Designing advanced biochar products for maximizing greenhouse gas mitigation potential

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Abstract

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

Keywords

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

1. Introduction

Rising emission of greenhouse gases (GHG) from agricultural lands, due to anthropogenic activities of burning fossil fuels and land-use changes (deforestation) are major contributors to global warming [1]. Agricultural activities collectively contribute between 5 to 6 petagrams carbon dioxide (CO_2) equivalents (approximately 10 to 12%) of the total global GHG emissions [2]. This is primarily due to nitrous oxide (N_2O) emissions from mineral and organic fertilizers applied in soils. Additionally, burning of fossil fuels and deforestation have resulted in an increase of global surface temperature up to 0.8 °C during the 20th century, which likely will increase to 1.4 ˚C–5.8 °C in the 21st century [3, 4]. This increase in global temperature is attributed to the greenhouse effect caused by CO_2 as the major source of GHG. However, the global warming potential (GWP) of N_2O is 298 times greater than CO_2 [4, 5], so the former can trap more heat in the atmosphere compared to the latter. Among all the sectors that are responsible for GHG production, agriculture contributes a significantly large share [3].

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

their various beneficial applications [11]. Char materials can (a) potentially sequester C in soil [12-14], (b) reduce nitrogen (N) loss from soil in terms of N_2O emission [15] and ammonia (NH_3) volatilization [16, 17], (c) improve nutrient retention capacity of soils and reduce runoff and leaching losses [18-21], (d) improve plant growth [9], (e) remediate contaminated soil and water [22-25], and (f) improve soil health [11, 18] by supplying nutrients to the roots and microbes directly from the source, or indirectly by their ability to sorb and retain nutrients [26, 27]. Chars have also been shown to increase N-use efficiency both in a short glasshouse study [28] and field scale studies [29]. The sorbed nutrients gradually release from char and become slowly available to plant roots and microorganisms. A meta-analysis of impacts of biochar on soil emissions of N_2O has shown that on average, a 54% lowering of emissions may be achieved [15]. It was shown that woody and herbaceous feedstock had a greater impact on lowering of emissions than biochars derived from manure or biosolid. Shafeeyan, Daud [13] reported that soil treated with AC (plum shell based granular AC) adsorbed more CO_2 than untreated soil. Aguilar-Chávez, Díaz-Rojas [14] also found that charcoal with an application rate of 4.5% could increase soil CO_2 sorption by more than 37%. Biochars have been shown to increase soil C density in the field both through the increased C added via biochar, and also through new plant C allocation [29]. Char materials are emerging as a low-cost sorbent for reducing risks of inorganic pollutants (lead, copper, arsenic, aluminum and chromium) in soils [30-32], and lowering the concentration or bioavailability of organic pollutants arising from various agricultural, industrial and farming activities [33, 34]

[Figure 1]

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

GHG and react with them (e.g., N_2O) thus reducing their emissions when compared to unamended soil [35]. To further improve the efficacy of char materials in lowering GHG emissions, they can be modified to obtain specific chemical characteristics, elemental composition and structural features [36]. Char materials can also be a suitable support/host matrix for incorporating highly reactive nanoparticles, which can enhance the mitigation of GHG emissions [37]. However, more research is required to identify the characteristics of chars that can be improved by combining other materials. Therefore, this paper aims to review the existing and potential innovative methodologies for improving char efficiency underpinning GHG mitigation and C sequestration in the context of a system where improved plant productivity is sought.

2. Greenhouse gasses and the environment

Increased GHG emission is a serious threat to our environment [38]. Due to anthropogenic activities, the temperature has increased by 0.6 °C–0.8 °C globally between 1951–2010 [3]. Emissions of GHG and changes in land use patterns including agriculture and urbanization are the most important elements which impact the climate [39]. Wastewater treatment plants and livestock are also important sources of GHG emission and onsite aerobic biological wastewater treatment is the highest contributor in an urban setting [40, 41]. Carbon dioxide contributes the highest proportion to the greenhouse effect because of its high concentration in the atmosphere [4]. Concentrations of the greenhouse gasses, e.g., CO_2, CH_4, and N_2O, due to anthropogenic activities are increasing at a rate of 0.4, 0.6 and 0.25% per year, respectively [42].

Because of different atmospheric half-lives and radiative forcing of the GHGs, they are assigned a different GWPs [43]. Trace gases including CH_4 and N_2O absorb nearly 300 and 25 times more infrared radiation, respectively, than CO_2, and contribute 15 and 5-6% anthropogenic greenhouse effect [44].

Among various sectors, agriculture contributes 20% of total GHG emissions (N_2O, CO_2, and CH_4) [45]. Land conversion from forests and pastures to croplands accounts for about 12-20% of the GHG emissions [46]. Waste management activities also contribute to the emissions (4%), while disposal of waste in landfills generates CH_4. Livestock are responsible for about 12% anthropogenic GHG emission [47, 48].

Climate change can have an adverse impact on agricultural production and environmental quality. For example, as estimated by statistical models, the wheat yield in India dropped by 36% in 2010 as compared to 1980, because of climate change and emissions of other pollutants [49]. The increasing concentrations of atmospheric GHGs have catalyzed the chances of drought and flood in different regions in India [49]. An overall reduction in the quality of available water runoff was also noted [50]. Furthermore, the increasing CO_2 levels affected soil microbial activity and water content. Furthermore, van Groenigen, Osenberg [51] found that increases in CO_2 level triggered N_2O emission from upland soils and CH_4 emission from paddy soils and natural wetlands.

Investments into field improvements of agriculture have avoided up to 161 gigatons of CO_2 emissions since 1961 [49]. Changing the food habits, for example, shifting from red meat and dairy products to chicken, fish, and vegetables based diets could potentially decrease the GHG emissions [52]. Also, changes in agricultural practices such as growing lignocellulosic energy crops, e.g., willow (*Salix* spp.) and elephant grass (*Miscanthus x giganteus*), which give much higher yield, would lower GHG emission in comparison to arable crops [53]. Adapting less intensive tillage operation is also a well-known strategy to tackle CO_2 emission from soils [54, 55].

3. Nitrogen dynamics and carbon cycle

3.1. Nitrogen dynamics and gaseous N emissions

It was reported that an average 4-6 teragram (Tg) of N_2O-N is being released into the atmosphere annually through agricultural activities, mainly from the use of mineral and organic N fertilizers [56]. An emerging pool of information shows that biochar, or indeed, a biochar system, is able to provide opportunities for mitigation of N_2O emissions through altered N and C cycling [59]. Nitrogen is an important nutrient for plant growth, development, and reproduction. Most plants access N from soil, either through uptake of mineral N, or through biological N_2 fixation. When N is added to the soil, it undergoes various transformation processes and can produce gaseous products including ammonia (NH_3), N_2O and N_2 (Figure 2). The loss of N through gaseous emissions decreases the amount of soil available N to plants and contributes to GHG inventories.

[Figure 2]

3.2. The carbon cycle and CO_2 emissions

Carbon is an important macro element for plant development, and plants usually take up C as CO_2 from air during photosynthesis [57]. Carbon circulates in an endless process between the earth's surface, oceans, plants and soils (Figure 3). Through this process C is converted into CO_2 as a natural component of the atmosphere that protects the earth's surface from radiation by reflecting it back into the atmosphere. This phenomenon causes some heat to be generated, which can result in rising temperatures. For this reason CO_2 is called a GHG [58]. When the production of CO_2 exceeds the buffer capacity of the earth's ecosystem, it can result in global warming, i.e., the earth retains heat.

Utilization of biofuel C (e.g., that from maize or sugar cane) instead of fossil fuel can reduce CO_2 emissions, because biofuel C is mainly derived from the atmosphere via current

photosynthesis (fossil fuels result from photosynthesis millions of years ago) [59]. Production of CO_2 due to various anthropogenic activities (industry and agricultural activities) have increased its concentration from 284 ppm in 1832 to 397 ppm in 2013 [60]. As noted, a large amount of CO_2 is produced from the agricultural sector. Schimel [61] reported that the agriculture sector contributes about 20% of total anthropogenic CO_2 emission. Anthropogenic CO_2 comes from several sources including biomass burning, tillage practice, accelerated soil organic matter (SOM) mineralization, and microbial decay [4]. Soil is a large global C sink being around 2500 gigatons (Gt C), including about 1550 Gt of soil organic carbon and 950 Gt of soil inorganic carbon [62].

[Figure 3]

4. Properties of biochar which alter N cycling, N_2O, and CO_2 emissions

Meta-analysis of the impacts of biochar on N_2O emissions have shown that the properties of biochar are critical in controlling emissions. For example, Cayuela, Van Zwieten [15] showed that biochars derived from crop and woody residues resulted in over a 50% decrease in emissions, while biochars from other feedstock might not provide, on average, any meaningful opportunities for lowering emissions. The quantity of biochar applied to soil has been shown to be important, with mitigation opportunities only becoming evident when biochar was amended at or above 2% w/w into soil [15]. Slight mitigation opportunities were detected in a meta-analysis by Cayuela, Van Zwieten [15] when biochar was amended at 1-2% w/w to the soil. Interestingly, biochar amendments were effective at lowering emissions in alkaline, neutral and slightly acid soils, but when pH was below 5.5, no effect was detected [15]. This may present opportunities for modification of biochars, or indeed selection of biochars that can modify soil pH to lower N_2O emissions. Most recently, Cayuela, Jeffery [63] updated the previous meta-analysis [15] with new data, and they showed that an important factor in the mitigation of N_2O was the molar H/C ratio of the biochar. Biochars

198 with a molar H:C_{org} ratio of <0.3, indicative of a high degree of aromatic condensation,
199 lowered N_2O emissions by 73%, while biochars with a molar H:C_{org} ratio of >0.5 were less
200 effective, lowering N_2O 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_2O.

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_2O. 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_2O. 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 µCT) 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

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

Some biochars were shown to carry organic compounds that could impact microbial toxicity in soil. For example, they might contain polycyclic aromatic hydrocarbons (PAHs), polychlorinated compounds, dibenzodioxins and furans, which would form during pyrolysis of the feedstock [71, 72]. PAHs were found to modify the nitrification processes and denitrifying bacterial communities in soil [73, 74]. Spokas [75] investigated the direct impact of biochar-released ethylene on N_2O production from the soil. The result supported the possibility of introducing compounds that modify N cycling, nitrification and denitrification reactions in the soil. For example, 3, 4-dimethylpyrazole phosphate (DMPP) is a nitrification inhibitor that has been studied extensively with the aim of improving N-use efficiency and lowering N_2O production from the soil. Opportunities exist to use biochar as a carrier for this nitrification inhibitor. However; biochar produced from eucalyptus wood with a large surface area (426.4 m^2 g^{-1}) reduced the inhibitory effect of another nitrification inhibitor dicyandiamide (DCD) in a neutral Cambisol [76]. This work demonstrated that sorptive biochars were more efficient at reducing the efficacy of the nitrification inhibitor than less sorptive ones.

Biochars' influence on the soil microbial communities that are involved in N cycling was reported [65], however, the authors suggested that changes in environmental conditions resulting in N_2O formation were more important than the changes in size or activity of soil microbial communities. Of particular interest are the redox or electron shuttling properties of biochar [77]. Iron (Fe) is an important element in N transformation in soil. Li, Yu [78] showed that reduction and oxidation of N compounds were enhanced when Fe and organic

matter were also oxidized or reduced. Reactions between Fe^{2+} and either NO_3^- or nitrite (NO_2^-) to produce N_2 (reduced species) were energetically favorable. These results suggested that Fe content of biochars should be enhanced before application to soil, or indeed, feedstock such as biosolids should be used [79] which would result in an increase of the Fe content. In the study by Van Zwieten, Kimber [79] lower emissions of N_2O from a Ferrosol were detected with a high Fe-biochar compared to other biochars produced from sludge and wood chips.

Pyrolysed biomass has created research interest as it has been shown to lower greenhouse gas emissions and increase soil C content. Carbon sequestration is one of the key benefits of using char materials as a soil amendment. It has been estimated that chars produced from natural wildfires may represent 15-20% of total C in temperate and coniferous forest soils [80]. In one study, Spokas, Koskinen [81] found that biochar application reduced soil CO_2 emissions. Another study by Case, McNamara [82] also reported that biochar addition at 49 t ha^{-1} in a field trial can suppress soil CO_2 emission up to 53%. The reason of lowering CO_2 emission following biochar amendment may be due to a negative priming effect (outlined in section 6) whereby new C (e.g. Root exudates etc.) in soil are stablished and not available for microbial degradation. However, other studies have observed that biochar addition in soil has little or no effect on CO_2; for example's Wu, Jia [83] found that biochar addition at 0.67, 1.68% rate did not affect soil CO_2 emissions but lowered N_2O emissions significantly.

This section has demonstrated pathways in which biochars may alter N cycling and hence emissions of N_2O (Figure 4). Modifications of biochars to optimize soil pH, soil physical characteristics, redox active elements and to reduce toxic components provide opportunities to mitigate N_2O and CO_2 emissions. It will be critical, however, to first understand the key processes of formation of modified biochars for each soil/climate/agroecosystem, before biochars can be designed to lower emissions of N_2O and CO_2.

[Figure 4]

5. Char materials for greenhouse gas mitigation

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

[Table 1]

5.1. Biochar

Biochar has multi-purpose properties that make it a unique amendment to improve soil health, and it also can remediate environmental contaminants [22, 23]. Biochar is used for mitigating GHG emissions due to its relative stability, ability to act as a long-term nutrient sink in the soil and higher nutrient retention capacity than other organic amendments [9, 86]. It has a range of surface functional groups that can adsorb heavy metals from soil and aquatic environments [32, 86, 88-90]. It can also reduce GHG emissions, such as N_2O, by adsorbing and retaining N in the soil. Woolf, Amonette [91] reported that the annual net emissions of GHG (CO_2, N_2O, and CH_4) were reduced up to 12% by adding biochar in the soil. In support of this estimate, many researchers have reported the successful application of biochar as a soil amendment for C sequestration [12, 92-94]. Biochar can also provide direct agronomic benefits to plants by supplying nutrients [N, phosphorus (P), potassium (K) and sulfur (S)], and provide indirect benefits through the sorption of elements to retain essential nutrients [26,

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

[Table 2]

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

5.2. Charcoal

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

The reduction of CO_2, N_2O, and CH_4 emissions by adding charcoals to the soil is not always uniform (Table 2). The addition can show no effect or even negative effects on the reduction of GHG emissions depending on feedstock types and soil properties [97, 103].

5.3. Activated carbon

Activated carbon is an important material because of its widespread use as an adsorbent, catalytic and catalyst support [104, 105]. This material can be modified in various ways to increase its surface characteristics and thus to enhance mitigation of GHG emissions as well as adsorption of heavy metals in soil. Activated carbon is an important adsorbent especially due to its high micro- and meso-porosity, surface acidic groups, and apparent surface area that increase its activity to adsorb heavy metals like Cd, Pb, and Cu [105, 106]. Two different methods can be used to prepare AC: physical and chemical activation. The physical activation method involves carbonization of raw materials and subsequent activation at high temperature in a CO_2 or steam environment. Steam activation flushes away the oil residues and it opens up the planar sheets. Steam activation method could increase the surface area, micro-porosity and mesopore volume of the products [107]. Chemical activation involves carbonization of previously activated raw materials by potassium hydroxide (KOH) and phosphoric acid (H_3PO_4) [107]. Adsorption of CO_2 requires solid sorbents with a high CO_2 selectivity and capacity. Activated carbon can capture CO_2 by solid adsorption because of its highly porous structure [108]. The adsorption capacity of AC is based on the short-term physical adsorption and it can be improved by introducing NH_3 on its surface for reducing CO_2 emission [108, 109] (Table 3). Ammonia decomposes at high temperatures and produces some radicals ($NH_2^{\bullet}$, $NH^{:}$, $H^{\bullet}$) and these radicals react with the C surface to form reactive functional groups (-NH_2-, -CN, pyridinic, pyrrolic and quaternary N) [108].

[Table 3]

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

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

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

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

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

[Figure 5]

7. Modification of biochar surface properties

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

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

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

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

[Table 4]

7.1. Modification processes

Biochars can be modified using several processes (Table 5). The selection of an individual modification method depends on feedstock type and the target problem (i.e., soil fertility, metal immobilization, etc.). Available feedstock for biochar production includes wood, coconut shells, peat, [129], grasses, nut shells, [130], animal manures [131], etc. The feedstock can be treated either pre- or post-pyrolysis to gain desirable properties. For example, biochars can be treated to have a higher capacity for specific interactions with organic and inorganic chemicals because they have a high surface area, high degree of physicochemical attraction between the adsorbate and C surface, and the appropriate pore size distribution. As shown in Table 5, during the physical processes of biochar treatment, gases (CO_2), air [132, 133] and steam [134] were introduced during the carbonization phase of pyrolysis (700 ^{0}C). Higher activation temperatures (700 to 900 ^{0}C) were needed to further attenuate the material to increase the surface area and O-containing functional groups [135].

[Table 5]

7.1.1. Impregnation

Impregnation is a process where guest elements (usually metals) are incorporated into the char surface through prolonged wet contact [136]. Following impregnation, char materials are likely to impact GHG emission through electrostatic interaction between the impregnated metal cations and negatively charged C containing functional groups in the SOM (e.g., carboxylic group and lactonic group) [137, 138]. Char modification by impregnation is likely to make them more active in terms of retaining heavy metals from aqueous solution [139, 140]. For example, Wang, Sheng [141] reported that manganese (Mn) impregnated biochar increased the removal efficiency of Pb from 6.4 to 98.9%. Agrafioti [138] also found that Ca^{2+} modified biochar demonstrated a high As removal capacity (>95%). Zhang, Gao [34] prepared iron impregnated biochar with ferric oxide (Fe_2O_3) and found that the modified biochar had a strong sorption of As in aqueous solutions. Nitric acid (HNO_3) is frequently used to remove intrinsic ash and tar of biochar before impregnation. Impregnation of biochar as a catalyst has been reviewed recently by Qian, Kumar [142]. The following reaction scheme shows (Figure 6) how Fe modified biochar can reduce N_2O emission.

[Figure 6]

7.1.2. Oxidation

Oxidation is another modification process where liquid or gaseous compounds (e.g., inorganic acids) are used to modify and purify chars [132, 143]. Two types of oxidation, liquid phase oxidation and gas phase oxidation are generally used. In the liquid phase oxidation process, strong acids like HNO_3 [143], a mixture of HNO_3 and sulfuric acid (H_2SO_4) [144], strong oxidants like potassium permanganate ($KMnO_4$) in acid solution, or other chemical mixtures, such as hydrogen peroxide/ sulfuric acid (H_2O_2/H_2SO_4) and

hypochlorite solution ($HClO_4$) [145, 146] have been used to modify, or purify chars. Gaseous phase oxidation includes the use of CO_2 and O_2 gas for modifications [132, 133]. The use of KOH is also known to increase the porosity and surface area of the biochar [142]. For example, Zhang, Gao [34] developed KOH-activated biochar with a surface area of up to 3,500 m^2/g with a large pore volume (1.3-1.94 cm^3/g).

Oxidation can modify chars in two different ways: firstly, by opening the pores in char products and subsequent filling with metals, and secondly, by the addition of new functional groups on the surface of chars. Chemical activation which utilizes acids [phosphoric acid (H_3PO_4), HNO_3, and H_2SO_4] and bases [KOH, sodium hydroxide (NaOH)], is used to modify biochars because they have both dehydration and oxidation characteristics. The feedstock is usually mixed or soaked in a solution of these chemicals before pyrolysis and activation (Table 4). The use of typical acids and bases modifies the biochar by introducing O-containing functional groups into the C matrices [143-145]. Strong oxidizers such as $KMnO_4$ and $HClO_4$ also can be used to modify or purify biochars [145, 146]. The degree of modification is also temperature dependent because at higher activation temperatures more O_2 is added to the rings.

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

7.1.3. Grafting

The last form of activation is grafting (Table 4). The basic premise of this method is that the surface properties of carbon nanotubes can be modified by the grafting of organic molecules onto them. The technique involves the immobilization of an initiator (Table 4; poly-styrene-N_3) onto the tubes followed by surface-initiated polymerization of an organic compound (sec-butyl L-Li) to form a dense polymer material [148]. In this way, the tubes were made more structurally dense and could enter into secondary reactions such as binding of pollutants [149]. Grafting involved the fusion of guest molecules/elements onto the chars surface functional groups, using the condensation reaction [150]. Grafting through chemical functionalization has resulted in an outstanding compatibility between nano-materials and chars. However, information concerning the grafting of complex polymers on the surface of char materials in order to improve their ability to remediate contaminated environments is scant [151]. Grafting can be done with or without pre-oxidation. There is a range of compounds/materials that can be used to graft a char material, e.g., chitosan (natural biopolymer), polyallylamine hydrocarbon, and various nanocrystals [cadmium selenide- zinc sulfide (CdSe-ZnS) in chloroform ($CHCl_3$), zinc oxide (ZnO) in ethanol and Fe_2O_3 in aqueous solution] [147, 148, 152]. Grafted char shows a wide range of potential application such as use in biomaterials, bioengineering and emerging biotechnology.

7.2. Materials for char modification

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

- Chitosan, a copolymer of 2-acetamido-2-deoxy-β-D-glucopyranose and 2-amino-2-deoxy-β-D-glucopyranose through a β-(1→4) linkage, is a naturally abundant 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 ($FeCl_3.6H_2O$) 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

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

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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_2 gas and reduced oxygen condition Time: Both slow and fast pyrolysis	Black in color	• Improved characteristics such as high surface area, pore volume, surface functional groups • Supply macro and micronutrients for plant growth • Reduce heavy metal toxicity • Improve soil physical, chemical, and biological properties	[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	• Act as a potential adsorptive material • Improve plant growth and development • Act as a soil conditioner • Positively affect seed germination, plant growth, and yield	[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_2, polymerization of hydroxylated benzene and aldehyde in a solvent, chemical activation includes HNO_3, H_2SO_4, NaOH, KOH, synthesis of a resorcinol- formaldehyde xerogel at specific condition to form AC	100µm to 600 mm, black in colour	• Improved physicochemical properties (surface area, extensive internal pore structure) • It can be used in various industries (pharmaceuticals, mining, chemical, petroleum etc.) because of its high adsorptive properties • Remove organic and inorganic species from industrial effluent • Remove pesticides from drinking water	[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 ≥ 2.5 µm)	• High specific surface area • Increase soil fertility by supplying a range of nutrients • It can cause serious health problem by carrying carcinogenic compounds	[166-169]

AC: Activated carbon

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 ($N_2O/NH_3/CO_2/CH_4$)**	**Nutrient retention/soil health**	**References**
Poultry manure and stem wood	15	400 and 550	All BC application reduced N_2O emission up to 73% due to increased sorptive capacity of biochars	Nutrient sorptive properties of biochar decreased NO_3 leaching and conserved N in the soil	[21]
Oakwood	5.5	650	Cumulative emissions of CH_4, CO_2, and N_2O 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_2O 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_2O emission (2.0 kg/ha N_2O/yr for control and 4.14 kg/ha N_2O/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_2O emission reduced up to 96% with 10% BC application and 47% with 2% BC	BC application enhanced microbial N_2O reduction and increased the abundance of microorganisms for N_2-fixation	[173]

Maize stover and eucalyptus wood	15	350 and 550	BC application reduced N_2O emission up to 10 to 41% and increased CH_4 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_2O 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_2O 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_2O 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_2O emission by 15.7% and CH_4 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_2O emission increased by 0.13 to 0.80 times but CH_4 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_2 emissions by 52% and net soil CO_2 eq. emissions by 55% but showed no significant reduction in N_2O 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_2O and CO_2 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_2O emissions by 41% and increased cumulative CO_2 emissions by 31-45%	Biochar application increased C:N ratio, total C, and P	[181]
Miscanthus × *giganteus* straw	9.3	550-600	Biochar application had no effect on CO_2 emission but it reduced N_2O 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_2O emission from 76% to 26% but no significant difference observed for CH_4 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_3 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_2O emission but it reduced CH_4 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_2O emission up to 55% with 10 ton/ha BC and 96% with 25t/ha BC application. No significant effect on CO_2 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_2, CH_4, N_2O) were observed in the field	BC application increased limited plant nutrients like P and Ca	[185]

BC: Biochar; GHG: Greenhouse gas

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_2O/NH_3/CO_2/CH_4)**	**References**
Charcoal	Wood	200 – 300	≥ 1.5% application of charcoal reduced CO_2 emission ≥ 37% and N_2O 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_2 mitigation but it can mitigate N_2O & CH_4 emission	[81]

Charcoal	Lump-wood	450	Decreased nitrate leaching significantly and increased CO_2 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_2O emission	[160]
Ammonia modified AC	Palm shell based granular AC	Ammonia modification with pre-oxidation- air introduced at 400	CO_2 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_2 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_3 and later AC impregnated with $Cu(NO_3)_2$ and $ZnSO_4$	AC was purchased and impregnated AC was dried at 110	Impregnated AC increased CO_2 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_2 adsorption capacity	[189]

AC: Activated carbon; GHG: Greenhouse gas

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_3) 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_2O_2) 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 $FeCl_3.6H_2O$ to produce BC/ɤ Fe_2O_3	Modified BC has excellent ferromagnetic properties which have strong sorption ability to aqueous As	[34]
Rice husk	300	Ca^{2+} as CaO, Fe^0 as iron powder and Fe^{3+} as $FeCl_3.6H_2O$ were used to modify BC	Modified BC with Ca^{2+} and Fe^{3+} showed higher As adsorption capacity (>95%), on the other hand, Fe^0 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^{-1} 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^{-1} 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, $ZnCl_2$, and NH_4Cl 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_2SO_4 and HNO_3. 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_2SO_4) 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_2 flow for 2 h	Electro modification was performed by using aluminium electrode (effect surface area75.56 cm^2)	Electro-modified BC with increased surface area and pore volume enhanced phosphate adsorption capacity from aqueous solution.	[196]
Cotton stalk	600	CO_2 and NH_3 gas used for modification. BC was heated up gradually to preset temperature (500-900 ˚C) and when the required temperature was reached, N_2 gas replaced with CO_2/NH_3 for modification	NH_3 modification introduced N-functional groups and CO_2 modification plays a significant role in pore formation. NH_3 modification increased CO_2 adsorption capacity of BC (99 mg/g)	[1]
Loblolly pine (*Pinus*	600 for 1 h (10	The Mn-oxide modification was conduction	Mn-oxide modified BC enhanced sorption of	[197]

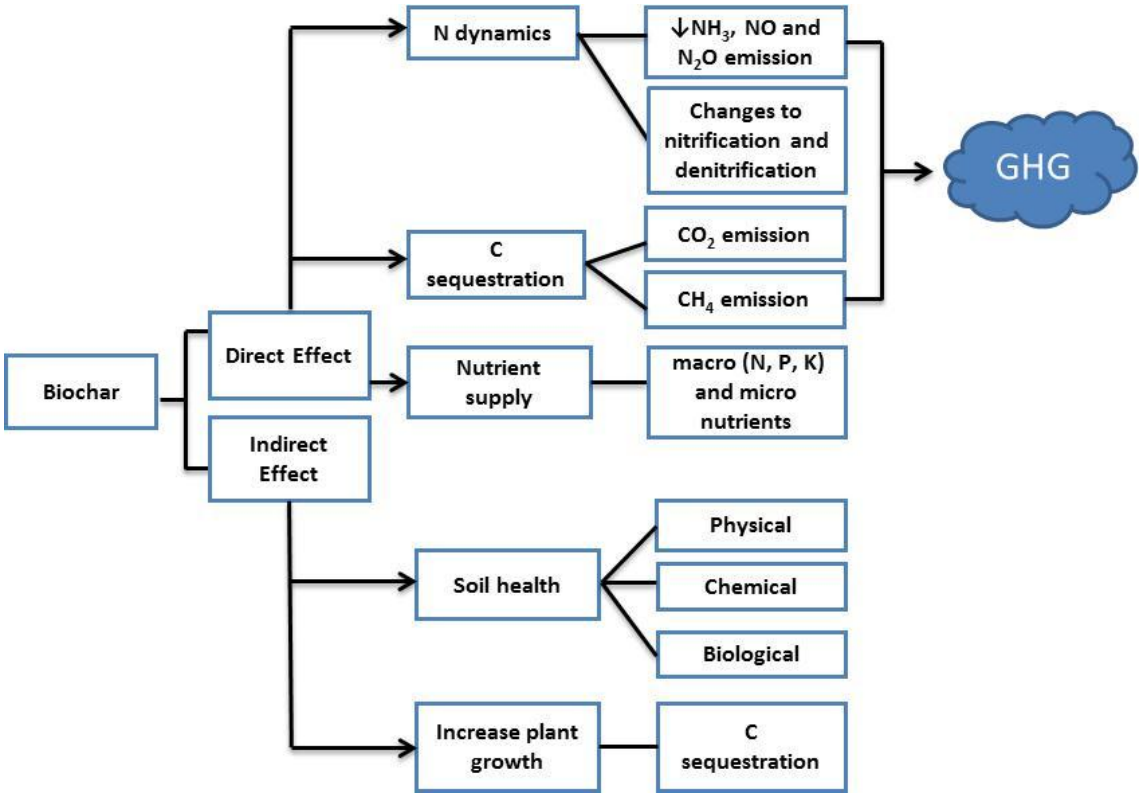
taeda) wood	˚C per min)	by using $MnCl_2.4H_2O$ for 2 h immersing. Final product was oven dried at 80 ˚C for overnight	As(V) and Pb (II). BC provides an effective way to produce low-cost C adsorbents for heavy metal remediation	
Pristine BC produced from *Eichhornia crassipes*	600	ɣ-Fe_2O_3 composite and chitosan were used for modification. Biomass dried and immersed in $FeCl_3$ 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_3 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_3 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_4I, and NH_4Br.	Impregnated activated BC improved Hg removal efficiency significantly compared to control	[201]

BC: Biochar

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

Agent	**Biochar modification**	**Pyrolysis (^{0} C)**	**Activation (^{0} C)**	**reference**
Physical				
Gases (CO_2, O_2, etc.)	Increases porosity and surface area	700	700 to 900	[132, 133]
Steam	Formation of O- functional groups	700	700 to 900	[134]
Chemical				
H_3PO_4, HNO_3, H_2SO_4 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]
$KMnO_4$, H_2O_2/$HClO_4$	Increase in O- functional groups	400, 700-750	150-200 (purification)	[145, 146]
Impregnation				
Mg	Increase in O functional groups	350	NA	[190]
Fe	Fe_2O_3 nanoparticles on surface	250 to 400	700 to 900	[23, 128]
Al	AlOOH/nanoparticles on surface	600	NA	[207]
Grafting				
Poly-styrene-N3	Initiator binding to C nanotubes to adhere 2^0 organic compound	NA	170	[148]

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1114 *C: Carbon, N: Nitrogen, P: Phosphorus, K: Potassium, CH_4: Methane, NH_3: Ammonia, N_2O:*

1115 *Nitrous oxide, NO: Nitrogen dioxide, and CO_2: Carbon dioxide*

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

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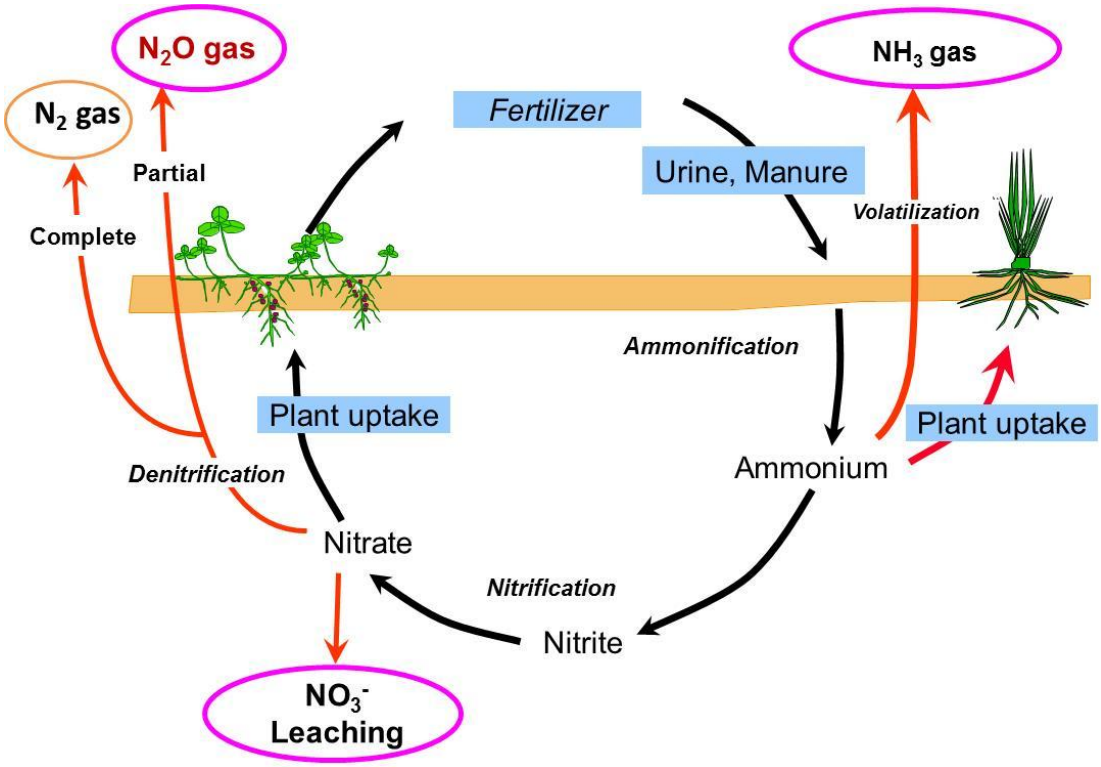
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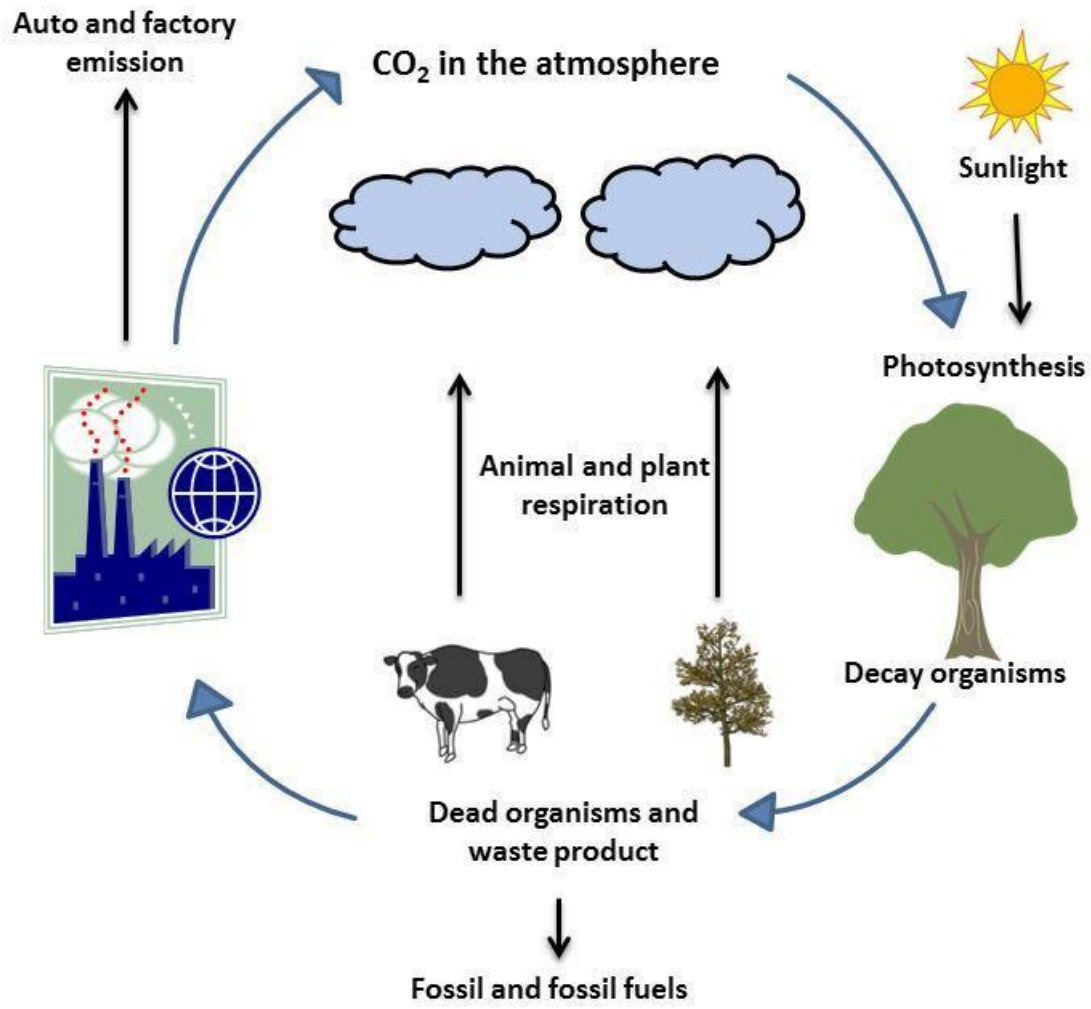
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1129 *NH_3: ammonia volatilization, N_2O: nitrous oxide emission and NO_3^-: nitrate leaching*

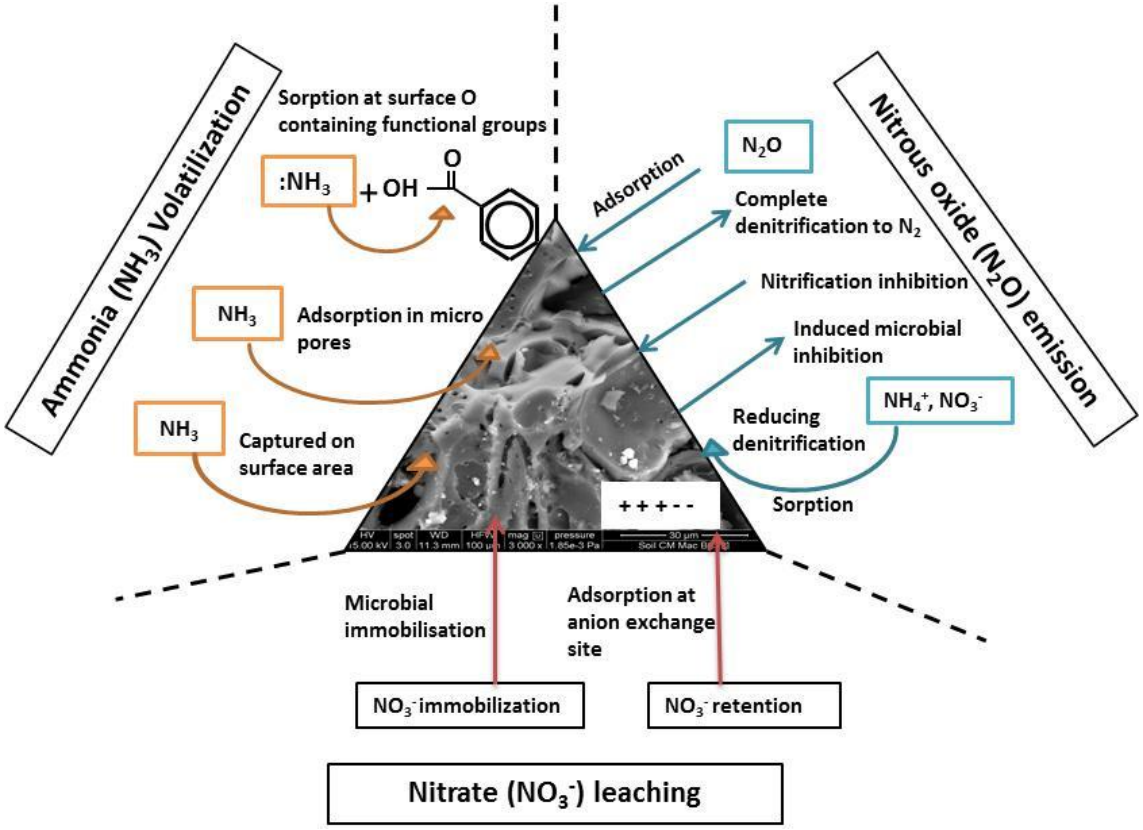
1130 Figure 2. Nitrogen dynamics and transformation in soil [adapted from [208]]



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1132 Figure 3: Carbon cycle and production of carbon dioxide (CO_2) throughout the earth

1133 involving various systems



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1135 Figure 4: Schematic diagram showing mechanisms for biochar induced mitigation of

1136 ammonia volatilization, nitrous oxide emission and nitrate leaching

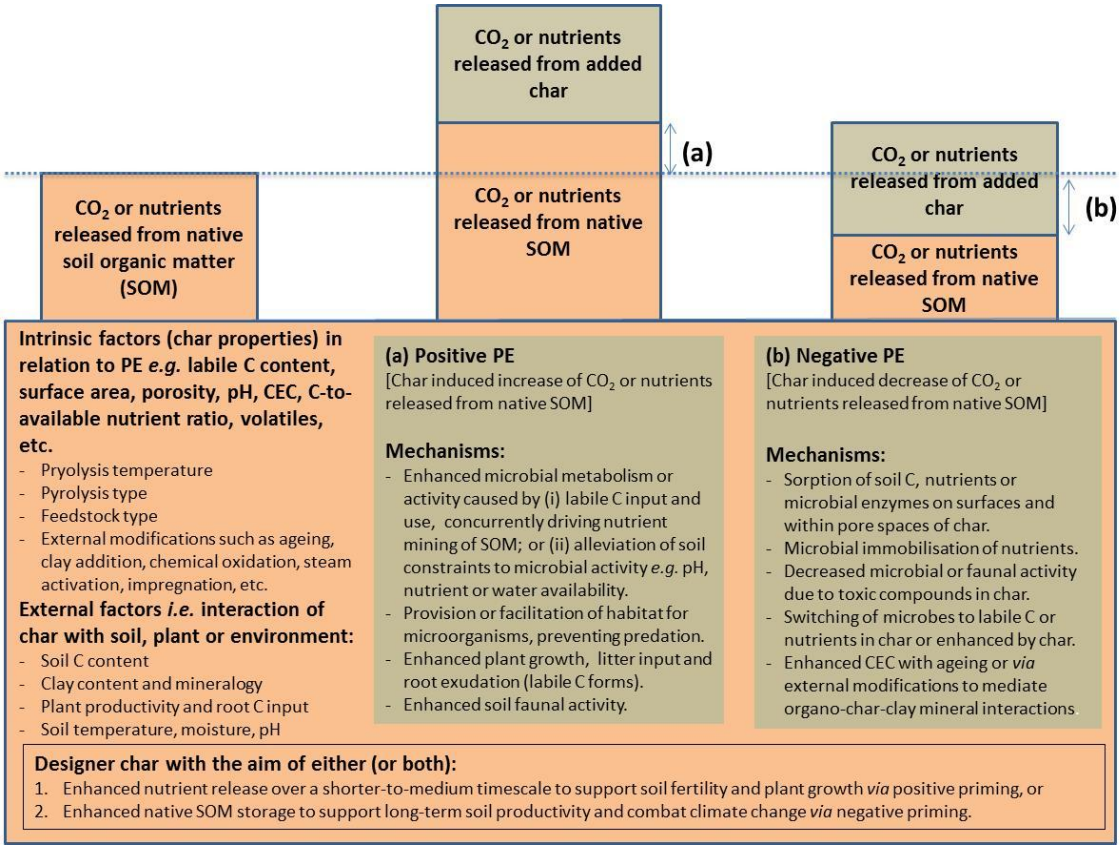
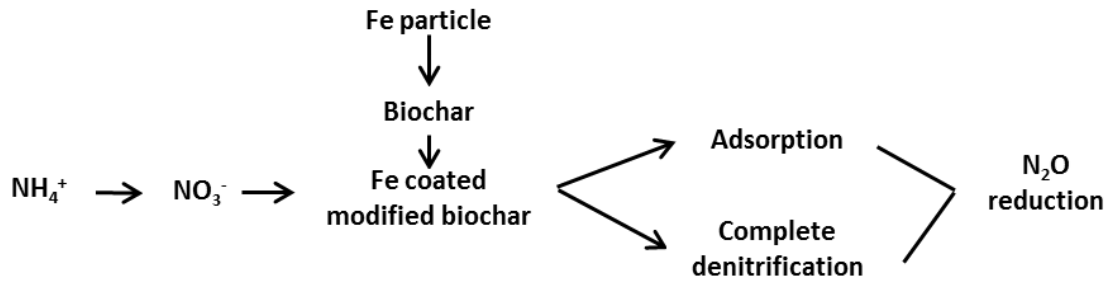


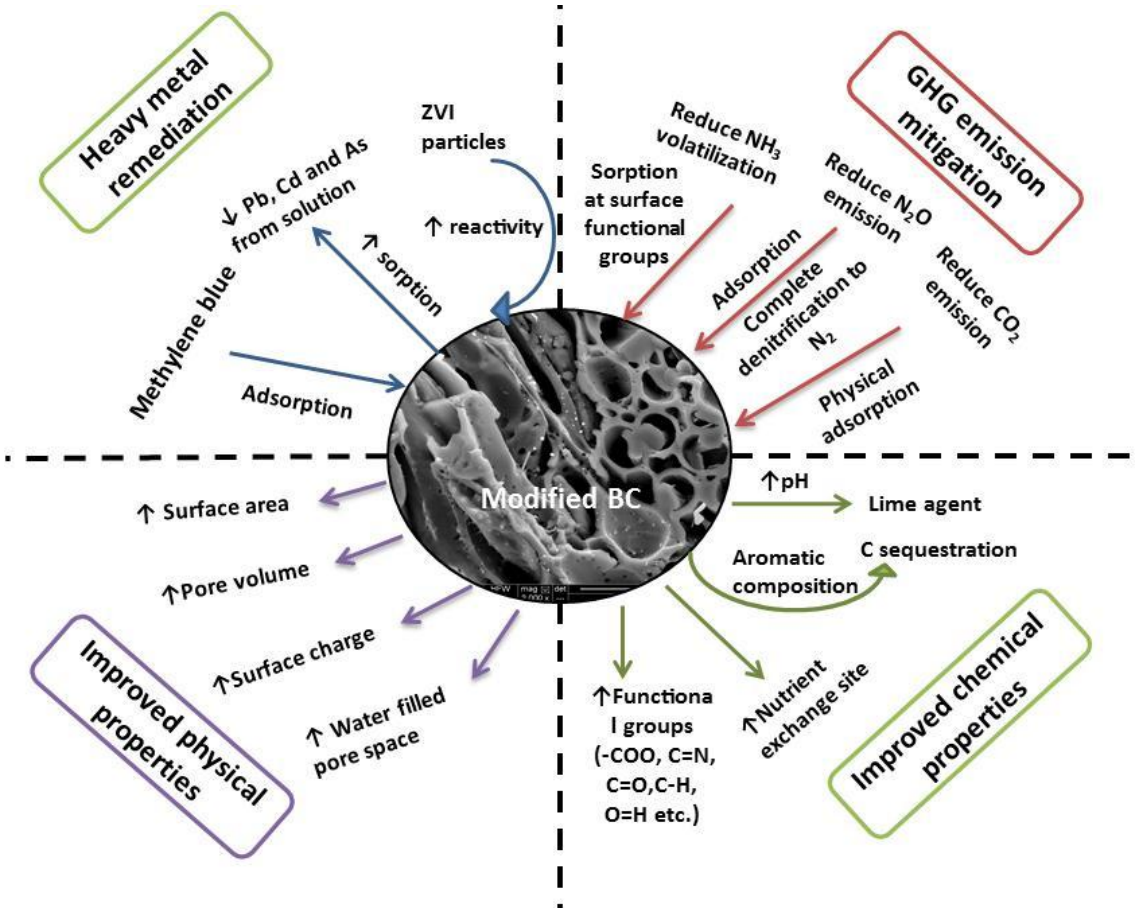
Figure 5: Overview of factors and mechanisms affecting the priming effect (PE) of native soil organic matter (SOM) by char/biochar addition in soil. Acceleration of SOM decomposition is referred to as positive PE and retardation of SOM decomposition is referred to as negative PE. Char intrinsic and external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



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1149 Figure 6: Reaction scheme showing iron (Fe)-modified biochar reduces N_2O emission



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

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