009;
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12 888 Cong et al., 2011; Jin et al., 2019; Lu et al., 2011; Zhou et al., 2020, 2018).

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15 889 Silos are appealing equipment to meet process storage demand that also provides complete
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18 890 isolation from the external environment, minimizing biochar loss due to humidity degradation,
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20 891 pests' contamination, or dust. Jenike's method is often used to design cylindrical or wedge-
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23 892 shaped silo hoppers aiming at appropriate mass- or funnel-flow discharge of bulk solids with
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25 893 different properties (Enstad, 1975; Massaro Sousa et al., 2021; Oginni and Fasina, 2018).
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27 894 However, to the best of our knowledge, the flow properties of biochar required for the design
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30 895 of silos have not been fully assessed in the literature, which is of great interest for future studies.

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33 896 Despite this, successful design and operation of silo hoppers with pulverized coals are reported
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36 897 for both gravity-driven and air-assisted discharge of powders (Guo et al., 2015; Lu et al., 2015,
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38 898 2012). Depending on samples' particle-size distribution and moisture content, minimum hopper
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41 899 inclination for mass-flow discharge ranges from 11 to 22°, whereas the outlet diameter must be
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43 900 higher than 0.3 m (Chen et al., 2012; Y. Liu et al., 2015). Biochar generally presents better
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45 901 flowability classification than pulverized coal under consolidated conditions (Toloue Farrokh
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48 902 et al., 2020, 2018), thus using steeper silos with cone angles of 10° and outlet diameter higher
49
50 903 than 0.3 m might be sufficient to handle most biochar powders. However, measuring bulk and
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52
53 904 flow properties is highly encouraged to optimize the silo design and prevent flow issues,
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55 905 significantly whether the silo wall material or the biochar particle size and moisture content
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57
58 906 deviate from the ones shown in the previous studies.

1 907 In principle, biochar can be dispersed in soil with equivalent techniques for spreading fertilizers
2
3 908 and pH correctors. However, these methods should be optimized considering farm
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5 909 particularities, business size, terrain conditions (e.g., slopes and soil wettability), local climate,
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7 910 and duration of rainy seasons, among other aspects. Dust emissions can be reduced, for
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9 911 example, with wet soil applications (Li et al., 2018). Moreover, using pelletized biochar might
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11 912 be an alternative to prevent excessive biochar loss by wind action or water leaching. While
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13 913 some papers reported the successful biochars densification for solid fuel applications (Bazargan
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15 914 et al., 2014; Hu et al., 2016; Ranzi et al., 2018), future studies should consider pellet properties
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17 915 for field applicability. Some relevant factors include pellet resistance when in contact with
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19 916 different environmental conditions, total contact area for pesticide sorption, and optimal pellet
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21 917 size to perform an economic and homogeneous distribution of biochar in soil.
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27 918 In general, adding biochar to the soil can result in several benefits, including improvements in
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29 919 carbon sequestration, greenhouse gas mitigation, soil fertility, plant growth, and crop yields
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31 920 (Ding et al., 2016; Hussain et al., 2017), solid advantages for agricultural areas. Besides, plant
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33 921 growth stimulation could improve ecological restoration and ecosystem services (Rey Benayas
34
35 922 et al., 2009). The productivity increases due to more significant water holding capacity and
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37 923 lower infiltration, which could also be an alternative for degraded or arid soils (Diatta et al.,
38
39 924 2020). The feedstock for biochar production is varied, including crop residues, wood biomass,
40
41 925 leaves, animal manure, solid waste, sewage, and industrial sludge (Ahmad et al., 2014;
42
43 926 Lehmann and Joseph, 2015). The alternative for applying crop residues to biochar production
44
45 927 could concatenate agricultural waste management and environmental remediation techniques.
46
47 928 Finally, note that the best selection of units and methods for handling biochars is intrinsically
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49 929 related to the regional technology development, farm business size, and field particularities;
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51 930 hence, performing techno-economic assessment under different farm contexts is encouraged to
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53 931 clarify this point.
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932 8. Final considerations

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3 933 The increase in crop production had led to a demand for residue management, which could be
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5 934 coupled with biochar production. Biochar has a potential for pesticide sorption in agricultural
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8 935 soils in this scenario, and studies have increased in the last few years. Particularly maize, rice,
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10 936 and wheat residues are appropriate feedstocks for biochar production and contaminated soil
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13 937 amendment. In this review, we highlighted some advantages of these applications, such as:

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16 938 ● Biochar amendments improved soil quality, restored soil properties, and contributed to
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18 939 carbon sequestration.
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21 940 ● Biochar amendments have the potential sorption of pesticides, reducing their soil
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23 941 mobility and bioavailability.
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26 942 ● Moreover, studies have shown several benefits from biochar application, including the
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28 943 potential to ameliorate soil quality and properties (e.g., organic matter). Thus, biochar
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30 944 could promote soil restoration and ecosystem services maintenance.
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33 945 ● Agricultural cooperatives can manage biochar production and logistics, and this could
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35 946 benefit mini-farms as a low-cost amendment.
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37
38 947 ● Multiple feedstocks for biochar production could be used in rotation systems, as residue
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40 948 management in the long-term could improve carbon sequestration in agriculture.

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42
43 949 On the other hand, these applications still need further research and development, mainly due
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45 950 to some limitations and gaps, including:

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48 951 ● Most research focused on batch experiments in lab-scale, highlighting a need for field
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50 952 application research and study of other contaminants. Also, there is a need to study the
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52 953 long-term effects of biochar application and its potential desorption.
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55 954 ● Retrieved studies were mainly for a few pesticides (only 21 different active substances).
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57 955 Therefore, biochar sorption should be evaluated for different pesticides and co-
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956 contaminations since they behave differently depending on their chemical
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2 957 characteristics.

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5 958 ● Studies should consider the entire biochar life cycle. Monitoring all steps is essential to
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7 959 ensure the biochar production meets the proposed goals for its application. Also, this
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9 960 approach can avoid the risks of biochar containing contaminants (e.g., PAHs).

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11 961 ● Future studies should evaluate the influence of biochar particle size on remediation
12
13 962 dynamics, especially *in situ*. Micro- and nano-particles can show more significant
14
15 963 horizontal movement (runoff) and vertical movement. Thus, once they have absorbed
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17 964 pesticides, they can be transported to greater distances.

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19 965 ● There is still limited knowledge about the aging process of biochar. A more systematic
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21 966 understanding of the complexity of physical and chemical changes is needed, and also
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23 967 the influence of different soil types and climate changes (e.g., wet/dry and
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25 968 freezing/melting cycles).

26
27 969 ● Biochar can reduce pesticide bioavailability and, consequently, its biodegradation.
28
29 970 Nonetheless, the microbiological processes still need investigation.

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31 971 ● Ecological risk assessment is still a gap regarding research on biochar applications.
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33 972 Thus, bioassays are encouraged since several bioindicators are sensitive to pesticides,
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35 973 besides the potential to assess desorption.

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37 974 ● Characterizing biochar bulk and flow properties is fundamental for designing solids
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39 975 feeders, transport, and storage equipment. In addition, pelletized biochar's flow,
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41 976 mechanical, and structural properties should be assessed to achieve cost-effective
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43 977 dispersion of this material in farm soils.

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45 978 ● No studies showed an economic analysis of biochar applications. Therefore, performing
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47 979 process techno-economic analysis under different farm contexts is encouraged.
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- 980 ● Restoration methods must be feasible, technically achievable, and socially acceptable.

981 In addition, governments should provide financial incentives for environmental
982 remediation in rural areas.

983

984 **Disclosure Statement**

985 No potential conflict of interest was reported by the authors.

986

987 **Author Contributions**

988 Conceptualization: A.P.O., J.Z.L., J.P.M., L.M.S.; Methodology: A.P.O., J.Z.L., J.P.M.;

989 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.;

990 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.;

991 Writing – Review & Editing: V.G.S.R., E.L.G.E.; Visualization: A.P.O., J.Z.L., J.P.M.,

992 L.M.S.; Supervision: A.P.O.; Project administration: A.P.O.; Funding Acquisition: V.G.S.R.,

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