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Review

Modified Biochars and Their Effects on Soil Quality: A Review

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Abstract: Biochar (BC) has attracted attention due to its impacts on soil quality by enhancing soil fertility, carbon storage and contaminants immobilization. BC also induces changes in microbial community structure and enhances crop productivity in long term scenarios compared to many other organic amendments. However, information related to the role of modified BCs in altering the soil quality is still scarce. BC can be modified by using physical, chemical and microbial methods. Modified BC can change the functional groups, pore size, pore structure, surface area and chemical properties of soil, which plays a key role in changing the soil quality. The addition of modified BCs as soil amendment increased soil CEC (cation exchange capacity), EC (electron conductivity), pH, organic matter, hydraulic conductivity, soil porosity, infiltration rate, microbial activities (enzymes and community), nutrient profile and gas exchange properties, but it varies according to the soil structure and pervading environmental conditions. This study provides a basis for effective practical approaches to modifying BCs for improving soil quality.

Keywords: modified biochar; soil quality; physiochemical properties; microbial community; EC; CEC

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1. Introduction

Biochar (BC) is charcoal produced from plant matter and stored in the soil as a means of removing carbon dioxide from the atmosphere. BC application as soil amendment has achieved promising results for higher crop growth and production [1–3], disposal of large scale waste biomass [4], an approved role in climate change mitigation in the long run [5], and soil biochemical property enhancement [6]. Previous studies have shown that adding BC to soil can increase saturate hydraulic conductivity and water infiltration, reduce the soil bulk density and improve the soil structure [7–9].

To improve the efficiency of BC, recent studies have focused on the use of modified BC to improve soil quality and performance for better plant growth and productivity [10–13] by playing a key role as media to provide attachment sites for microbial communities [14,15] and effectively enhance soil physicochemical properties by regulating soil pH [10], electron conductivity (EC) [16], cation exchange capacity (CEC) [14], organic matter [17], and hydraulic conductance, porosity and soil aggregates [14,15]. However, the chemical and physical properties of modified BCs greatly depend on the type of modification reagent, modification method, pyrolysis temperature, pyrolysis process and type of raw material. Generally, the properties of BC are determined by its physical structure (surface area and porosity) [18]. However, only a few studies are present to assess the effect of modified BC on soil quality [14,15,19–21], and a comprehensive review is still missing to address the effect of various modified BCs on soil quality. The main objective of this study is to expose the properties of various modified BCs and their effect on soil physiochemical properties, and their relationship with plant growth and development. The effect of modified BC on plant growth, yield attributes and soil physio-chemical properties (such as soil physical and hydraulic properties, soil organic matter, gas exchange parameters and nutrient profile, soil pH, EC and CEC and soil biological activities) are briefly discussed in this study.

2. Effect of Biochar on Plant Growth and Yield Attributes

BC can be used as a promising soil-amendment to increase crop growth and productivity by modulating soil properties [22–25], because of its unique characteristics such as cation exchange capacity (CEC), abundant (O)-containing functional groups, rich pore structure and large surface area [26,27]. Meta-analysis based on 153 studies and 1254 pair comparisons revealed that plant productivity varies from −31.8% to 974% under different BC conditions [23]. Moreover, they also observed that BC properties including bulk density, ash, pH, carbon content and CEC significantly modified the plant productivity by improving the nutrient uptake and soil physical structure.

Although amending soil with BC has been regarded as an effective approach for improving crop growth and productivity, it is not clear by which mechanism BC increases crop yield. Liu et al. [11] compared the relative contribution of three different BC components, such as mineral nutrient form BC ash (BA), washed BC residue (WB) and water-soluble BC extract (BE) by using *Zea mays* L. (Maize) as a model plant in two soil types Prismosol and Anthrosol. In the Primosol and Anthrosol, WB, BA and BE application increased maize biomass by 18.2%, 24.4% and 41.3%, and 27.1%, 32.7% and 41.6%, respectively. They suggested that BE had a higher plant growth promoting effect as compared to other BCs. In addition, with BE-amendment the number of maize roots, surface area, total volume and biomass were significantly improved, particularly the fine roots diameter (<0.2 mm). Intriguingly, meta-analysis of 81.3% of the dataset from 47 studies showed that BC amendment increased the root growth up to 32%, and the increment of root biomass were 12.7%, +26.9%, +66.0% and +101.6% for cereals, vegetables, grasses and trees, respectively [28]. They suggested that the rate of application and feedstocks of BC were the main factors contributing to plant growth and production. The highest positive effect was noted for gramineous (+46.2%), followed by woody plants (+25.8%) and green waste (+21.1%). Tarin et al. [29] reported that the rice BC amendment significantly increased the photosynthetic rate of *Fokienia hodginsii* (conifer tree) in all four seasons. The rice BC amendment with 80 g kg^{-1} improved 36% biomass compared to control plants. Pristine and acidified rice husk-BC produced 80.5% and 110.7% root dry matter [30]. However, Bonanomi et al. [3] explored the effect of BC on the growth of lettuce (*Lactuca sativa*). They noted that BC had both a strong inhibiting and stimulating effect on plant growth. In conclusion, the application of BC effectively increased the plant biomass, photosynthetic efficiency, root diameter, surface area and root total volume by improving the soil physical structure and nutrient uptake, resulting in higher economical yield. Meta-analysis of BC application showed that BC increased the crop yield up to 10–15%, with concurrent decreases in N_2O emissions [31].

3. Effect of Pristine Biochar on Soil Physiochemical Properties

The BC amendment effectively changed the soil CEC, bulk density, texture, pore structure and surface area [26,27]. However, according to Blanco-Canqui [32], BC generally increased the soil wet aggregate stability (3 to 32.26%), porosity (14 to 64%), soil bulk density (3 to 31%), and soil water availability (4 to 130%), but had a non-significant effect on soil penetration resistance. Additionally, soil pore distribution, size and volume differ in BC feedstock source and pyrolysis temperature. Mesopores (2–50 nm) and macropores (>50 nm) of BC are helpful for water retention and act as the sole habitat for microorganisms. Besides, the nanopores or micropores (<0.9 nm) of BC govern the sorption and chemical properties of BC [33]. Soil particles can easily interact with the fine particles of BC and form the soil aggregates by modulating the water retention and interpore shape [32,34].

During pyrolysis, many volatile compounds are released in the form of gases that increase the surface area of BC and generate honey bee like porous structures that result in higher nutrient retention and water holding capacity [35,36]. Moreover, the feedstock source of BC can also affect these properties. For instance, Weber and Quicker [37] found that the majority of BC possess biomass surface areas ranging from 100–800 m^2 g^{-1}, while BC produced from sewage sludge has a surface area of 100 m^2 g^{-1}. In another case, BC of cottonwood or aspen (populus species) had a lower surface area as compared to BC produced from maize straw [38]. Studies revealed that BC did not equally increase soil porosity, and was mostly dependent upon soil texture class and soil type. Generally, fine textured soil showed less improvement in soil porosity as compared to coarse texture soil by BC application [39].

Blanco-Canqui [32] noted that an addition of BC increased soil properties, minimized the soil water repellency, moderated soil thermal properties, altered water infiltration, and reduced the particle density and tensile strength. Tarin et al. [29] reported the effect of rice straw on the physicochemical properties of soil and suggested that BC amendment can be used to combat soil acidification and phosphorous (P) availability in P deficient soils. In another study, Sadegh-Zadeh et al. [40] found that rice BC application with 50 g kg^{-1} remediates the saline-sodic soil. They noted that Mg^{2+} and Ca^{2+} in the BC surface could exchange Na^{+} on the soil colloids, which thereby resulted in Na^{+} leaching from saline-sodic soils. In addition, it is anticipated that BC is a significant source of carbon (C), and its application improves the soil aggregation properties [41]. Qayyum et al. [30] reported that apristine BC application substantially increased soil pH between 3.8 to 7.5%. In conclusion, BC soil amendment increased soil CEC, bulk density, texture, pore structure, interpose shape and surface area, soil aggregate stability and soil water availability as compared to untreated soil. Moreover, BCs application helps to combat the effect of soil acidification, P deficiency and soil salinity, and act as the sole habitat for microorganism.

4. Biochar Modification and Its Properties

Besides the sorption mechanism, recent developments in BC modification by loading with nanoparticles, organic functional groups, reductants, minerals, bio-materials and activation with an alkali solution in improving sorption capacity is briefly discussed below (Figure 1).

4.1. Biochar Physical Modification

BC modification by using physical methods is an environmentally-friendly and cost-effective approach as compared to chemical modification. It improves the physio-chemical properties of BC including permeability and porosity with controllable measures. The common techniques in the physical modification of BC include magnetization, ball milling, microwave irradiation and steam/gas activation that improves the BC properties to enhance the soil quality. For instance, in ball milling the pristine BC is broken into small powder that increases its surface area and adsorption capacity while reducing its particle size [42]. Ball milling can be classified into chemical ball milling and physical ball milling. Chemical ball milling modifies the microporous structure and functional groups, whereas physical ball milling greatly influences the surface area and particle size of BC [43]. Magnetic BC synthesized from chemical ball milling can easily be recovered with the help of an external magnetic field [44]. The catalytic activity and surface charge of BC improve with the magnetization process, which thereby result in better environmental remediation.

Another emerging technique for BC modification is microwave irradiation, which raises the temperature of BC up to 200–300 °C by microwave heating within a short time. The microwave-modified BC showed the higher surface area and absorption capacity for many pollutants with its hydraulic functional groups. The integration of steam activation with microwave irradiation significantly improved the physiochemical properties of BC, including water holding capacity and CEC [45]. Gas/steam activation also induce porosity and increase the surface area of BC by removing the trapped residues inside the porous structure of BC due to partial combustion. This process of BC modification activates carbon dioxide and hydrogen through surface reactions [46] and, as a consequence, it shows greater adsorption capacity for nitrogen dioxide and methane over the pristine BC [47]. In conclusion, physical modifications of BCs through ball milling increases surface area, adsorption capacity and microporous structure of BCs, while microwave irradiation modification improves BCs surface area and absorption capacity for many pollutants, and gas/steam activation is important for improving BC porosity, surface area, physiochemical properties and adsorption capacity for different gasses as compared to pristine BCs.

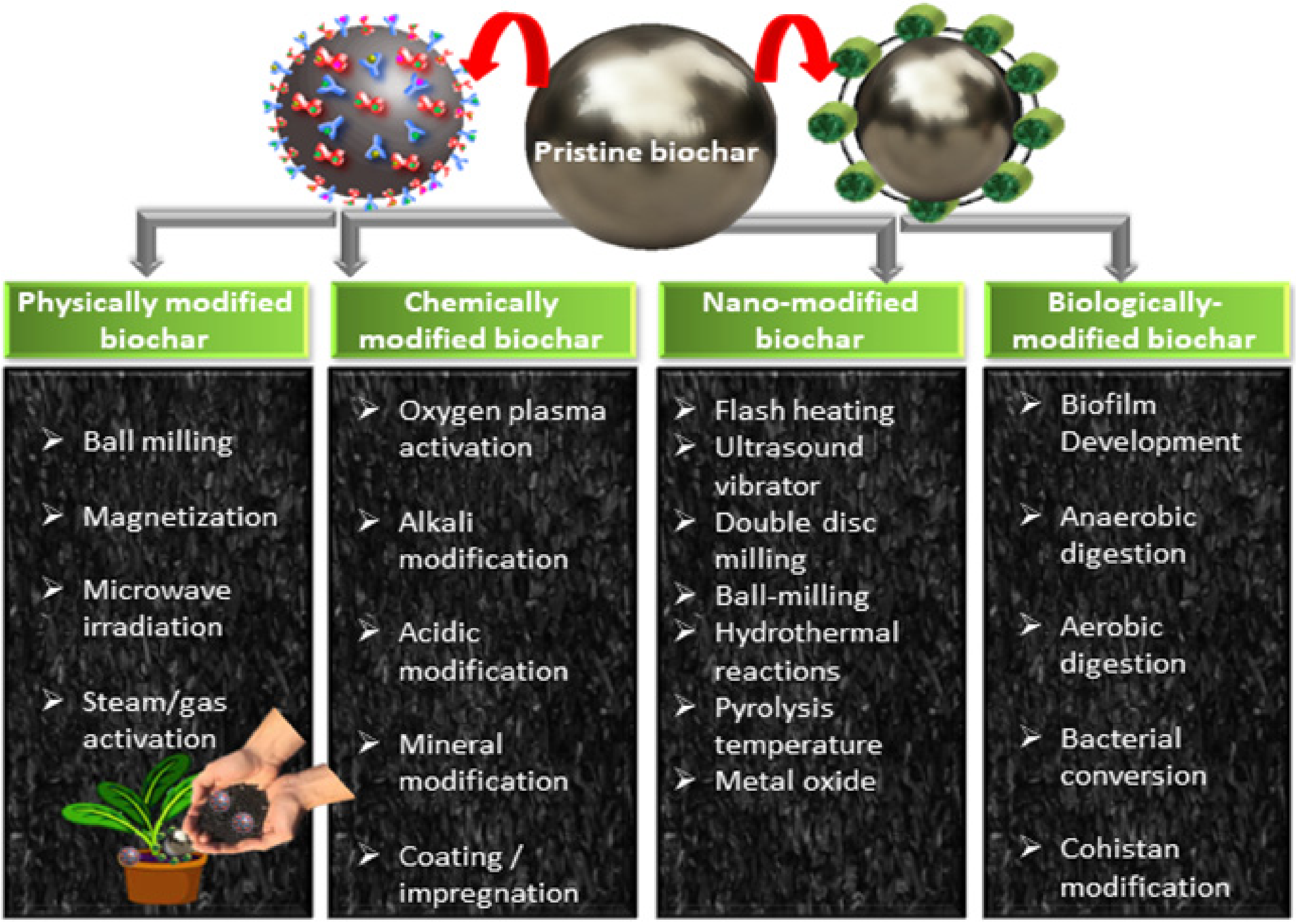

Figure 1. Depiction of different ways for conversion of pristine biochar to modified biochar for improving soil quality.

4.2. Biochar Modification with Mineral Fertilizers and Chemicals

Biochar can be modified through reactions with different mineral fertilizers and chemicals to make them more efficient at performing specific applications by enhancing their physiochemical properties [48]. Chemical modification can be done with a range of processes, such as oxygen plasma activation, coating/impregnation, mineral coating, and acid/alkali modifications. Bamboo hardwood modified with carbon disulfide (CS_2) and sodium hydroxide (NaOH) at 45 °C for 8 h showed greater effectiveness for chromium (Cr) remediation. It was also observed that the sulfur-iron modified BC had more surface roughness and granular massive structure as compared to pristine BC [49]. In addition, Yin et al. [50] reported that poplar chips BC modified with 20% aluminium chloride ($AlCl_3$) at 80 °C for 48 h increased the BC yield and BET surface area (96.7%), while decreasing the carbon content (55.88) as compared to pristine. They noted that BC modified with 15% $AlCl_3$ showed optimum adsorption for nitrate, whereas the 20% $AlCl_3$ was best for phosphate adsorption.

In another study, swine manure modified BC with phosphoric acid (H_3PO_4) at 25 °C for 24 h showed higher mesopore, micropore volume and total pore area, while rice straw modified with the same acid showed non-significant modifications [51]. Cow manure and wheat straw BC modified with nitric acid (HNO_3) at 90 °C for 4 h showed negative surface charge, higher COO groups and enhanced U(VI) adsorption than in unmodified BC. The maximum U(VI) adsorption capacity of wheat straw was 40 times higher than pristine BC treatment [52]. Moreover, 3.0% cetyltrimethyl ammonium bromide (CTAB) modification with 5 g of dried Auricularia auricula dreg increased the surface area and pore diameter up to 6.1% and 16.5%, respectively. Consequently, the number of micropores and mesoporous in the unit area also increased. The adsorption quantity and rate of the modified BC were 8.0% and 6.4% higher than pristine BC [53]. In addition, NaOH (sodium hydroxide) modification in dairy manure BC showed higher oxygen-containing functional groups, ion exchange capacity and surface area, and increased the adsorption capacity of BC for Cd and Pb (lead) as compared to untreated BC. The highest sorption capacity was 68.08 and 175.53 mg g^{-1} for Cd and Pb, respectively [54].

HCl+ ultra-sonication of coconut shell BC increased the microcosmic pore area (6.1%), and the average pore diameter (16.5%) structure and surface functional groups as compared to the untreated BC [55]. Moreover, potassium hydroxide (KOH) and sodium sulfide (Na_2S) based modification of corn straw increased BET surface area up to 59.23 and 55.58 m^2 g^{-1}, respectively, as compared to pristine BC (32.85 m^2 g^{-1}). They deduced that these types of modified BC can be effectively used for remediating mercury (Hg) pollution. Besides, Li et al. [56] used NaOH, H_3PO_4, HNO_3, NH_4OH and sulphuric acid (H_2SO_4) to carry out treatment on coconut shell-based carbon. They noted that higher adsorption capacity (o-xylene, a hydrophobic volatile organic compound) was obtained with alkali-treated carbon as compared to acid-treated BC. The reason is that total oxygen containing functional groups diminished, and pore volume and surface area increased by alkali treatment, while it was opposite for acid application. BC activation with NaOH and KOH is quite different, KOH activation in situ showed an interaction between K and layers of the carbon crystalline, while Na did not show any interaction for carbon. In another case, Sajjadi et al. [57] noted that H_3PO_4, HNO_3, H_2SO_4 and HCl contains higher amounts of oxygen containing functional groups (such as carbonyl, quinone, ether, carboxylic anhydride, lactone, carboxylic acid, phenol and intercalated oxygen), while alkali modified NaOH and KOH have a greater carbon content [58].

Moreover, oxidizing agents Fe(III) and $KMnO_4$ significantly improved the specific area and pore size of BC [57]. According to Lin et al. [59], Fe-Mn modified BC increased pH, surface area, rich C content and a certain frame structure. In another case, Li et al. [47] reported that cadmium-binding BC increased surface area and increased oxygen-containing functional groups. BC modified by combining BC with nano-zero-valent iron increased the phosphorous and decreased the methane and nitrous oxide emission. Conversely, the nitrous oxide and carbon dioxide emission increased by phosphorous modified BC [60]. Moreover, *Thalia dealbata* BC modified with magnesium chloride ($MgCl_2$) showed higher surface area (110.6 m^2 g^{-1}) as compared to unmodified BC (7.1 m^2 g^{-1}) [61], mostly Mg-BC used to remediate soil from Cd and sulfamethoxazole. Additionally, oxygen gas flow through a plasma chamber that has dielectric barrier discharge under certain pressure converts plasma into oxygen ions, excited atoms, electrons and many reactive oxygen species [62], which react with BC functional groups and renders the oxygen plasma-activated BC more active as compared to chemically modified BC. The new insight of these chemical modification methods and BC properties can pave the way to improve the soil quality and sustainable agriculture. In a nutshell, the use of chemical and mineral modified BCs are most important due to their functional groups, which effectively interact with soil pollutants and improve soil quality by improving mineral uptake and soil gas exchange properties. Besides, higher adsorption capacity and greater carbon content was observed by using alkali-treated chemicals, while acid containing BCs have higher oxygen containing functional groups.

4.3. Biochar Modification with Nano-Particles

Nano-BC is currently used as it amalgamates the advantage of nanotechnology in BC modification. Decreasing BC particle size to the micro range (10–600 μm) led to enhancement of the available sites for adsorption, thus resulting in improved adsorption capacity [63–65], and further decreasing of BC size to nano-range (100 nm) increases its properties, such as biological effectiveness, adsorption potential, surface energy and surface to volume ratio [63,64,66]. The nano-particle size range is controlled by pyrolysis temperature or perhaps through exfoliation [66,67], flash heating [68], ultrasound vibrator [69], ball-milling [70], double disc milling [71], and hydrothermal reactions using agriculture residue as by product [72]. Metal nanoparticles increase the CEC, porosity, surface area and functional groups as compared to unmodified BCs. The impregnation can be achieved through pre-treating feedstock biomass with metal salts, supporting BC with functional nano-particles or forming composites with metal oxide nano-particles, which renders them high affinity to various pollutants [26,73]. In short, nano-modified BCs increased the adsorption capacity, biological effectiveness, functional groups efficiency, CEC, porosity, surface area, and surface to volume ratio of BCs as compared to pristine BCs.

4.4. Biochar Modification with Microbes

Biological modification of BC can be achieved by pre-treating the feedstock with anaerobic digestion and constructing a film on the internal and external surface of BC [43]. Digestion of waste material by aerobic and anaerobic bacteria increases the economy by producing bio-fertilizers and biofuel. BCs generated from bacterial digestion play a key role in improving hydrophobicity, CEC, and surface area, and are mostly utilized to remove heavy metals, pharmaceuticals, and pollutants from contaminated soils by developing biofilms [47,74]. BC-modified bioasphalt improves biomass utilization and enhances environmental protection [75]. In another case, Tao et al. [76] used the feasibility of combining anaerobic pyrolysis to produce biologically modified BC (corn stalk). Anaerobic ensiling improved biodegradation into non-fermented residue after 24 h of fermentation. This process's non-fermented material was pyrolyzed at 500 °C to synthesize biologically active BC. They observed that modified BC had higher oxygen-containing functional groups, mineral components and surface area as compared to pristine BC. Modified BC with anaerobic bacteria also enhanced the Cd (II) sorption up to 2.2 times as compared to unmodified BC. Moreover, chitosan (a sugar obtained from the outer skeleton of fish) modified bamboo BC, and improved the sorption of Pb on the chitosan modified BC and reduced its uptake (60%) and metal toxicity [77]. They suggested that the presence of chitosan on the BC surface increased alkalinity due to the presence of amine functional groups (weak bases), thus its amendment helps to overcome soil acidity. In addition, it also greatly lowered the C/N ratio of the BC up to 15.5 to 27.1, which make it a better choice for soil reclamation. Muhammad et al. [78] modified the wheat straw BC with soil indigenous-microbes and noted higher biosorption capacity (14.42 mg g^{-1}) as compared to pristine BC (6.28 mg g^{-1}) and wheat straw soil amendment (4.20 mg g^{-1}). They noted that biologically modified wheat straw BC had higher C, N, H content and surface area (6.5%), and porous morphology due to microbial degradation. In another case, a periphyton-based system comprising a BC column and a periphyton bioreactor presented a strong ability to entrap As(III) by biosorption. The calcite, -OH and -C, =O groups on the periphytic biofilm surfaces played an important role in As(III) entrapment and reduced the As toxicity and avoided microorganism poisoning [79]. Conclusively, biological modified biochar improved hydrophobicity, CEC, surface area, oxygen-containing functional groups, mineral components, and alkalinity and decreased the C/N ratio of BC as compared to pristine BC. These types of BC are mostly used to overcome heavy metal stress and other pollutants from soil.

5. Effect of Modified Biochar on Soil Quality

Modified BC can change the functional groups, pore size, pore structure, surface area and chemical properties of BC that play a key role in changing the soil quality by responding to its physical and hydraulic properties, nutrient profile, gas exchange properties, organic matter, soil pH, EC, CEC, and biological activities (bacteria, fungus and enzymes). The detail of soil quality with the addition of modified BC as soil amendment is briefly described below.

5.1. Effect of Modified Biochar on Soil Physical and Hydraulic Properties

BC as a soil amendment can influence the soil's physical and chemical properties, thus providing a means to improve soil fertility. According to Chen et al. [80], small-sized BC particles change the soil pore structure and affect soil aggregates' stability, porosity, fractal dimension, and the degree of anisotropy. Duan et al. [14] compared pristine BC with composite modified BC, particle-sized BC and acidified BC and noted that all BC modifications improved the soil water-stable aggregate contents. The soil-water aggregate content was higher with acid-modified BC at the 0–15 cm soil layer, being 1.45–1.80 and 1.59–1.96 times higher than unmodified BC and control treatments, respectively. They also found that acidified BC resulted in higher soil water holding capacity and soil infiltration rate. In another case, An et al. [15] mixed the H_3PO_4 and KOH modified BC of peach shell and pig manure BC with four dosages (0, 2, 3, and 8%) and noted that the H_3PO_4-modified BC had higher water retention as compared to KOH and pristine BCs. Instead, KOH showed reduced hydraulic functional groups on the surface of BC. They observed that pig manure BCs showed higher crack suppression intensity than functional BCs. They generally suggested a 5 to 8% BC dosage for improving water retention and reducing cracks. In conclusion, H_3PO_4, composite, peach shell, pig manure, particle-sized, and acidified BCs effectively improved the soil physical and hydraulic properties as compared to other modified BCs.

5.2. Effects of Modified Biochar on Soil Organic Matter

Soil organic matter is the component of soil that consists of plant and animal detritus at various stages of decomposition, soil microbe cells and tissues, and substances synthesized by soil microbes and play an important role in the survival of fauna and flora. The modified BC also increased the presence of the organic matter [19,20]. For instance, Li et al. [47] found that Cd-binding BC increased soil C/N ratios and soil organic carbon. Moreover, Wang et al. [81] noted higher organic matter accumulation of soil organic matter and organic carbon with the application of rice husk BC that was successively modified with NaOH, HNO_3 and dimethyl dithiocarbamate sodium (3% *w*/*w*) as compared to unmodified BC. Moreover, Moradi & Karimi [17] also noted higher soil organic matter and organic carbon with the soil amendment of Fe modified BC (2% *w*/*w*). Similarly, higher organic matter was also noted with the application of Fe-Mn BC (2% *w*/*w*) [46], S-BC (1% *w*/*w*), S-Fe BC (1% *w*/*w*) [49], iron-modified BC (3% *w*/*w*) [20], thiourea-modified BC (8% *w*/*w*), carrot pulp BC (8% *w*/*w*) [19], and iron-zinc oxide composite modified corn straw BC (3% *w*/*w*) [10] as compared to pristine BC (Table 1). In short, chemical and mineral modified BCs can play a key role in improving soil organic matter and C/N ratios.

Table 1. Efficacy of modified biochar in improving soil heath.

Modified BC	BC Dose	Soil Properties	Reference
Mn oxide BC	4% (*w*/*w*)	Increased adsorption capacity of As and pH of soil	[82]
Poultry manure BC	5% (*w*/*w*)	Reduction of toxic Cr (VI) in soil	[83]
Sheep manure BC	5% (*w*/*w*)	Reduction of toxic Cr (VI) in soil	[83]
Coconut shell BC	5% (*w*/*w*)	Increased soil pH, CEC, bacteria, fungal and actinomyces counts, acid phosphatase, dehydrogenase, and urease while invertase was not affected.	[55]
S-modified rice husk BC	5% (*w*/*w*)	Leachate total Hg concentrations decreased while increased Leachate total Hg removal	[84]
Magnetic BC	2% (*w*/*w*)	Decreased Cd acid soluble fraction, and Cd reducible fraction, while no effect on Cd oxidizable fraction and Cd residual fraction were observed. Decreased Zn acid soluble fraction, and increased Zn residual fraction, while no effect on Zn oxidizable fraction and Zn reducible fraction were observed. Increased Pb acid soluble fraction, Pb reducible fraction, and Pb residual fraction, while no effect on Pb oxidizable fraction was observed. Increased Cu oxidizable fraction, Cu reducible fraction, and Cu residual fraction, while no effect on Cu acid soluble fraction was observed.	[33]
Fe-Mn BC	2 wt%	Increased soil enzymes (UE, ALP/AKP, CAT, and POD) and the abundances of Proteobacteria and Firmicutes phyla. Moreover, decreased soil pH and bioavailable arsenic concentration	[59]
Fe-Mn BC	2% (*w*/*w*)	Decreased pH, bioavailability of antimony and cadmium, while increased EC, available P, available K, total N, and organic matter. Moreover, UE and CAT did not affect but acid phosphatase activity was decreased	[46]
MgO-BC	4.5 Mg ha^{-1}	Increased available P	[12]
S BC	1% (*w*/*w*)	Increased soil organic matter content and microbial community while decreased available Cd concentrations	[49]
S-Fe BC	1% (*w*/*w*)	Increased soil organic matter content and microbial community while decreased available Cd concentrations	[49]
Fe-Mn-Ce modified BC	2 wt%	Increased S-CAT, S-UE, S-POD and S-AKP/ALP activity. Moreover, microbial activities increased, especially Gemmatimonadaceae and Oxalobacteraceae families.	[21]
Multiple modified BC	3% (*w*/*w*)	Decreased DTPA-extractable Cd, and Cu, pH, and available P while increased CEC, available K, organic matter, and dehydrogenase in soil	[85]
Rhamnolipid-modified BC	2 wt%	Increased dehydrogenase activity, bacterial and fungal diversity indices, emission of CO_2 and CH_4, while reduced the emission of N_2O	[86]
Iron-modified BC	3% (*w*/*w*)	Decreased soil pH, available Fe, available As, available Cd, available Pb, S-CAT, and UE while increased total organic carbon	[20]
Thiourea-modified BC	8% (*w*/*w*)	Increased soil pH, CEC, soil organic carbon, and EC. Decreased acid soluble fraction of Cu and reducible fraction of Cu while increased oxidizable fraction of Cu and residual fraction of Cu. Decreased acid soluble fraction of Zn while increased reducible fraction of Zn, oxidizable fraction of Zn and residual fraction of Zn	[19]

Table 1. *Cont.*

Modified BC	BC Dose	Soil Properties	Reference
Carrot pulp BC	8% (*w*/*w*)	Increased soil pH, CEC, soil organic carbon, and EC. Decreased acid soluble fraction of Cu and reducible fraction of Cu while increased oxidizable fraction of Cu and residual fraction of Cu. Decreased acid soluble fraction of Zn while increased reducible fraction of Zn, oxidizable fraction of Zn and residual fraction of Zn	[19]
Fe–Mn–La-modified BC	2 wt%	Decreased soil As concentration and increased S-CAT, S-UE, S-POD and S-AKP/ALP activity. Moreover, microbial activities increased especially γ-Proteobacteria, α-Proteobacteria, Acidobacteria, and Gemmatimonadetes.	[87]
Modified BC (rice husk BC and successively modified with NaOH, HNO_3 and dimethyl dithiocarbamate sodium)	3% (*w*/*w*)	Increased soil pH, dissolved organic carbon, organic matter, K, Ca, Mg, Na, and available K, while reduced available P, CEC, DTPA-extractable Cd, Pb, Cu and Zn. Moreover, increased S-CAT and dehydrogenase	[81]
Fe modified BC	2% (*w*/*w*)	Increased pH, soil organic carbon, microbial biomass carbon, dehydrogenase activity, Cd bound to organic matter, residual Cd and Cd bound to iron–manganese oxides while decreased Cd bound to carbonates, DTPA-extractable Cd, exchangeable Cd, and Cd mobility factor	[17]
Brassica napus BC-UV	0.6% (*w*/*w*)	Increased soil pH and EC and decreased $CaCl_2$-extractable Cd	[16]
Lolium perenne BC-UV	0.6% (*w*/*w*)	Increased soil pH and EC and decreased $CaCl_2$-extractable Cd	[16]
Iron-zinc oxide composite modified corn straw BC	3% (*w*/*w*)	Increased pH, CEC, and dissolved organic carbon (DOC), bacterial community, i.e., Chao1 Shannon and Simpson while decreased DTPA-Cd	[10]
Particle size modified BC	1% (*w*/*w*)	Soil soluble K^+, Ca^{2+}, and Mg^{2+} increased while soil soluble Na^+ and Na^+ adsorption ratio decreased	[14]
Composite modified BC	1% (*w*/*w*)	Soil soluble K^+, Ca^{2+}, and Mg^{2+} increased while soil soluble Na^+ and Na^+ adsorption ratio decreased	[14]

5.3. Gas Exchange Parameters and Nutrient Profile

Nutrient profile and gas exchange properties of soil can precisely elaborate its current quality status both for bacterial community and plant growth and development. Currently, Chen et al. [88] observed the application of nano-modified BC soil amendment reduced soil runoff, sediment and nutrient loss on sloped farmland. They reported that nano-BC (1.0%) reduced nitrate loss up to 13.6–59.8% in the sloping fields of Loess Plateau. They noted that the peak value of nitrate distribution in the soil profile moved downward, and the maximum was observed at 10 to 15 cm. In addition, Lin et al. [59] reported that Fe-Mn modified BC increased crystalline hydrous-oxide bound, soil redox-potential, amorphous-hydrous bound, while reducing the arsenic content in soil. In another case, Li et al. [47] found that Cd modified BC increased soil pH, organic carbon/total nitrogen and C/N, and decreased the nitrate nitrogen, available phosphorus, ammonium nitrogen and total nitrogen. Moreover, Qayyum et al. [30] reported that acidified BC has potential to improve phosphorous content in soil.

Additionally, Yin et al. [50] observed that $AlCl_3$-modified BC significantly improved the PO_4^{3-} and NO_3^- adsorption as compared to pristine BC. A 2% application of magnetic BC decreased the Zn acid-soluble fraction, and increased the Zn residual fraction, while having no effect on the Zn oxidizable fraction and Zn reducible fraction [33]. In addition, it increased the copper (Cu) oxidizable fraction, Cu reducible fraction, and Cu residual fraction, while having no effect on the Cu acid-soluble fraction. Gholami and Rahimi et al. [19] reported that thiourea-modified BC (8% *w*/*w*) decreased the acid-soluble fraction of Cu and a reducible fraction of Cu, while increasing the oxidizable fraction of Cu and a residual fraction of Cu. While a decreased acid-soluble fraction of Zn and increased reducible fraction of Zn was observed, an oxidizable fraction of Zn and a residual fraction of Zn was observed after thiourea-modified BC application. They also noted that carrot pulp BC modification decreased the acid soluble fraction of Cu and reducible fraction of Cu, while increasing the oxidizable fraction of Cu and residual fraction of Cu. Besides, a decreased acid soluble fraction of Zn and increased reducible fraction of Zn, oxidizable fraction of Zn and residual fraction of Zn was observed with carrot pulp BC modification. Moreover, Wang et al. [46] reported that available P, available K and total N decreased with soil amendment with modified Fe-Mn BC (2%). An increase in P content was found with the application of Mg-O modified and multiple modified BC as compared to pristine BC [12,85]. In another case, an iron-modified BC application (3%) reduced the availability of Fe in soil as compared to unmodified BC [20]. According to Wang et al. [81], modified rice husk BC increased the K, Ca, Mg, Na, and available K, while reducing the available P, Pb, Cu and Zn.

According to Duan et al. [14], particle size modified BC (1%) and composite modified BC (1%) increased the soil soluble K^+, Ca^{2+}, and Mg^{2+}, while decreasing the soil soluble Na^+ and Na^+ adsorption ratio. In addition, the treatment of 1% poultry manure BC at 550 °C changed the gas exchange properties by increasing the CO_2 emission from soil up to 91.4% as compared to poultry manure treatment [89] (Figure 2). Similarly, the increased emission of CO_2 and CH_4, and reduced emission of N_2O was obtained with application of rhamnolipid-modified BC (2 wt%) [86] (Table 1). In brief, Fe-Mn, Cd, $AlCl_3$, magnetic, thiourea, carrot pulp, composite, Mg-O, rice husk and nano-modified BCs can improve the soil nutrient profile and prevent their leaching even in sloppy landscapes, while poultry manure and rhamnolipid modified BCs proved to be highly important for enhancing soil gas exchange properties.

5.4. Effects of Modified Biochar on Soil pH

Qayyum et al. [30] reported that BC acid modification with the addition of acid (1 N HCl) did not decrease the soil alkalinity. In another case, He et al. [90] modified rice straw BC with 1:1 HNO_3/H_2SO_4 and 15% H_2O_2, and used HCl-treated and unmodified BC as control to observe the acid paddy soil properties. They noted that pH buffering capacity and resistance to paddy soil acidification were effectively improved with the addition of HNO_3/H_2SO_4 and H_2O_2-modified BC. The surface functional groups were responsible for increasing the soil resistance to acidification. The generation of protonation of organic anions through dissociation of these functional groups retarded the decline in soil pH under acidification. They suggested that BC incorporation with HNO_3/H_2SO_4 led to higher carboxyl functional groups as compared to H_2O_2-modified BC, which is why it showed more soil resistance to acidification. The application of HNO_3/H_2SO_4-modified BC after the wet–dry cycle appeared to increase the pH of acidic paddy soil. Their work suggested that HNO_3/H_2SO_4-BC modification is a paramount solution to remediate acidic soil. The basic mechanism is that the weak acid functional group on the surface of BC mainly occurs in the form of organic anions under alkaline and neutral soils. Under soil acidification, these organic anions protonated with H^+ and converted into neutral molecules, inhibiting the soil acidification and declining the soil pH [91,92]. According to Yu et al. [82], soil pH increased with the application of Mn oxide modified BC (4%). Similar results were obtained with soil amendments of modified coconut shell BC (5%) [55], thiourea-modified BC (8%), carrot pulp BC (8%) [19], modified rice husk BC (successively modified with NaOH, HNO_3 and dimethyl dithiocarbamate sodium (3%) [81]. Iron-zinc oxide composite modified corn straw BC (3%) [10], Fe modified BC (2%) [17], *Brassica napus* BC-UV (0.6%) [16], *Lolium perenne* BC-UV (0.6%) [16], while decreases in pH were obtained with the use of modified Fe-Mn BC (2%) [59], Fe-Mn BC (2%) [46], multiple modified BC (3%) [85], and iron-modified BC (3%) [20] as compared to pristine BC. In short, acid modified BCs have pH buffering capacity and resistance to soil acidification due to the generation of higher protonation of organic anions, while metal-oxides and alkaline modified BCs showed a higher affinity to increased soil pH.

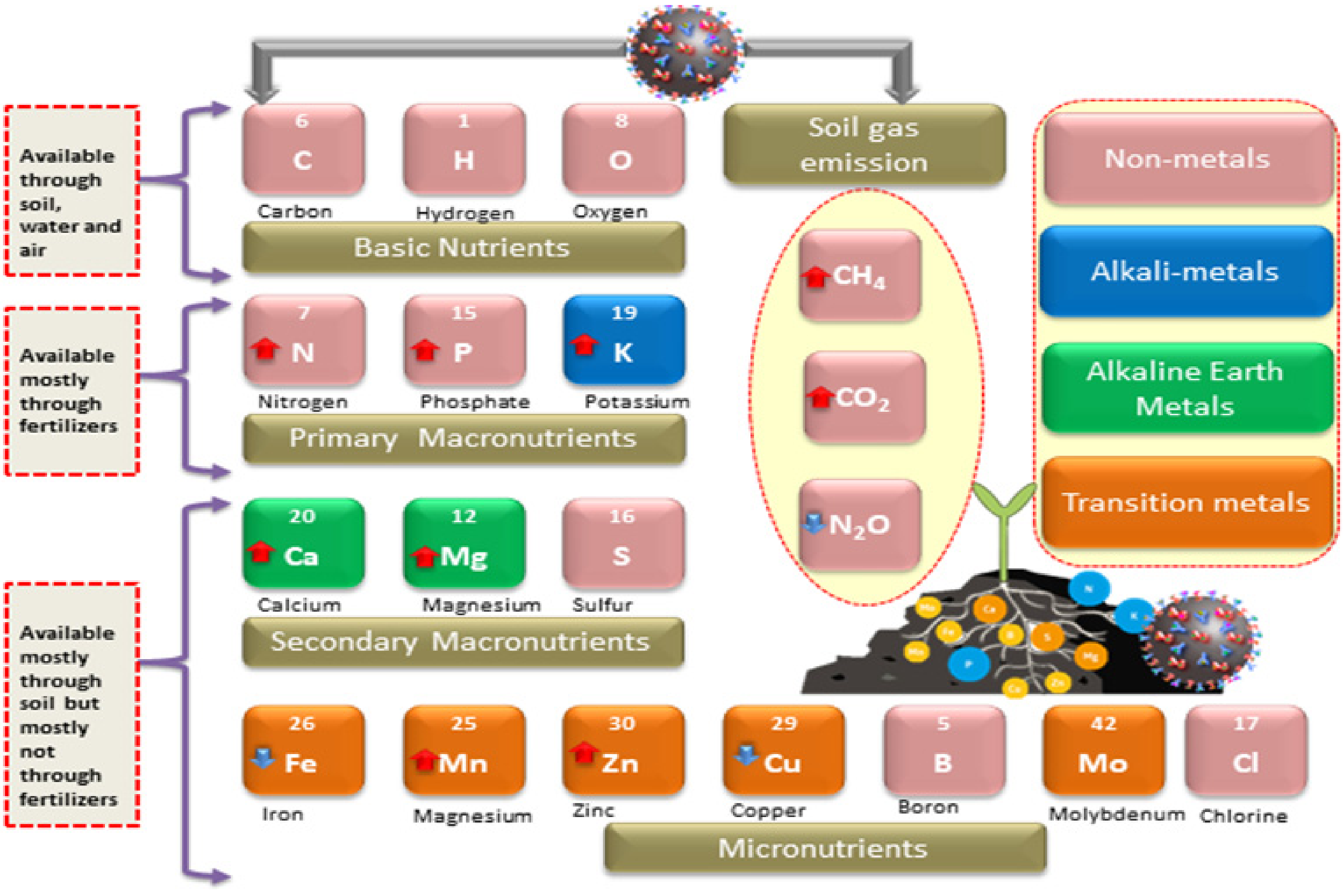

Figure 2. The effect of modified biochar on soil gas exchange and nutrient profile. The red color arrow represent increase, while blue arrow shows decrease in the nutrient content and gas emission.

5.5. Effects of Modified Biochar on Soil EC and CEC

Qayyum et al. [30] reported that pristine BC and acidified BC had a non-significant effect on soil EC as compared to the control. The rice straw BC modified with HCl reduced the soil EC by inducing $CaCO_3$ dissolution, which added H^+ and Ca^{2+} ions to soil, which replaced the Na^+ from the soil colloidal surface to facilitate the Na^+ leaching from the saline-sodic soil [40]. In another case, Zhang et al. [16] found that *Brassica napus* and *Lolium perenne* BC modified with UV (0.6%) showed higher soil EC as compared to pristine BC. Moreover, Gholami and Rahimi [19] also noted a higher EC with the application of modified carrot pulp BC (8%) as compared to unmodified BC. Similarly, the application of Fe-Mn modified BC also increased the soil EC [46]. In another study, thiourea-modified BC (8%) also increased soil EC as compared to untreated BC [19]. Additionally, Liu et al. [55] noted high CEC with the application of modified coconut shell BC (5% w/w). Similarly, an increase in EC was also found with the application of multiple modified BC (3% w/w) [85], thiourea-modified BC (8% w/w), carrot pulp BC (8% w/w) [19], rice modified BC [81], and iron-zinc oxide composite modified corn straw BC 3% (w/w) [10]. In summary, HCl, UV, Fe-Mn, thiourea and carrot pulp modified BCs can be used to increase the soil EC and CEC. However, new studies are vital to further elucidate the effect of modified BCs to enhance the soil EC and CEC.

5.6. Effect of Modified Biochar on Soil Biological Activities

Nano-BC application appreciably increased the microbial activity, such as the biomass of Bacteroidetes and Actinobacteria in soil, and decreased the activity of Proteobacteria, which was predominately present in contaminated soil [60]. In another study, Wu et al. [93] reported that calcium based magnetic BC significantly increased the abundance of microbial taxa and size of the bacterial population that thereby resulted in composition shift. Moreover, Lin et al. [59] reported that Fe-Mn modified BC increased the soil enzyme activity, with the exception of lower alkaline phosphatase activity and abundance of Bacteroidetes, while increasing the population of Firmicutes and Proteobacteria as compared to the control and sole addition of BC.

Moreover, Li et al. [47] found that BC aging by Cd increased microbial abundance, gram-negative bacteria, altered gram-positive/gram-negative bacteria, and decreased gram positive bacteria and microflora. In another study, Liu et al. [60] reported that nano-zero-valent iron increased the *Gemmatimanas* and *Sphingomonas* bacterial species, which resulted in higher nitrogen transformation and metabolism. They also increased the community structure of fungus composite with *Fusarium*. In addition, increased microbial activity (bacteria and fungus) was also found by the modified BC with sulfur (S) (1%) and S-Fe (1%) [49] and rhamnolipid-modified BC (2%) [86], Fe modified BC (2%) [17] and iron-zinc oxide composite modified corn straw BC (3%) [10].

In addition, Liu et al. [55] reported that coconut shell modified BC (5%) increased the bacterial and fungal community and soil enzymes including acid phosphatase, dehydrogenase, and urease, while non-significant changes were noted for invertase. Furthermore, Lin et al. [59] reported that soil amendment of Fe-Mn modified BC (2%) increased soil enzymes alkaline phosphatase/ ALP/AKP, urease (UE), peroxidase (POD), catalase (CAT) and the abundances of *Proteobacteria* and *Firmicutes* phyla. In another case, Fe-Mn-Ce modified BC (2%) increased S-CAT, S-UE, S-POD and S-AKP/ALP activity, and modified microbial activities especially increased the abundance of *Gemmatimonadaceae* and *Oxalobacteraceae* families as compared to pristine BC [21]. Similarly, Lin et al. [87] reported increased S-CAT, S-UE, S-POD and S-AKP/ALP activity and microbial population especially γ-Proteobacteria, α-Proteobacteria, *Acidobacteria*, and *Gemmatimonadetes* with soil amendment of the Fe–Mn–La-modified BC (2 wt%). Moreover, Wen et al. [20] noted decreased activity of S-CAT, and UE with application of iron-modified BC (3%). Conversely, Wang et al. [46] reported that Fe-Mn BC (2%) had a non-significant effect on UE and CAT activities, while decreasing the phosphatase activity. In addition, dehydrogenase activity was increased with the application of multiple modified BC (3%) [85], rhamnolipid-modified BC (2%) [86], rice husk modified BC (3%) [81] and Fe modified BC (2%) [17] (Figure 3). The detailed study of soil enzymes and soil microbes changed through the application of modified-BC effectively improving the soil quality, so intensive research is direly needed to explore this field. To summarize, modified BCs effectively changed the microbial communities, increased microbial diversity and developed a microbial co-occurrence network, implied to increase soil dwelling behavior and soil ecosystem function related to nutrient- and C-cycling that results in better soil structure and quality.

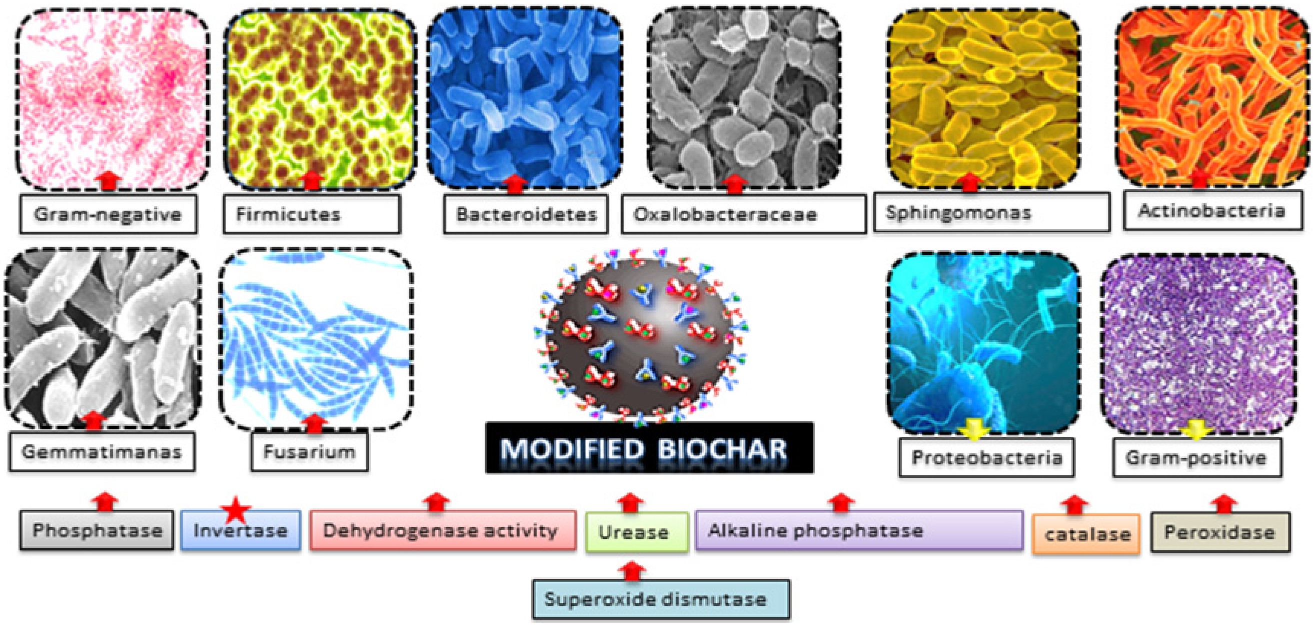

Figure 3. The effect of modified biochar on soil microbial community and enzymatic activity. The red arrows highlight the increase in activities, while yellow arrows show a decrease in specific activity. The star mentioned the non-significant changes.

6. Conclusions and Future Prospects

Modified BCs-based fertilizer addition enabled changes in the keystone taxa (algae and fungi), in the network topology structure, active participation in soil C- and nutrient-cycling, enhanced gas exchange attributes, improved soil productivity and properties including soil physical structure, enhanced soil hydraulic properties, altered soil pore structure, managed soil EC, CEC and pH, and combatted soil-based abiotic stresses. So, modified BCs soil amendments appeal from a carbon accounting and soil condition perspective. The modified BCs with mineral fertilizers, chemicals, nano-particles and biological material effectively improved the soil quality and can be used as an effective technique to promote plant growth and development. Further research is urgently required to determine how modified BCs influence the fate of the environment and to verify the proposed mechanisms involved in modifying BC properties for soil quality improvement. For instance, Li et al. [47] reported that BC modification risked the Cd desorption due to aging. The major disadvantage of ball milling modified BC is their finer size, which poses potential risk of ground water pollution. In addition, the stability of BC after pollutant absorption is also a main concern [43]. Recently, little effort has been made to explore the effect of modified BCs on soil born microbes and plants, so further studies are deliberately required to expose their environmental risk before their more intensive exploitations. Moreover, new development in the analysis of BCs properties and surface functional groups will no doubt be pivotal to uncovering the hidden dimensions of microbe interactions and soil nutrients, and pave the way for sustainable agriculture development. However, there are also some risks in using modified BCs that must be considered for developing BCs.

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