

**Designing advanced biochar products for maximizing greenhouse gas mitigation potential**

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28 **Abstract**

29 Greenhouse gas (GHG) emissions from agricultural operations continue to increase. Carbon  
30 (C) enriched char materials like biochar have been described as a mitigation strategy.  
31 Utilization of biochar material as a soil amendment has been demonstrated to provide  
32 potentially greater soil GHG suppression due to its interactions in the soil system. However,  
33 these effects are variable and the duration of the impact remains uncertain. Various (nano)  
34 materials can be used to modify chars to obtain surface functionality to mitigate GHG  
35 emissions. This review critically focusses on the innovative methodologies for improving  
36 char efficiency underpinning GHG mitigation and C sequestration.

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38 **Keywords**

39 Activation, Charcoal, Carbon dioxide, Grafting, Soil health, Nitrous oxide, Plant nutrients

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## 49 **1. Introduction**

50 Rising emission of greenhouse gases (GHG) from agricultural lands, due to anthropogenic  
51 activities of burning fossil fuels and land-use changes (deforestation) are major contributors  
52 to global warming [1]. Agricultural activities collectively contribute between 5 to 6  
53 petagrams carbon dioxide (CO<sub>2</sub>) equivalents (approximately 10 to 12%) of the total global  
54 GHG emissions [2]. This is primarily due to nitrous oxide (N<sub>2</sub>O) emissions from mineral and  
55 organic fertilizers applied in soils. Additionally, burning of fossil fuels and deforestation have  
56 resulted in an increase of global surface temperature up to 0.8 °C during the 20<sup>th</sup> century,  
57 which likely will increase to 1.4 °C–5.8 °C in the 21<sup>st</sup> century [3, 4]. This increase in global  
58 temperature is attributed to the greenhouse effect caused by CO<sub>2</sub> as the major source of GHG.  
59 However, the global warming potential (GWP) of N<sub>2</sub>O is 298 times greater than CO<sub>2</sub> [4, 5],  
60 so the former can trap more heat in the atmosphere compared to the latter. Among all the  
61 sectors that are responsible for GHG production, agriculture contributes a significantly large  
62 share [3].

63 Application of organic amendments in agricultural soils can alter GHG emissions, while  
64 improving soil physical, chemical, and biological properties [6]. To mitigate GHG emission,  
65 carbonized biomass such as biochar, graphite, charcoal and activated carbon (AC) can be  
66 used [7, 8]. Biochar materials are solid residuals from pyrolysis processes, and can contain up  
67 to and indeed beyond 80% C, representing around 30-50% of the original biomass C. They  
68 can lower GHG emissions, both directly and indirectly. These direct and indirect effects and  
69 their outcomes are summarized in Figure 1. The nomenclature of char materials has not been  
70 standardized fully across all scientific fields. They can be produced during combustion,  
71 gasification and pyrolysis of any C containing material, like burning of biomass, incomplete  
72 combustion of fossil fuel (black carbon; soot), and production of hydrocarbons (carbon black;  
73 soot) [9, 10]. Since the mid-1990s char materials attracted enormous attention because of

74 their various beneficial applications [11]. Char materials can (a) potentially sequester C in  
75 soil [12-14], (b) reduce nitrogen (N) loss from soil in terms of N<sub>2</sub>O emission [15] and  
76 ammonia (NH<sub>3</sub>) volatilization [16, 17], (c) improve nutrient retention capacity of soils and  
77 reduce runoff and leaching losses [18-21], (d) improve plant growth [9], (e) remediate  
78 contaminated soil and water [22-25], and (f) improve soil health [11, 18] by supplying  
79 nutrients to the roots and microbes directly from the source, or indirectly by their ability to  
80 sorb and retain nutrients [26, 27]. Chars have also been shown to increase N-use efficiency  
81 both in a short glasshouse study [28] and field scale studies [29]. The sorbed nutrients  
82 gradually release from char and become slowly available to plant roots and microorganisms.  
83 A meta-analysis of impacts of biochar on soil emissions of N<sub>2</sub>O has shown that on average, a  
84 54% lowering of emissions may be achieved [15]. It was shown that woody and herbaceous  
85 feedstock had a greater impact on lowering of emissions than biochars derived from manure  
86 or biosolid. Shafeeyan, Daud [13] reported that soil treated with AC (plum shell based  
87 granular AC) adsorbed more CO<sub>2</sub> than untreated soil. Aguilar-Chávez, Díaz-Rojas [14] also  
88 found that charcoal with an application rate of 4.5% could increase soil CO<sub>2</sub> sorption by more  
89 than 37%. Biochars have been shown to increase soil C density in the field both through the  
90 increased C added via biochar, and also through new plant C allocation [29]. Char materials  
91 are emerging as a low-cost sorbent for reducing risks of inorganic pollutants (lead, copper,  
92 arsenic, aluminum and chromium) in soils [30-32], and lowering the concentration or  
93 bioavailability of organic pollutants arising from various agricultural, industrial and farming  
94 activities [33, 34]

95 [Figure 1]

96 Salient characteristics of char materials for GHG reduction include surface area, functional  
97 groups, pore size, pore space, elemental composition, pH, and sorption sites. The presence of  
98 functional groups such as the carboxylic or hydroxyl groups on biochar surfaces can adsorb

99 GHG and react with them (e.g., N<sub>2</sub>O) thus reducing their emissions when compared to  
100 unamended soil [35]. To further improve the efficacy of char materials in lowering GHG  
101 emissions, they can be modified to obtain specific chemical characteristics, elemental  
102 composition and structural features [36]. Char materials can also be a suitable support/host  
103 matrix for incorporating highly reactive nanoparticles, which can enhance the mitigation of  
104 GHG emissions [37]. However, more research is required to identify the characteristics of  
105 chars that can be improved by combining other materials. Therefore, this paper aims to  
106 review the existing and potential innovative methodologies for improving char efficiency  
107 underpinning GHG mitigation and C sequestration in the context of a system where improved  
108 plant productivity is sought.

## 109 **2. Greenhouse gasses and the environment**

110 Increased GHG emission is a serious threat to our environment [38]. Due to anthropogenic  
111 activities, the temperature has increased by 0.6 °C–0.8 °C globally between 1951–2010 [3].  
112 Emissions of GHG and changes in land use patterns including agriculture and urbanization  
113 are the most important elements which impact the climate [39]. Wastewater treatment plants  
114 and livestock are also important sources of GHG emission and onsite aerobic biological  
115 wastewater treatment is the highest contributor in an urban setting [40, 41]. Carbon dioxide  
116 contributes the highest proportion to the greenhouse effect because of its high concentration  
117 in the atmosphere [4]. Concentrations of the greenhouse gasses, e.g., CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>O, due  
118 to anthropogenic activities are increasing at a rate of 0.4, 0.6 and 0.25% per year, respectively  
119 [42].

120 Because of different atmospheric half-lives and radiative forcing of the GHGs, they are  
121 assigned a different GWPs [43]. Trace gases including CH<sub>4</sub> and N<sub>2</sub>O absorb nearly 300 and  
122 25 times more infrared radiation, respectively, than CO<sub>2</sub>, and contribute 15 and 5-6%  
123 anthropogenic greenhouse effect [44].

124 Among various sectors, agriculture contributes 20% of total GHG emissions (N<sub>2</sub>O, CO<sub>2</sub>, and  
125 CH<sub>4</sub>) [45]. Land conversion from forests and pastures to croplands accounts for about 12-  
126 20% of the GHG emissions [46]. Waste management activities also contribute to the  
127 emissions (4%), while disposal of waste in landfills generates CH<sub>4</sub>. Livestock are responsible  
128 for about 12% anthropogenic GHG emission [47, 48].

129 Climate change can have an adverse impact on agricultural production and environmental  
130 quality. For example, as estimated by statistical models, the wheat yield in India dropped by  
131 36% in 2010 as compared to 1980, because of climate change and emissions of other  
132 pollutants [49]. The increasing concentrations of atmospheric GHGs have catalyzed the  
133 chances of drought and flood in different regions in India [49]. An overall reduction in the  
134 quality of available water runoff was also noted [50]. Furthermore, the increasing CO<sub>2</sub> levels  
135 affected soil microbial activity and water content. Furthermore, van Groenigen, Osenberg  
136 [51] found that increases in CO<sub>2</sub> level triggered N<sub>2</sub>O emission from upland soils and CH<sub>4</sub>  
137 emission from paddy soils and natural wetlands.

138 Investments into field improvements of agriculture have avoided up to 161 gigatons of CO<sub>2</sub>  
139 emissions since 1961 [49]. Changing the food habits, for example, shifting from red meat and  
140 dairy products to chicken, fish, and vegetables based diets could potentially decrease the  
141 GHG emissions [52]. Also, changes in agricultural practices such as growing lignocellulosic  
142 energy crops, e.g., willow (*Salix* spp.) and elephant grass (*Miscanthus x giganteus*), which  
143 give much higher yield, would lower GHG emission in comparison to arable crops [53].  
144 Adapting less intensive tillage operation is also a well-known strategy to tackle CO<sub>2</sub> emission  
145 from soils [54, 55].

146

147

148 **3. Nitrogen dynamics and carbon cycle**

149 **3.1. Nitrogen dynamics and gaseous N emissions**

150 It was reported that an average 4-6 teragram (Tg) of N<sub>2</sub>O-N is being released into the  
151 atmosphere annually through agricultural activities, mainly from the use of mineral and  
152 organic N fertilizers [56]. An emerging pool of information shows that biochar, or indeed, a  
153 biochar system, is able to provide opportunities for mitigation of N<sub>2</sub>O emissions through  
154 altered N and C cycling [59]. Nitrogen is an important nutrient for plant growth,  
155 development, and reproduction. Most plants access N from soil, either through uptake of  
156 mineral N, or through biological N<sub>2</sub> fixation. When N is added to the soil, it undergoes  
157 various transformation processes and can produce gaseous products including ammonia  
158 (NH<sub>3</sub>), N<sub>2</sub>O and N<sub>2</sub> (Figure 2). The loss of N through gaseous emissions decreases the  
159 amount of soil available N to plants and contributes to GHG inventories.

160 [Figure 2]

161 **3.2. The carbon cycle and CO<sub>2</sub> emissions**

162 Carbon is an important macro element for plant development, and plants usually take up C as  
163 CO<sub>2</sub> from air during photosynthesis [57]. Carbon circulates in an endless process between the  
164 earth's surface, oceans, plants and soils (Figure 3). Through this process C is converted into  
165 CO<sub>2</sub> as a natural component of the atmosphere that protects the earth's surface from radiation  
166 by reflecting it back into the atmosphere. This phenomenon causes some heat to be generated,  
167 which can result in rising temperatures. For this reason CO<sub>2</sub> is called a GHG [58]. When the  
168 production of CO<sub>2</sub> exceeds the buffer capacity of the earth's ecosystem, it can result in global  
169 warming, i.e., the earth retains heat.

170 Utilization of biofuel C (e.g., that from maize or sugar cane) instead of fossil fuel can reduce  
171 CO<sub>2</sub> emissions, because biofuel C is mainly derived from the atmosphere via current

172 photosynthesis (fossil fuels result from photosynthesis millions of years ago) [59].  
173 Production of CO<sub>2</sub> due to various anthropogenic activities (industry and agricultural  
174 activities) have increased its concentration from 284 ppm in 1832 to 397 ppm in 2013 [60].  
175 As noted, a large amount of CO<sub>2</sub> is produced from the agricultural sector. Schimel [61]  
176 reported that the agriculture sector contributes about 20% of total anthropogenic CO<sub>2</sub>  
177 emission. Anthropogenic CO<sub>2</sub> comes from several sources including biomass burning, tillage  
178 practice, accelerated soil organic matter (SOM) mineralization, and microbial decay [4]. Soil  
179 is a large global C sink being around 2500 gigatons (Gt C), including about 1550 Gt of soil  
180 organic carbon and 950 Gt of soil inorganic carbon [62].

181 [Figure 3]

#### 182 **4. Properties of biochar which alter N cycling, N<sub>2</sub>O, and CO<sub>2</sub> emissions**

183

184 Meta-analysis of the impacts of biochar on N<sub>2</sub>O emissions have shown that the properties of  
185 biochar are critical in controlling emissions. For example, Cayuela, Van Zwieten [15] showed  
186 that biochars derived from crop and woody residues resulted in over a 50% decrease in  
187 emissions, while biochars from other feedstock might not provide, on average, any  
188 meaningful opportunities for lowering emissions. The quantity of biochar applied to soil has  
189 been shown to be important, with mitigation opportunities only becoming evident when  
190 biochar was amended at or above 2% w/w into soil [15]. Slight mitigation opportunities were  
191 detected in a meta-analysis by Cayuela, Van Zwieten [15] when biochar was amended at 1-  
192 2% w/w to the soil. Interestingly, biochar amendments were effective at lowering emissions  
193 in alkaline, neutral and slightly acid soils, but when pH was below 5.5, no effect was detected  
194 [15]. This may present opportunities for modification of biochars, or indeed selection of  
195 biochars that can modify soil pH to lower N<sub>2</sub>O emissions. Most recently, Cayuela, Jeffery  
196 [63] updated the previous meta-analysis [15] with new data, and they showed that an  
197 important factor in the mitigation of N<sub>2</sub>O was the molar H/C ratio of the biochar. Biochars

198 with a molar H:C<sub>org</sub> ratio of <0.3, indicative of a high degree of aromatic condensation,  
199 lowered N<sub>2</sub>O emissions by 73%, while biochars with a molar H:C<sub>org</sub> ratio of >0.5 were less  
200 effective, lowering N<sub>2</sub>O emissions by 40%. This was not a surprising result in light of  
201 previous information showing that woody biomass and crop residue biochars (which tend to  
202 have lower molar H/C ratios) were more effective than manure-based biochars. Clearly, there  
203 are both physicochemical and biological controlling factors in the mitigation of N<sub>2</sub>O.

204 Denitrification, a biologically “broad process” [64], requires both a labile C and N supply to  
205 function in soil, therefore biochars that limit the bioavailability of either of these substrates  
206 may be expected to lower emissions of N<sub>2</sub>O. Evidence exists that biochar can limit the supply  
207 of mineral N [35, 65], thus lowering the substrate needed by denitrifiers. Similarly, biochars  
208 were shown to induce negative priming effect [66, 67] and to sorb labile C in soil. For  
209 example, Sarmah, Srinivasan [68] showed that biochars with higher production temperatures  
210 and associated surface areas exhibited a greater sorption capacity of hormones when amended  
211 into dairy farm soils. Similarly, Martin, Kookana [33] showed that biochar amended soils  
212 sorbed a greater amount of herbicides. Optimizing the sorptive capacity of biochars presents  
213 opportunities to restrict C and N substrates required by denitrifiers, and therefore provides an  
214 opportunity to lower the emission of N<sub>2</sub>O. However, the longevity of these traits in soil  
215 remains unknown. Biochar addition to soil can change soil properties that influence  
216 denitrification. For example, biochars were shown to ameliorate soil compaction and bulk  
217 density [69] which would affect denitrification. A wood based biochar at 5% w/w increased  
218 porosity (measured by X-ray computed tomography or  $\mu$ CT) in a Vertisol from 7.5 to 13.4%  
219 [70]. Importantly, increases in pore connectivity were observed across two clay-dominated  
220 soils (Vertisol and Ferralsol) and a sand-dominated soil (Arenosol) over 15-month  
221 incubation. Soil with 1% biochar had an increase in the rate of drainage in the Vertisol and a  
222 20% increase in the available water content of an Arenosol [70]. These changes in the soil

223 physical characteristics suggested that biochar might allow faster drainage in clay soils and  
224 allow an improved air flow into the soil profile, and therefore reduce waterlogging conditions  
225 that are conducive to denitrification. This requires further exploration and testing at both the  
226 laboratory and field scales.

227 Some biochars were shown to carry organic compounds that could impact microbial toxicity  
228 in soil. For example, they might contain polycyclic aromatic hydrocarbons (PAHs),  
229 polychlorinated compounds, dibenzodioxins and furans, which would form during pyrolysis  
230 of the feedstock [71, 72]. PAHs were found to modify the nitrification processes and  
231 denitrifying bacterial communities in soil [73, 74]. Spokas [75] investigated the direct impact  
232 of biochar-released ethylene on N<sub>2</sub>O production from the soil. The result supported the  
233 possibility of introducing compounds that modify N cycling, nitrification and denitrification  
234 reactions in the soil. For example, 3, 4-dimethylpyrazole phosphate (DMPP) is a nitrification  
235 inhibitor that has been studied extensively with the aim of improving N-use efficiency and  
236 lowering N<sub>2</sub>O production from the soil. Opportunities exist to use biochar as a carrier for this  
237 nitrification inhibitor. However; biochar produced from eucalyptus wood with a large surface  
238 area (426.4 m<sup>2</sup> g<sup>-1</sup>) reduced the inhibitory effect of another nitrification inhibitor  
239 dicyandiamide (DCD) in a neutral Cambisol [76]. This work demonstrated that sorptive  
240 biochars were more efficient at reducing the efficacy of the nitrification inhibitor than less  
241 sorptive ones.

242 Biochars' influence on the soil microbial communities that are involved in N cycling was  
243 reported [65], however, the authors suggested that changes in environmental conditions  
244 resulting in N<sub>2</sub>O formation were more important than the changes in size or activity of soil  
245 microbial communities. Of particular interest are the redox or electron shuttling properties of  
246 biochar [77]. Iron (Fe) is an important element in N transformation in soil. Li, Yu [78]  
247 showed that reduction and oxidation of N compounds were enhanced when Fe and organic

248 matter were also oxidized or reduced. Reactions between  $\text{Fe}^{2+}$  and either  $\text{NO}_3^-$  or nitrite ( $\text{NO}_2^-$   
249 ) to produce  $\text{N}_2$  (reduced species) were energetically favorable. These results suggested that  
250 Fe content of biochars should be enhanced before application to soil, or indeed, feedstock  
251 such as biosolids should be used [79] which would result in an increase of the Fe content. In  
252 the study by Van Zwieten, Kimber [79] lower emissions of  $\text{N}_2\text{O}$  from a Ferrosol were  
253 detected with a high Fe-biochar compared to other biochars produced from sludge and wood  
254 chips.

255 Pyrolysed biomass has created research interest as it has been shown to lower greenhouse gas  
256 emissions and increase soil C content. Carbon sequestration is one of the key benefits of  
257 using char materials as a soil amendment. It has been estimated that chars produced from  
258 natural wildfires may represent 15-20% of total C in temperate and coniferous forest soils  
259 [80]. In one study, Spokas, Koskinen [81] found that biochar application reduced soil  $\text{CO}_2$   
260 emissions. Another study by Case, McNamara [82] also reported that biochar addition at  $49 \text{ t}$   
261  $\text{ha}^{-1}$  in a field trial can suppress soil  $\text{CO}_2$  emission up to 53%. The reason of lowering  $\text{CO}_2$   
262 emission following biochar amendment may be due to a negative priming effect (outlined in  
263 section 6) whereby new C (e.g. Root exudates etc.) in soil are established and not available for  
264 microbial degradation. However, other studies have observed that biochar addition in soil has  
265 little or no effect on  $\text{CO}_2$ ; for example's Wu, Jia [83] found that biochar addition at 0.67,  
266 1.68% rate did not affect soil  $\text{CO}_2$  emissions but lowered  $\text{N}_2\text{O}$  emissions significantly.

267 This section has demonstrated pathways in which biochars may alter N cycling and hence  
268 emissions of  $\text{N}_2\text{O}$  (Figure 4). Modifications of biochars to optimize soil pH, soil physical  
269 characteristics, redox active elements and to reduce toxic components provide opportunities  
270 to mitigate  $\text{N}_2\text{O}$  and  $\text{CO}_2$  emissions. It will be critical, however, to first understand the key  
271 processes of formation of modified biochars for each soil/climate/agroecosystem, before  
272 biochars can be designed to lower emissions of  $\text{N}_2\text{O}$  and  $\text{CO}_2$ .

273 [Figure 4]

## 274 **5. Char materials for greenhouse gas mitigation**

275 Char materials may be used to mitigate climate change resulting from agricultural GHG  
276 emissions [9, 12]. The degradation rate of char materials is slow and these properties may be  
277 exploited in the development of slow release fertilizers [84]. Chars are generally produced as  
278 a by-product during biofuel processing or during the pyrolysis of organic residues from  
279 various biomasses, woods and hydrocarbons to make bioenergy [85]. The properties of char  
280 materials can vary depending on varieties of feedstock materials used for their preparation  
281 and pyrolysis (or burning) conditions [11, 28, 35, 86, 87]. Table 1 shows specific production  
282 methods and characteristics of various char materials.

283 [Table 1]

### 284 **5.1. Biochar**

285 Biochar has multi-purpose properties that make it a unique amendment to improve soil  
286 health, and it also can remediate environmental contaminants [22, 23]. Biochar is used for  
287 mitigating GHG emissions due to its relative stability, ability to act as a long-term nutrient  
288 sink in the soil and higher nutrient retention capacity than other organic amendments [9, 86].  
289 It has a range of surface functional groups that can adsorb heavy metals from soil and aquatic  
290 environments [32, 86, 88-90]. It can also reduce GHG emissions, such as N<sub>2</sub>O, by adsorbing  
291 and retaining N in the soil. Woolf, Amonette [91] reported that the annual net emissions of  
292 GHG (CO<sub>2</sub>, N<sub>2</sub>O, and CH<sub>4</sub>) were reduced up to 12% by adding biochar in the soil. In support  
293 of this estimate, many researchers have reported the successful application of biochar as a  
294 soil amendment for C sequestration [12, 92-94]. Biochar can also provide direct agronomic  
295 benefits to plants by supplying nutrients [N, phosphorus (P), potassium (K) and sulfur (S)],  
296 and provide indirect benefits through the sorption of elements to retain essential nutrients [26,

297 27, 88, 95]. Table 2 shows a compilation of some recent reports on the effect of different  
298 types of biochars on GHG emissions and soil health.

299 [Table 2]

300 Biochar can induce microbial immobilization of nutrients such as N, P, and S in soil, thereby  
301 reducing loss of these nutrients through leaching and gaseous emission (e.g., N). Overall,  
302 biochar not only improves the agricultural productivity but also sequesters C in the soil, and  
303 thus protects the global environment by reducing GHG emissions as well as nutrient leaching  
304 from the soil [96].

305

## 306 **5.2. Charcoal**

307 Charcoal is generally used as a fuel source and it is produced from wood [97]. Charcoal is a  
308 much better fuel than wood because of its lower transport and handling cost compared to  
309 firewood [98]. Charcoal has been used for domestic purposes for manufacturing of various  
310 industrial chemicals like carbon tetrachloride, sodium cyanide, and carbon disulfide [99], and  
311 as a reductant in steel manufacturing. During thermal degradation and carbonisation, the  
312 volatile components are removed from the biomass. Charcoal has 85-90% fixed C that can  
313 provide a major C sink in the soil [100]. It has specific properties that can help improve soil  
314 health (e.g., appropriate pH and water holding capacity) and reduce the rate of N  
315 mineralization [101]. Zimmerman [102] reported that charcoal is resistant to microbial  
316 degradation, and hence can store C in the soil for long periods of time.

317 The reduction of CO<sub>2</sub>, N<sub>2</sub>O, and CH<sub>4</sub> emissions by adding charcoals to the soil is not always  
318 uniform (Table 2). The addition can show no effect or even negative effects on the reduction  
319 of GHG emissions depending on feedstock types and soil properties [97, 103].

### 320 **5.3. Activated carbon**

321 Activated carbon is an important material because of its widespread use as an adsorbent,  
322 catalytic and catalyst support [104, 105]. This material can be modified in various ways to  
323 increase its surface characteristics and thus to enhance mitigation of GHG emissions as well  
324 as adsorption of heavy metals in soil. Activated carbon is an important adsorbent especially  
325 due to its high micro- and meso-porosity, surface acidic groups, and apparent surface area  
326 that increase its activity to adsorb heavy metals like Cd, Pb, and Cu [105, 106]. Two  
327 different methods can be used to prepare AC: physical and chemical activation. The physical  
328 activation method involves carbonization of raw materials and subsequent activation at high  
329 temperature in a CO<sub>2</sub> or steam environment. Steam activation flushes away the oil residues  
330 and it opens up the planar sheets. Steam activation method could increase the surface area,  
331 micro-porosity and mesopore volume of the products [107]. Chemical activation involves  
332 carbonization of previously activated raw materials by potassium hydroxide (KOH) and  
333 phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) [107]. Adsorption of CO<sub>2</sub> requires solid sorbents with a high CO<sub>2</sub>  
334 selectivity and capacity. Activated carbon can capture CO<sub>2</sub> by solid adsorption because of its  
335 highly porous structure [108]. The adsorption capacity of AC is based on the short-term  
336 physical adsorption and it can be improved by introducing NH<sub>3</sub> on its surface for reducing  
337 CO<sub>2</sub> emission [108, 109] (Table 3). Ammonia decomposes at high temperatures and produces  
338 some radicals (NH<sub>2</sub><sup>•</sup>, NH<sup>•</sup>, H<sup>•</sup>) and these radicals react with the C surface to form reactive  
339 functional groups (-NH<sub>2</sub>-, -CN, pyridinic, pyrrolic and quaternary N) [108].

340 [Table 3]

### 341 **6. Priming effect of char materials on soil carbon and nutrient cycling**

342 The priming effect (PE) refers to stimulation or stabilization of native soil C through the  
343 application of nutrients or organic residues [110]. The PE can be both positive or negative  
344 and may occur simultaneously in soil [111]. A positive PE means a net increase in the release

345 of C and nutrients from native SOM caused by added substrates, and the opposite effect (i.e.,  
346 immobilization of C and nutrients) for a negative PE [111, 112]. Both positive and negative  
347 PE can be caused by direct or indirect alterations of biotic and abiotic processes in the soil.  
348 Because char materials contain C and other nutrients such as N and P, they can cause a PE on  
349 C and these nutrients in the soil. Most of the times the PE refers only to C and nutrients that  
350 undergo microbial transformation (e.g., N, P, and S) [110, 113]. Figure 5 presents an  
351 overview of intrinsic char properties and external factors (that char interacts with) and  
352 mechanisms leading to either a positive or negative PE in soil.

353 Certain char properties such as labile C content, surface area, porosity, pH, CEC, C-to-  
354 available nutrient ratios, and volatile organics can directly impact priming of native SOM  
355 [67, 97, 114, 115]. These properties can be altered by the condition of char production (e.g.,  
356 pyrolysis temperature, slow or fast pyrolysis), feedstock type (e.g., C-rich and nutrient poor  
357 vs. C poor and nutrient rich biomass), or external modifications of char surfaces, pore spaces,  
358 or chemistry. The external modifications of char can result from natural ageing, clay addition,  
359 chemical oxidation, steam activation, or impregnation during or post-pyrolysis of feedstock  
360 biomass [87]. Char in soil could interact with soil C content, texture, clay mineralogy, pH,  
361 temperature, and root C input to alter the magnitude and direction of PE, which may vary  
362 with char type, char ageing, and soil type [115, 116]. A recent meta-analysis by Maestrini,  
363 Nannipieri [117] showed that labile C components in char would induce positive priming  
364 (increase native SOM decomposition by 15%) by triggering the microbial activity within a  
365 few days to weeks, while physicochemical protective mechanisms may induce negative  
366 priming over a longer term. A range of mechanisms have been proposed in a recent review  
367 [112] for the PE of char involving changes in biotic processes (e.g., acceleration of microbial  
368 metabolism, enzyme production and activity, shifts in microbial community) or abiotic  
369 processes (e.g., sorption or immobilization of native substrates, microbial enzymes, biochar-

370 clay interactions) (Figure 5). The char products and their properties could be modified during  
371 or after pyrolysis with the aim to either enhance (i) nutrient release and availability over a  
372 short-to-medium timescale to support soil fertility and plant growth *via* positive priming, or  
373 (ii) native SOM (C and nutrients) storage to support long-term soil productivity and combat  
374 climate change *via* negative priming. However, nutrients would become less available to  
375 plants if certain properties such as char's sorption ability are enhanced, e.g., by pyrolysis at  
376 high temperatures or *via* physical (steam) or chemical activation without altering certain  
377 properties or introducing substrates that enhance labile C components to promote positive  
378 priming. It is important to alter char properties in such a way that the modified products  
379 enhance both positive and negative PE. However, limited research has been conducted to  
380 understand the PE of modified chars on native or freshly added SOM.

381 [Figure 5]

## 382 **7. Modification of biochar surface properties**

383 Global interest in using biochar soil amendments has risen predominantly to improve soil  
384 fertility [27] and crop productivity [118, 119] as well as to increase C sequestration [12].  
385 Biochar can boost soil fertility levels by the release of nutrients [120] and through improved  
386 nutrient retention via the reactive functional groups [121, 122]. Char materials are rich in C  
387 content and stable in form so that they can create a long term C or another nutrient sink in the  
388 soil [123]. As noted, biochar addition could improve soil quality as well as reduce GHG  
389 emissions [12, 85, 124]. The addition of biochar materials in soils could also act as an ideal  
390 immobilizer of various contaminants such as antibiotics.

391 Biochars are increasingly being recognized as multi-functional materials. As such, the  
392 chemical characteristics of biochar surfaces are now more closely scrutinized to maximize  
393 their role in abiotic and biotic reactions [125]. For example, biochars are known to impact  
394 reactions involving nutrient cycling, metal chelation and stabilization, and redox reactions,

395 which are known to be important for altering plant and microbial responses [125]. Because of  
396 these interactions, there is considerable interest in applying biochar technology into new  
397 areas including environmental and energy sectors [91].

398 Recently, the concept of designing biochars for specific application purpose has been  
399 proposed [37]. Creating designer biochars is reported to be a more effective approach than  
400 simply applying biochar indiscriminately [126]. Scientists have advanced the designer  
401 biochar concept by modifying the biochar surface using physical, chemical, and nano-sized  
402 materials (Table 4). The purpose of this strategy is to improve the physicochemical and  
403 sorptive characteristics of biochars for novel uses such as heavy metal binding [23, 89],  
404 organic pollutant sorption [127], and water purification [128].

405 [Table 4]

#### 406 **7.1. Modification processes**

407 Biochars can be modified using several processes (Table 5). The selection of an individual  
408 modification method depends on feedstock type and the target problem (i.e., soil fertility,  
409 metal immobilization, etc.). Available feedstock for biochar production includes wood,  
410 coconut shells, peat, [129], grasses, nut shells, [130], animal manures [131], etc. The  
411 feedstock can be treated either pre- or post-pyrolysis to gain desirable properties. For  
412 example, biochars can be treated to have a higher capacity for specific interactions with  
413 organic and inorganic chemicals because they have a high surface area, high degree of  
414 physicochemical attraction between the adsorbate and C surface, and the appropriate pore  
415 size distribution. As shown in Table 5, during the physical processes of biochar treatment,  
416 gases (CO<sub>2</sub>), air [132, 133] and steam [134] were introduced during the carbonization phase  
417 of pyrolysis (700 °C). Higher activation temperatures (700 to 900 °C) were needed to further  
418 attenuate the material to increase the surface area and O-containing functional groups [135].

419 [Table 5]

### 420 7.1.1. Impregnation

421 Impregnation is a process where guest elements (usually metals) are incorporated into the  
422 char surface through prolonged wet contact [136]. Following impregnation, char materials are  
423 likely to impact GHG emission through electrostatic interaction between the impregnated  
424 metal cations and negatively charged C containing functional groups in the SOM (e.g.,  
425 carboxylic group and lactonic group) [137, 138]. Char modification by impregnation is likely  
426 to make them more active in terms of retaining heavy metals from aqueous solution [139,  
427 140]. For example, Wang, Sheng [141] reported that manganese (Mn) impregnated biochar  
428 increased the removal efficiency of Pb from 6.4 to 98.9%. Agrafioti [138] also found that  
429  $\text{Ca}^{2+}$  modified biochar demonstrated a high As removal capacity (>95%). Zhang, Gao [34]  
430 prepared iron impregnated biochar with ferric oxide ( $\text{Fe}_2\text{O}_3$ ) and found that the modified  
431 biochar had a strong sorption of As in aqueous solutions. Nitric acid ( $\text{HNO}_3$ ) is frequently  
432 used to remove intrinsic ash and tar of biochar before impregnation. Impregnation of biochar  
433 as a catalyst has been reviewed recently by Qian, Kumar [142]. The following reaction  
434 scheme shows (Figure 6) how Fe modified biochar can reduce  $\text{N}_2\text{O}$  emission.

435 [Figure 6]

### 436 7.1.2. Oxidation

437 Oxidation is another modification process where liquid or gaseous compounds (e.g.,  
438 inorganic acids) are used to modify and purify chars [132, 143]. Two types of oxidation,  
439 liquid phase oxidation and gas phase oxidation are generally used. In the liquid phase  
440 oxidation process, strong acids like  $\text{HNO}_3$  [143], a mixture of  $\text{HNO}_3$  and sulfuric acid  
441 ( $\text{H}_2\text{SO}_4$ ) [144], strong oxidants like potassium permanganate ( $\text{KMnO}_4$ ) in acid solution, or  
442 other chemical mixtures, such as hydrogen peroxide/ sulfuric acid ( $\text{H}_2\text{O}_2/\text{H}_2\text{SO}_4$ ) and

443 hypochlorite solution ( $\text{HClO}_4$ ) [145, 146] have been used to modify, or purify chars. Gaseous  
444 phase oxidation includes the use of  $\text{CO}_2$  and  $\text{O}_2$  gas for modifications [132, 133]. The use of  
445  $\text{KOH}$  is also known to increase the porosity and surface area of the biochar [142]. For  
446 example, Zhang, Gao [34] developed  $\text{KOH}$ -activated biochar with a surface area of up to  
447  $3,500 \text{ m}^2/\text{g}$  with a large pore volume ( $1.3\text{-}1.94 \text{ cm}^3/\text{g}$ ).

448 Oxidation can modify chars in two different ways: firstly, by opening the pores in char  
449 products and subsequent filling with metals, and secondly, by the addition of new functional  
450 groups on the surface of chars. Chemical activation which utilizes acids [phosphoric acid  
451 ( $\text{H}_3\text{PO}_4$ ),  $\text{HNO}_3$ , and  $\text{H}_2\text{SO}_4$ ] and bases [ $\text{KOH}$ , sodium hydroxide ( $\text{NaOH}$ )], is used to modify  
452 biochars because they have both dehydration and oxidation characteristics. The feedstock is  
453 usually mixed or soaked in a solution of these chemicals before pyrolysis and activation  
454 (Table 4). The use of typical acids and bases modifies the biochar by introducing O-  
455 containing functional groups into the C matrices [143-145]. Strong oxidizers such as  $\text{KMnO}_4$   
456 and  $\text{HClO}_4$  also can be used to modify or purify biochars [145, 146]. The degree of  
457 modification is also temperature dependent because at higher activation temperatures more  
458  $\text{O}_2$  is added to the rings.

459 Chemical phase oxidation through impregnation of biochars can be completed using metals  
460 [e.g., Magnesium ( $\text{Mg}$ ), iron ( $\text{Fe}$ ), aluminium ( $\text{Al}$ )] that are incorporated into the structural  
461 makeup of the biochars [136]. This process also improved the compatibility of chars with  
462 other materials such as nanomaterials [145-147]. Following impregnation, biochars can enter  
463 into abiotic and biotic reactions that impact nutrient availability [125], GHG production [137,  
464 138], and metal binding [139, 140].

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### 467 7.1.3. Grafting

468 The last form of activation is grafting (Table 4). The basic premise of this method is that the  
469 surface properties of carbon nanotubes can be modified by the grafting of organic molecules  
470 onto them. The technique involves the immobilization of an initiator (Table 4; poly-styrene-  
471 N<sub>3</sub>) onto the tubes followed by surface-initiated polymerization of an organic compound (sec-  
472 butyl L-Li) to form a dense polymer material [148]. In this way, the tubes were made more  
473 structurally dense and could enter into secondary reactions such as binding of pollutants  
474 [149]. Grafting involved the fusion of guest molecules/elements onto the chars surface  
475 functional groups, using the condensation reaction [150]. Grafting through chemical  
476 functionalization has resulted in an outstanding compatibility between nano-materials and  
477 chars. However, information concerning the grafting of complex polymers on the surface of  
478 char materials in order to improve their ability to remediate contaminated environments is  
479 scant [151]. Grafting can be done with or without pre-oxidation. There is a range of  
480 compounds/materials that can be used to graft a char material, e.g., chitosan (natural  
481 biopolymer), polyallylamine hydrocarbon, and various nanocrystals [cadmium selenide- zinc  
482 sulfide (CdSe-ZnS) in chloroform (CHCl<sub>3</sub>), zinc oxide (ZnO) in ethanol and Fe<sub>2</sub>O<sub>3</sub> in  
483 aqueous solution] [147, 148, 152]. Grafted char shows a wide range of potential application  
484 such as use in biomaterials, bioengineering and emerging biotechnology.

## 485 7.2. Materials for char modification

486 A range of compounds/materials can be used to modify chars (Figure 7). However, selection  
487 of materials depends on the specific char characteristics that may need to be changed.  
488 Various types of materials that can be used to modify chars are listed below:

- 489 • Chitosan, a copolymer of 2-acetamido-2-deoxy- $\beta$ -D-glucopyranose and 2-amino-2-  
490 deoxy- $\beta$ -D-glucopyranose through a  $\beta$ -(1 $\rightarrow$ 4) linkage, is a naturally abundant  
491 polysaccharide and generally, it can be obtained by extensive deacetylation of chitin

492 [147]. Chitosan can be used as an organic glue to attach other materials on char  
493 surfaces [32].

494 • Zero-valent iron (ZVI) can be used to modify char. ZVI particles are inexpensive  
495 reducing agents and thus can be used to remediate various contaminants [32, 151,  
496 153]. An additional benefit is that the modified chars could be collected from solution  
497 by magnetic separation [154].

498 • Peroxide ( $H_2O_2$ ) could be used to modify chars. It was observed that application of  
499  $H_2O_2$  can increase the O-containing surface functional groups like the carboxylic  
500 group that can improve heavy metal sorption capacity [155].

501 • Some nanocrystals such as ZnO, CdSe-ZnS, ferrous oxide (FeO), calcium oxide  
502 (CaO), and ferric chloride ( $FeCl_3 \cdot 6H_2O$ ) can be used to modify chars to improve their  
503 physical, chemical, and biological properties [147, 148, 152].

504 [Figure 7]

## 505 **8. Summary and future research need**

506 This review presents multiple opportunities to optimize the efficacy of biochars for a range of  
507 purposes including mitigation of  $N_2O$ , stabilization of C in the soil and for reducing the  
508 toxicity of heavy metals in soil. Future research is required concerning the following topics:

509 • Production of chars from sewage sludge and waste materials that can be used to  
510 conserve nutrients in the soil and increase soil fertility.

511 • The introduction of cost-effective modification methods that can lower GHG  
512 emissions.

513 • The performance of field experiments with appropriate controls to get more realistic  
514 information.

515 • Modification of biochar properties using the methods impregnation, grafting, and  
516 oxidation to optimize outcomes for lowering GHG emissions. In particular, reactive

517 surfaces need to be studied in detail because they are critical for capturing and  
518 adsorbing GHGs and in improving the pore structure. These parameters are also  
519 important in developing slow release fertilizers and increasing water retention in soil.  
520 Nanomaterials may also increase the reactivity of char surfaces which may result in  
521 improved mitigation of soil GHGs.

522

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1094 Table 1: Different types of char materials, their production methods and applications

Product name	Raw materials/feed stock	Manufacture conditions (temperature/ time/ environment)	Size/shape/colour	Key properties/application	References
Biochar	A range of organic biomasses (plant residues, animal manures, waste materials etc.)	Temperature range: from 100 to below 800 °C (using pyrolyzer unit) Environment: N <sub>2</sub> gas and reduced oxygen condition Time: Both slow and fast pyrolysis	Black in color	<ul style="list-style-type: none"> <li>Improved characteristics such as high surface area, pore volume, surface functional groups</li> <li>Supply macro and micronutrients for plant growth</li> <li>Reduce heavy metal toxicity</li> <li>Improve soil physical, chemical, and biological properties</li> </ul>	[22, 156, 157]
Charcoal	Wood and other substance (animal and vegetable substance)	Temperature range: general range from 200 to < 700 °C Peak temperature: between 500 to 600 °C Environment: reduced oxygen condition Time: slow pyrolysis (12 to 14 days sometimes)	Light and black residue	<ul style="list-style-type: none"> <li>Act as a potential adsorptive material</li> <li>Improve plant growth and development</li> <li>Act as a soil conditioner</li> <li>Positively affect seed germination, plant growth, and yield</li> </ul>	[158-161]
AC	Chemical, physical, and heating of various carbonaceous materials	Temperature: High temperature (> 500 °C to 1000 °C) Time: > 10 h Activation: Steam/ CO <sub>2</sub> , polymerization of hydroxylated benzene and aldehyde in a solvent, chemical activation includes HNO <sub>3</sub> , H <sub>2</sub> SO <sub>4</sub> , NaOH, KOH, synthesis of a resorcinol- formaldehyde xerogel at specific condition to form AC	100µm to 600 mm, black in colour	<ul style="list-style-type: none"> <li>Improved physicochemical properties (surface area, extensive internal pore structure)</li> <li>It can be used in various industries (pharmaceuticals, mining, chemical, petroleum etc.) because of its high adsorptive properties</li> <li>Remove organic and inorganic species from industrial effluent</li> <li>Remove pesticides from drinking water</li> </ul>	[106, 162-165]

		xerogel			
Black carbon	An organic material ranges from slightly charred biomass to charcoal. It is chemically heterogeneous, biologically refractory class of carbon compound	Temperature: incomplete combustion of plant biomass, fossil fuel and biofuel (muffle furnace) Environment: Open burning Time: >8 h	Fine particulate matter (PM $\geq$ 2.5 $\mu$ m)	<ul style="list-style-type: none"> <li>• High specific surface area</li> <li>• Increase soil fertility by supplying a range of nutrients</li> <li>• It can cause serious health problem by carrying carcinogenic compounds</li> </ul>	[166-169]

1095 *AC: Activated carbon*

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1101 Table 2: Effect of biochar (BC) on greenhouse gas (GHG) mitigation and soil health

Stock material	Biochar application rate (ton/ha)	Pyrolysis temperature (°C)	Effect on GHG emission (N <sub>2</sub> O/NH <sub>3</sub> /CO <sub>2</sub> /CH <sub>4</sub> )	Nutrient retention/soil health	References
Poultry manure and stem wood	15	400 and 550	All BC application reduced N <sub>2</sub> O emission up to 73% due to increased sorptive capacity of biochars	Nutrient sorptive properties of biochar decreased NO <sub>3</sub> leaching and conserved N in the soil	[21]
Oakwood	5.5	650	Cumulative emissions of CH <sub>4</sub> , CO <sub>2</sub> , and N <sub>2</sub> O from biochar amended soils were reduced by 56, 92 and 43% respectively	BC application significantly increased soil C by 7%, increased surface area of soil by 15% and reduced bulk density by 13%	[170]
Willow, pine, maize and wood mixture (Spruce, Silver fir, Scots pine, Beech, Oak)	20	350, 450, 480, 550 and 650	Decreased N <sub>2</sub> O emission by 52% with BC treatment (on average)	BC application decreased N availability through biotic and abiotic immobilization processes	[171]
Walnut shell and pine chip biochar	10	Pine chip at 550 and wall nutshell at 900	BC application increased N <sub>2</sub> O emission (2.0 kg/ha N <sub>2</sub> O/yr for control and 4.14 kg/ha N <sub>2</sub> O/yr for BC)	Soil pH increased up to 0.5 to 1 unit, combination of increased N supply and increased rates of nitrification and denitrification	[172]
Green waste biochar	0 and 24	700	N <sub>2</sub> O emission reduced up to 96% with 10% BC application and 47% with 2% BC	BC application enhanced microbial N <sub>2</sub> O reduction and increased the abundance of microorganisms for N <sub>2</sub> -fixation	[173]

Maize stover and eucalyptus wood	15	350 and 550	BC application reduced N <sub>2</sub> O emission up to 10 to 41% and increased CH <sub>4</sub> emission up to 14-70%	Steam activated BC affect soil pH-buffer capacity, specific chemical toxins, metal complexes and precipitation produces resulting from BC application	[174]
Oil seed rape and wheat	28	400	Cumulative soil N <sub>2</sub> O production reduced by 91% and reduced cumulative denitrification by 37% with BC	BC application increased mineralization/nitrification, reduced denitrification and induced inorganic N immobilization	[175]
Cornstalk biochar	0, 3.2, 16 and 32	400	Increased N <sub>2</sub> O emissions by 17.5%, 92.3% biochar carbon and 16.8% of corn stalk carbon sequestered into the soil within 1 year	BC application increased soybean biomass up to 24% and wheat 32%	[176]
Poultry litter biochar	10	550	BC along with urea reduced N <sub>2</sub> O emission up to 69.4%	BC application with urea increased N uptake by corn plant, also increased plant available P and pH	[177]
Pine chip	5.7 and 18.8	550	Biochar application reduced N <sub>2</sub> O emission by 15.7% and CH <sub>4</sub> emission by 38.6%	Carbon content was increased about 74%. Soil properties like pH, CEC, N mineralization also increased with biochar application	[178]
Rice straw	7.5, 22.5, 24 and 48	-	N <sub>2</sub> O emission increased by 0.13 to 0.80 times but CH <sub>4</sub> emission reduced with biochar addition	Biochar application increased rice yield during two growing seasons	[179]

Hardwood (Oak, cherry, and ash)	50	400	Biochar application suppressed soil CO <sub>2</sub> emissions by 52% and net soil CO <sub>2</sub> eq. emissions by 55% but showed no significant reduction in N <sub>2</sub> O emissions	Biochar application increased carbon used efficiency and bioenergy crop production due to GHG balance	[82]
Bamboo char	20	700-800	Biochar application affects N <sub>2</sub> O and CO <sub>2</sub> emissions significantly throughout two years of cropping	Biochar with cow manure plot increased crop production by 110% in 2009 and 160-180% in 2010	[180]
Pig manure	1.2	550	Biochar with compost application reduced N <sub>2</sub> O emissions by 41% and increased cumulative CO <sub>2</sub> emissions by 31-45%	Biochar application increased C:N ratio, total C, and P	[181]
<i>Miscanthus × giganteus</i> straw	9.3	550-600	Biochar application had no effect on CO <sub>2</sub> emission but it reduced N <sub>2</sub> O emissions by 54%	Biochar application increased soil pH and showed significant positive effect on growth of forbs	[182]
Beech, hazel, birch and oak	33 and 66	500	BC application reduced N <sub>2</sub> O emission from 76% to 26% but no significant difference observed for CH <sub>4</sub> emission	Increased soil pH but there is no significant improvement of mineral N content after adding BC, also there is no negative impact on soil microorganisms	[183]
Macadamia nutshell and poultry litter	25	460 and 550	Poultry litter BC reduced NH <sub>3</sub> volatilization up to 70%	Increased N uptake capacity of wheat plant up to 76% with poultry litter BC	[17]

Wheat straw and corn stalk	13.22	250, 300, 350 and 400	Negative impact on GHG emission. BC application significantly increased N <sub>2</sub> O emission but it reduced CH <sub>4</sub> emission to some extent	No significant increase in rice yield with BC application and only 2% of BC N was available for plant uptake but it increased C and N content of soils	[184]
Wheat straw	0, 10 and 25	450	Reduced N <sub>2</sub> O emission up to 55% with 10 ton/ha BC and 96% with 25t/ha BC application. No significant effect on CO <sub>2</sub> emission	Activity of urease enzyme was increased with BC application compared to dehydrogenase and β-glycosidase	[83]
Maple and spruce sawdust	5	350 and 450	No significant treatment effects on fluxes of GHG (CO <sub>2</sub> , CH <sub>4</sub> , N <sub>2</sub> O) were observed in the field	BC application increased limited plant nutrients like P and Ca	[185]

1102 BC: Biochar; GHG: Greenhouse gas

1103 Table 3: Effect of charcoal and activated carbon (AC) on greenhouse gas (GHG) emissions

Char material	Stock material	Pyrolysis temperature (°C)	Effect on GHG emission (N <sub>2</sub> O/NH <sub>3</sub> /CO <sub>2</sub> /CH <sub>4</sub> )	References
Charcoal	Wood	200 – 300	≥ 1.5% application of charcoal reduced CO <sub>2</sub> emission ≥ 37% and N <sub>2</sub> O by 44% when 4.5% was the application rate	[14]
Charcoal	Wood	>200	There is no significant effect of adding charcoal on GHG mitigation	[103]
Charcoal	Coconut shell	450	There is no significant effect on CO <sub>2</sub> mitigation but it can mitigate N <sub>2</sub> O & CH <sub>4</sub> emission	[81]

Charcoal	Lump-wood	450	Decreased nitrate leaching significantly and increased CO <sub>2</sub> emission while the rate of charcoal application was higher also increased losses of C	[186]
Charcoal	Organic residue, wood	200 and 300	Lowest C mineralization was observed after charcoal treatment and there was no effect of charcoal on N <sub>2</sub> O emission	[160]
Ammonia modified AC	Palm shell based granular AC	Ammonia modification with pre-oxidation- air introduced at 400	CO <sub>2</sub> adsorption by AC increased with pre-heat treated aminated samples	[13]
AC	Agricultural waste like coconut shell, coconut fibre, rice husk, plan mesocarp fibre and plan kernel shell	Waste materials were synthesised in a vertical pyrolysis reactor	Adsorption of CO <sub>2</sub> by AC increased and it's greatly varied with factors like temperature, precursors products and particle size	[104]
AC	Steam AC made from lignite coal	300	Activated biochar has higher affinity to organics and removed 75% of TOC from steam-assisted-gravity-drainage	[187]
AC	Pre-treatment was done by HNO <sub>3</sub> and later AC impregnated with Cu(NO <sub>3</sub> ) <sub>2</sub> and ZnSO <sub>4</sub>	AC was purchased and impregnated AC was dried at 110	Impregnated AC increased CO <sub>2</sub> adsorption up to 49% when 20% Cu/Zn was loaded on AC	[188]
AC from eucalyptus wood	AC was functionalised with pure gaseous ammonia	Carbonisation temperature was 450	Incorporation of N groups in AC due to functionalization increased its CO <sub>2</sub> adsorption capacity	[189]

1104 AC: Activated carbon; GHG: Greenhouse gas

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1107 Table 4: Effect of biochar (BC) modification on char's properties

Stock material	Pyrolysis temperature (°C)	Modification	Effect of char modification	References
Bamboo, sugarcane bagasse, hickory wood and peanut hull	600	Chitosan (naturally abundant polysaccharide) used for modification	Chitosan modified BC removed 150% more Pb, 316% more Cd and 233% more Cu than unmodified BC	[89]
Bamboo	600	Chitosan used as an organic glue to attach zerovalent iron onto BC surface	ZVI coated BC increased removal of Pb(II) from 23.9% to 59.6% and Cr (VI) from 0% to 27.8% from aqueous solution	[32]
Cottonwood	600	Synthetic graphite powder, methylene blue and 1, 3, 6, 8-pyrenetetrasulfonic acid (Py-SO <sub>3</sub> ) tetrasodium salt hydrate were used to coat BC	Graphene-coated BC improved adsorption of PAH by 20 times than untreated BC	[190]
Peanut hull	300	Hydrogen peroxide (H <sub>2</sub> O <sub>2</sub> ) used to modify BC	Increased oxygen-containing functional group of BC like carboxylic group and enhanced Pb sorption ability 20 times more than untreated BC	[155]
Cottonwood	600	Biomass was pre-treated with FeCl <sub>3</sub> .6H <sub>2</sub> O to produce BC/γ Fe <sub>2</sub> O <sub>3</sub>	Modified BC has excellent ferromagnetic properties which have strong sorption ability to aqueous As	[34]
Rice husk	300	Ca <sup>2+</sup> as CaO, Fe <sup>0</sup> as iron powder and Fe <sup>3+</sup> as FeCl <sub>3</sub> .6H <sub>2</sub> O were used to modify BC	Modified BC with Ca <sup>2+</sup> and Fe <sup>3+</sup> showed higher As adsorption capacity (>95%), on the other hand, Fe <sup>0</sup> showed only 58%, but the Cr adsorption was not so high as As	[138]
Tea waste	300 & 700	Steam activation was used to modify BC Samples were treated with 5 mL min <sup>-1</sup> of steam for an additional 45 min under the peak temperature	Steam activated BC produced at 700 °C showed the highest sulfamethazine sorption among all BCs studied due to its largest surface area and pore volume	[24]

Invasive plant (Burcucumber)	300 & 700	Steam activation was used to modify BC Samples were treated with 5 mL min <sup>-1</sup> of steam for an additional 45 min under the peak temperature	The steam activated BC produced at 700 °C showed 55% increase in sorption capacity of sulfamethazine compared to that of non-activated BC produced at the same temperature	[191]
Invasive plant (Burcucumber)	700	BCs were activated with 30% sulphuric and oxalic acids	Modified BC showed an extensive increase in the BET surface area and enhancement in the sorption of sulfamethazine	[192]
Raw medicinal residue from a Chinese herb pharmaceutical factory	600 because this temperature is optimum when the Hg removal capacity was considered	Physical activation involved quartz tube reactor and then physically activated BC used for chemical activation by using HCl, ZnCl <sub>2</sub> , and NH <sub>4</sub> Cl through impregnation	Modification improved physicochemical properties of BC and increased removal rate of elemental Hg from fuel gas. Also its considered as a cost effective sorbent with high activity	[193]
Pristine (sawdust char)	500 (fast pyrolysis)	Amino modification involved H <sub>2</sub> SO <sub>4</sub> and HNO <sub>3</sub> . Desired product was dried overnight at 90 °C	Modification increased Cu(II) adsorption capacity of BC from water solution. The Cu(II) combined with the amino groups through surface complexation	[194]
Rick husk	450-500 (fast pyrolysis)	Raw BC was modified by specified acid (H <sub>2</sub> SO <sub>4</sub> ) and alkali (KOH). Final wet BC was dried at 80 °C for 12h and termed as acid BC and alkali bio-char	Alkali BC increased tetracyclic adsorption capacity (58.8 mg/g). Also, modified BC has graphite-like structure, higher surface area, pore volume and these properties of BC plays an important role in TC adsorption	[195]
Brown marine macroalgae	450 under N <sub>2</sub> flow for 2 h	Electro modification was performed by using aluminium electrode (effect surface area 75.56 cm <sup>2</sup> )	Electro-modified BC with increased surface area and pore volume enhanced phosphate adsorption capacity from aqueous solution.	[196]
Cotton stalk	600	CO <sub>2</sub> and NH <sub>3</sub> gas used for modification. BC was heated up gradually to preset temperature (500-900 °C) and when the required temperature was reached, N <sub>2</sub> gas replaced with CO <sub>2</sub> /NH <sub>3</sub> for modification	NH <sub>3</sub> modification introduced N-functional groups and CO <sub>2</sub> modification plays a significant role in pore formation. NH <sub>3</sub> modification increased CO <sub>2</sub> adsorption capacity of BC (99 mg/g)	[1]
Loblolly pine ( <i>Pinus</i> )	600 for 1 h (10	The Mn-oxide modification was conduction	Mn-oxide modified BC enhanced sorption of	[197]

<i>taeda</i> ) wood	°C per min)	by using MnCl <sub>2</sub> .4H <sub>2</sub> O for 2 h immersing. Final product was oven dried at 80 °C for overnight	As(V) and Pb (II). BC provides an effective way to produce low-cost C adsorbents for heavy metal remediation	
Pristine BC produced from <i>Eichhornia crassipes</i>	600	γ-Fe <sub>2</sub> O <sub>3</sub> composite and chitosan were used for modification. Biomass dried and immersed in FeCl <sub>3</sub> solution and pyrolyzed. Later this product used for chitosan modification using acetic acid and NaOH solution	Modified BC was successfully synthesized and applied to remove Cr(VI) from aqueous solution. After modification, improved functional groups on BC surface increased its Cr(VI) sorption ability	[198]
Chicken manure	450	Amine modification by using anhydrous NH <sub>3</sub> gas for treating BC for 1 h at 450 °C	Amine-modified BC with higher surface area and amine functional groups increased Cu(II) adsorption capacity. Modification improved Cu-binding sites on the BC surface	[199]
Conocarpus green waste	600	Chemical modification with either Mg or Fe salts was done by a method of chemical co-precipitation. Treated BC was named as MgO-BC and FeO-BC	Modified BCs were assessed for removal of NO <sub>3</sub> from aqueous solution and MgO-BC showed better removal capacity due to high surface area and strong ionic complexation through chemisorption	[200]
Rice husk	450-500	Methanol modification was done by using NaOH as a pre-treatment agent. Chemical modification includes esterification and reaction between the carbonyl groups of BC and methanol	The adsorption capacity of BC for TC is enhanced after methanol modification. Modification improved O-containing group properties of BC for TC adsorption	[128]
Whitewood (spruce)	792 (fast pyrolysis)	Steam activation was done. Activated BC was impregnated with various additives KCl, KBr, KI, NH <sub>4</sub> I, and NH <sub>4</sub> Br.	Impregnated activated BC improved Hg removal efficiency significantly compared to control	[201]

1108 BC: Biochar

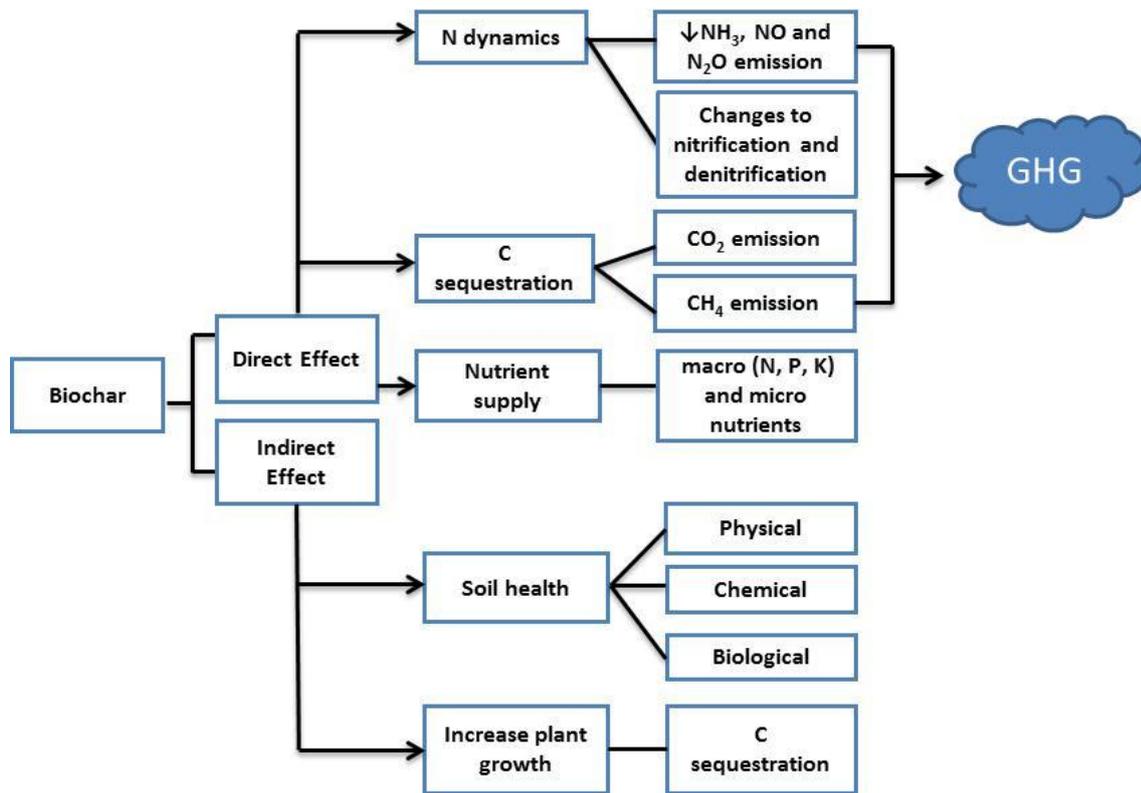
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1111 Table 5: Activation and pyrolysis methods for modification of biochar (BC) characteristics

Agent	Biochar modification	Pyrolysis (° C)	Activation (° C)	reference
<b>Physical</b>				
Gases (CO <sub>2</sub> , O <sub>2</sub> , etc.)	Increases porosity and surface area	700	700 to 900	[132, 133]
Steam	Formation of O- functional groups	700	700 to 900	[134]
<b>Chemical</b>				
H <sub>3</sub> PO <sub>4</sub> , HNO <sub>3</sub> , H <sub>2</sub> SO <sub>4</sub> NaOH, KOH	Loss of micropores due to deterioration, increase in O- functional groups	170	400 to 500	[202, 203]
	Increase in O- functional groups	700	700 to 900 with steam	[204-206]
KMnO <sub>4</sub> , H <sub>2</sub> O <sub>2</sub> /HClO <sub>4</sub>	Increase in O- functional groups	400, 700-750	150-200 (purification)	[145, 146]
<b>Impregnation</b>				
Mg	Increase in O functional groups	350	NA	[190]
Fe	Fe <sub>2</sub> O <sub>3</sub> nanoparticles on surface	250 to 400	700 to 900	[23, 128]
Al	AlOOH/nanoparticles on surface	600	NA	[207]
<b>Grafting</b>				
Poly-styrene-N3	Initiator binding to C nanotubes to adhere 2 <sup>o</sup> organic compound	NA	170	[148]

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1114 *C: Carbon, N: Nitrogen, P: Phosphorus, K: Potassium, CH<sub>4</sub>: Methane, NH<sub>3</sub>: Ammonia, N<sub>2</sub>O:*

1115 *Nitrous oxide, NO: Nitrogen dioxide, and CO<sub>2</sub>: Carbon dioxide*

1116 Figure 1. Direct and indirect effect of char materials on greenhouse gas (GHG) emissions

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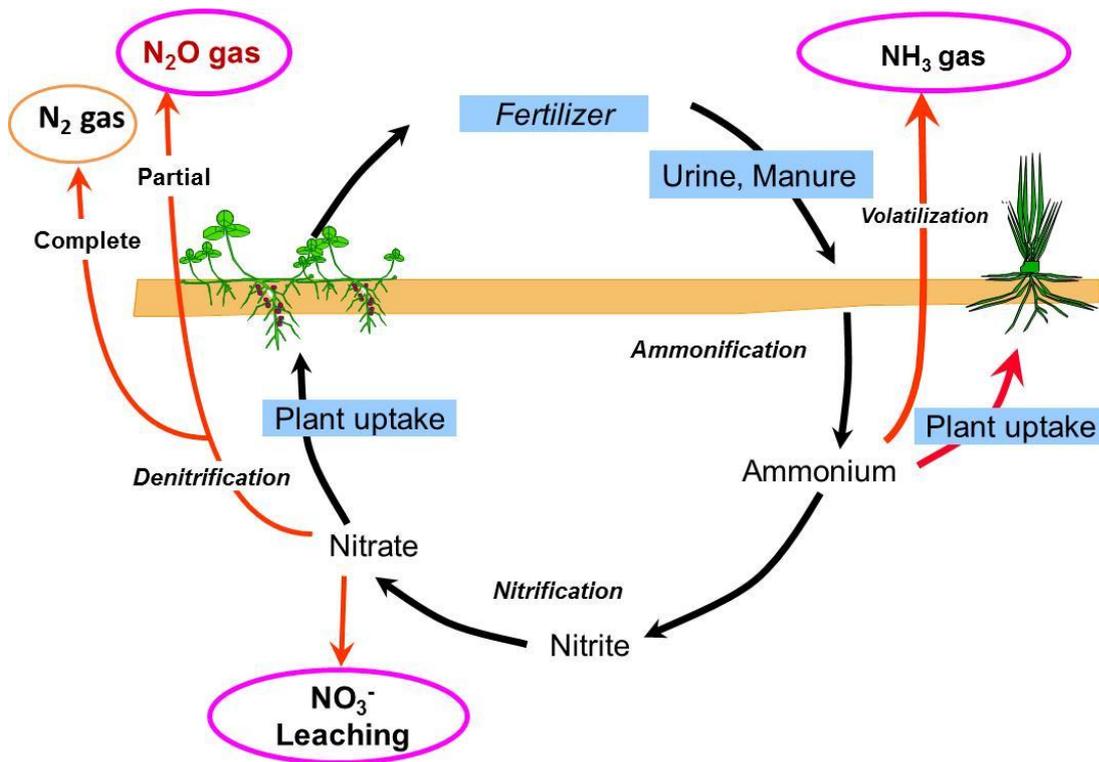
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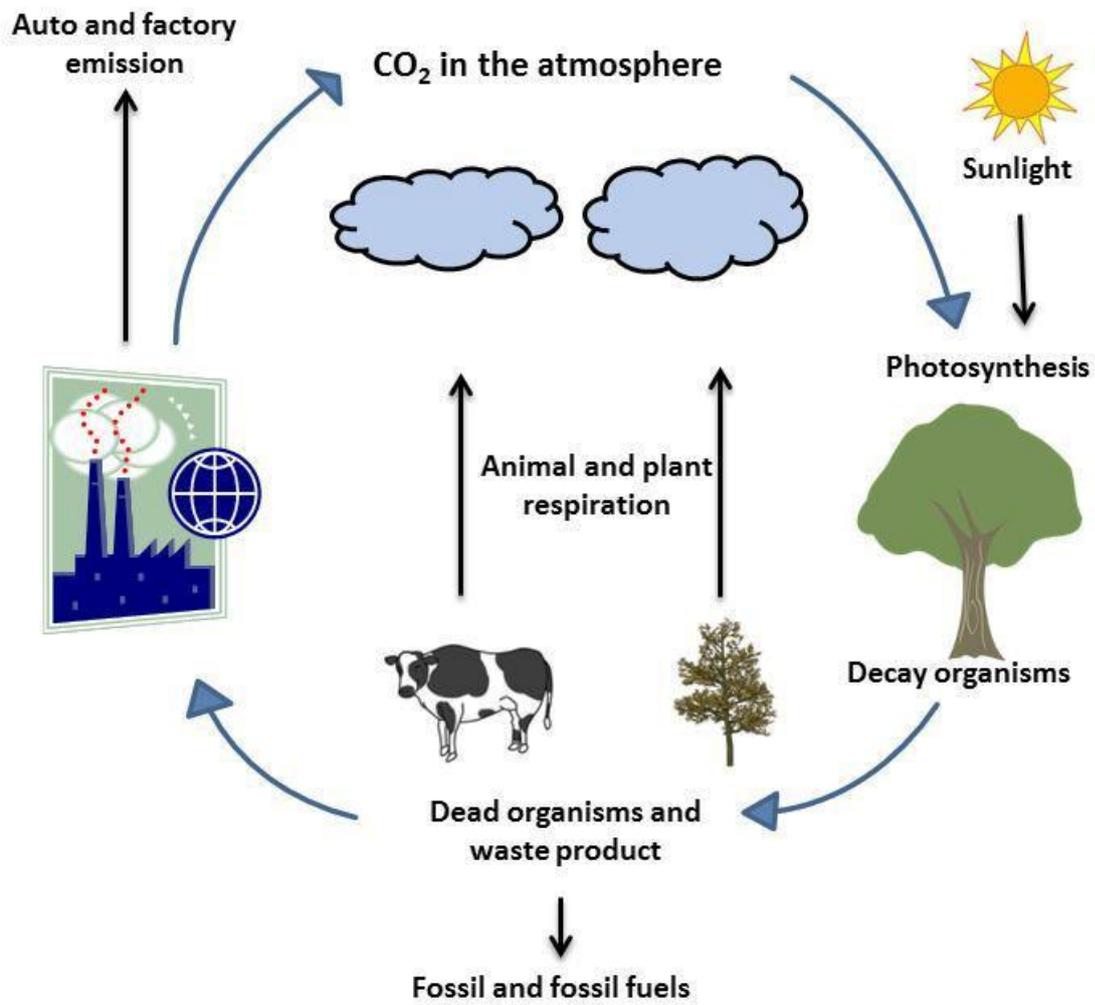
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1129 *NH<sub>3</sub>: ammonia volatilization, N<sub>2</sub>O: nitrous oxide emission and NO<sub>3</sub><sup>-</sup>: nitrate leaching*

1130 Figure 2. Nitrogen dynamics and transformation in soil [adapted from [208]]

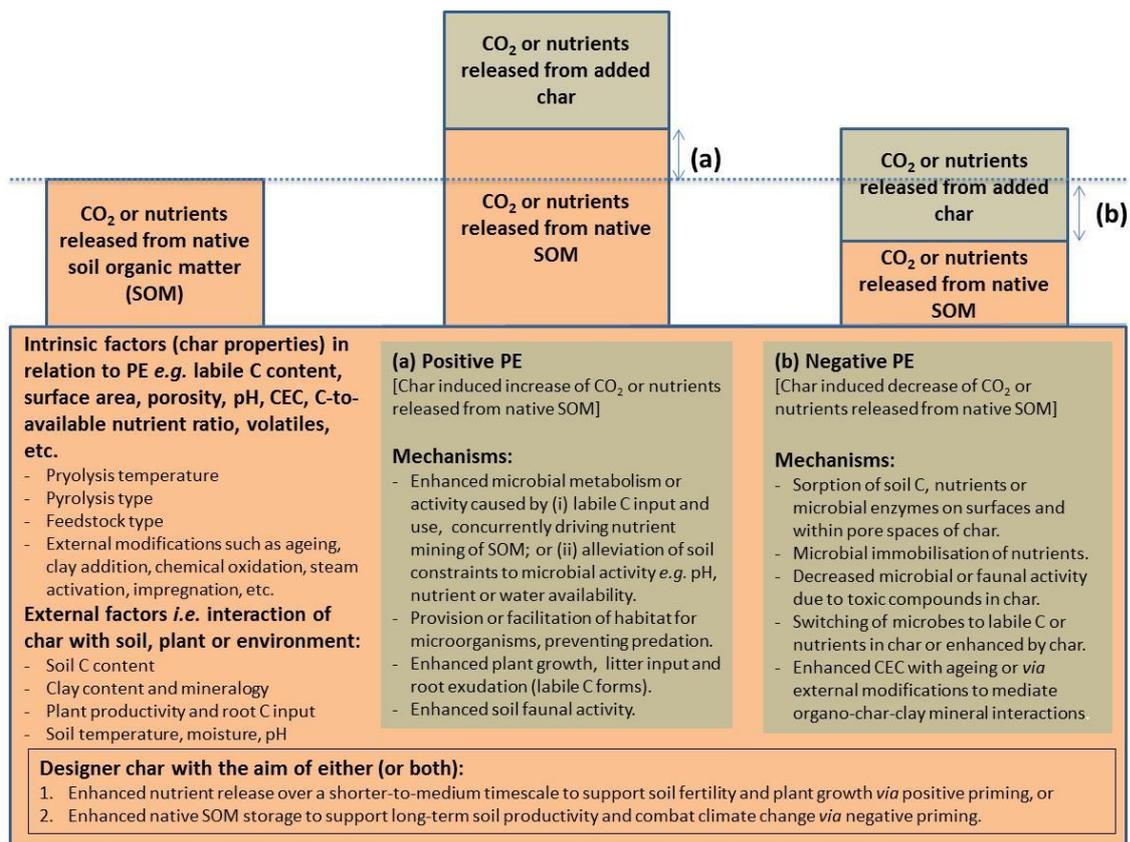


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1132 Figure 3: Carbon cycle and production of carbon dioxide (CO<sub>2</sub>) throughout the earth

1133 involving various systems



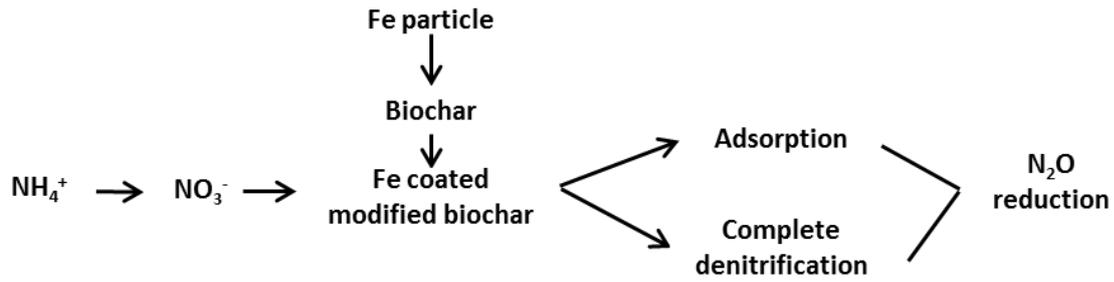


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1138 Figure 5: Overview of factors and mechanisms affecting the priming effect (PE) of native soil  
 1139 organic matter (SOM) by char/biochar addition in soil. Acceleration of SOM decomposition  
 1140 is referred to as positive PE and retardation of SOM decomposition is referred to as negative  
 1141 PE. Char intrinsic and external (soil, plant or environment) factors relating to PE have been  
 1142 listed. The likely biotic and abiotic processes for the positive or negative PE by direct or  
 1143 indirect mechanisms have been included. See the main text for the expanded explanation. The  
 1144 schematization of PE is adapted from [110]

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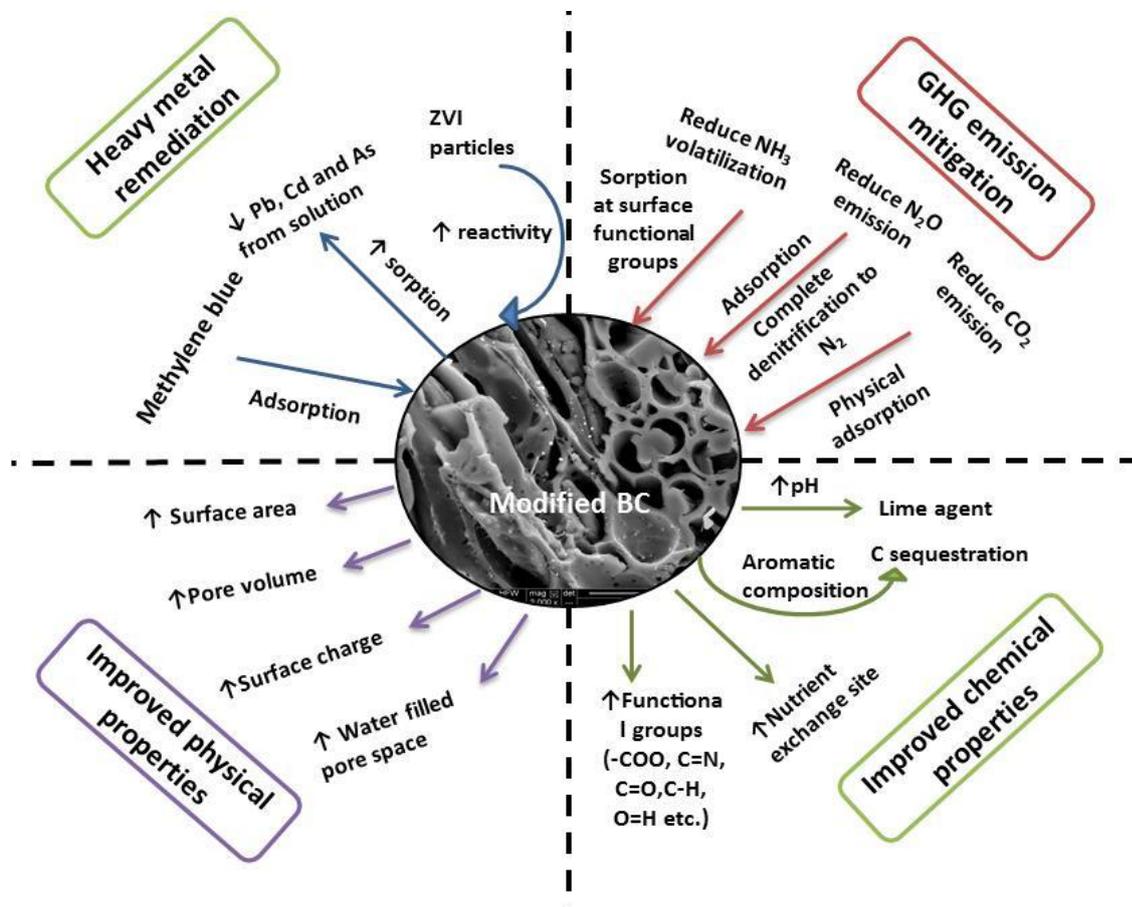
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1149 Figure 6: Reaction scheme showing iron (Fe)-modified biochar reduces  $\text{N}_2\text{O}$  emission



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1151 Figure 7: Schematic diagram showing enhanced characteristics of modified biochar

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