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REVIEW ARTICLE

Development of biomass-derived biochar for agronomic and environmental remediation applications

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Abstract

An increasing interest in biochar application has opened many multidisciplinary research areas in science. Biochar can be produced by thermochemical conversion of organic biomass in an oxygen-deficient condition. Extensive research has been conducted on the potential of biochar for agronomic applications, such as soil fertility improvement and carbon sequestration due to its specific mineralogical composition and long-term stability in the soil. Using biochar for environmental remediation has also been recognized recently as a promising area of research for its unique physicochemical characteristics, redox potential, and adsorption capacity. However, the published works are mostly focused only on the agronomic and environmental applications with little information presented to elucidate the different mechanisms involved. This study, therefore, aims to examine the influence of controlling parameters during biochar production, such as pyrolysis temperature, residence time, and types of feedstock on the characteristics of biochar. Various mechanisms explaining the potential of biochar for the environmental and agronomic applications are discussed in detail. The challenges faced in biochar development and its field applications for agronomic and environmental remediation purposes are also highlighted. Finally, recommendations for future research are given on the development of biochar with high redox functional groups and sorption potential as well as on understanding the behavior of biochar under the natural field conditions.

Keywords Pyrolysis · Biochar · Environment · Pollution · Soil · Carbon sequestration

1 Introduction

Biochar is defined as "a carbon (C) rich material produced when organic biomass such as crop residues, wood chips or manure are burnt in a closed container with little or no air" [80]. More descriptively, Shackley et al. [122, 123] explained biochar as "the carbonaceous porous solid material obtained from the thermochemical conversion of organic biomass in oxygen-deficient conditions with the physicochemical characteristics suitable for the long-term and safe carbon storage in the environment." Research on biochar is rooted in (a) research on Amazonian terra preta soils in the twentieth century

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(the pioneering work of Sombroek), (b) significant efforts during the 1970s and 1980s on research related to charcoal application on plant and soil, (c) research on the characteristics of naturally occurring charcoal and black carbon, and (d) research and development on biomass pyrolysis and gasification [13, 79].

The conversion of biomass to biochar could assist with waste management while also offering additional benefits to the environment [43, 150]. Those include soil amendment, carbon sequestration, and pollutant remediation (Fig. 1) [35, 150, 151]. Owing to the carbon sequestration capabilities of biochar, its application in soil has been recommended as a promising way for climate change mitigation [127]. Specifically, the atmospheric emissions of carbon dioxide (CO_2) are highly favorably affected due to the long-term biochar stability in soil [126]. Recent research studies on soil application have also claimed that biochar affected both abiotic and biotic processes and reduced the emissions of methane (CH_4) and nitrous oxide (N_2O) [86].

Recently, the successful application of biochar for environmental remediation has also been recognized [4]. Due to anthropogenic activities, the water and soil ecosystem are highly subjected to contamination from residential areas, industries, and other commercial sources [34]. Different technologies have been developed to remediate these contaminants. Among these, reducing the toxicity and accumulation of contaminants by lowering their bioavailability has been found as an effective strategy. To this end, biochar has been recognized as an outstanding ameliorant to reduce the bioavailability of contaminants due to its unique physicochemical characteristics along with the additional benefits leading to soil fertilization [128]. However, in the soil-biochar systems, the bioavailability of pollutants is highly affected by redox and adsorption reactions [32, 106]. Moreover, the published works have mainly explained the agronomic and environmental applications, while little information has been presented elucidating different mechanisms, which is the focus of the present review.

This critical review is aimed at examining the influence of biochar synthesis controlling parameters such as temperature, residence time, and types of feedstock on the characteristics of biochar. Moreover, the mechanisms explaining the potential of biochar for the environmental and agronomic applications are also discussed. This review also highlights the challenges

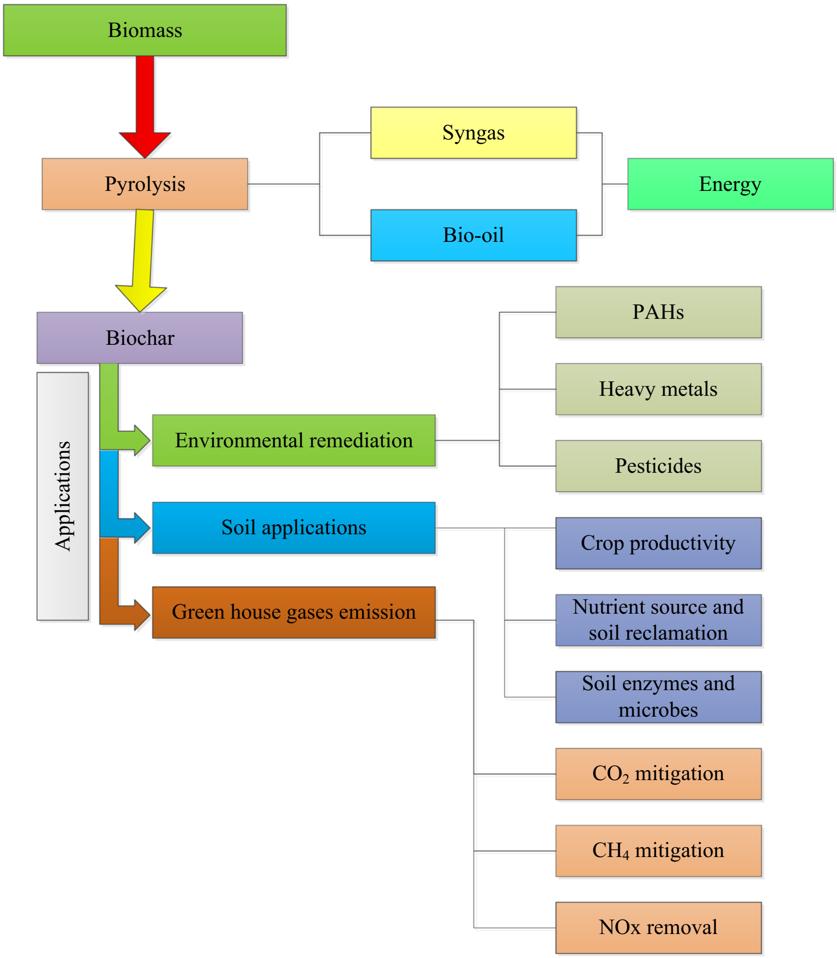


Fig. 1 Biochar production and its applications

faced in biochar development and its field applications for agronomic and environmental remediation purposes. Furthermore, several recommendations for future research are given on the development of biochar with high redox functional groups and sorption potential as well as on understanding the behavior of biochar under the natural field conditions.

2 Development of biochar

2.1 Feedstock characteristics

Any types of organic biomass, such as crop residues, yard wastes, forestry wastes, animal manure, and sludge, can be subjected to thermal treatment for biochar production [150]. During production, the high-temperature treatment degrades the organic components along with the removal of pathogens and organic toxins (aflatoxin) present in the feedstock. The physicochemical characteristics of the feedstock used have a strong influence on the composition, quality, and yield of biochar [46]. For instance, biochars are rich in potassium (K) if produced from animal manure as feedstock, whereas woody biomass produce a high C content biochar [75]. The use of cellulosic feedstocks results in low bio-oil yield with high ash content, whereas high lignin content feedstocks tend to give high bio-oil yields [44]. Moreover, high lignin biomass also results in higher biochar yields, along with gases and liquid products. In addition, mineral components can also have a catalytic-like effect to some extent and increase the char yield. The moisture content and particle size can also have a direct impact on char yield depending on operating conditions. The published research depicts that the moisture content $< 10\%$ is required for high-quality biochar [119]. Higher biochar yields can also be achieved by using large particle sizes of feedstocks through restricting vapor disengagement and boosting the secondary char forming reactions [124]. In contrast, to facilitate the pyrolysis process, different feedstocks also require size reduction by crushing or cutting [150]. Besides, some feedstocks are highly complex, with a heterogeneous composition that cannot be treated directly by pyrolysis. The use of such feedstocks needs pre-treatment that requires extra energy. Hence, the use of appropriate feedstocks should be considered for economic biochar production [150].

2.2 Biochar development through pyrolysis of biomass

Biochar can be produced through pyrolysis that is a process of biomass decomposition at a temperature range of 150 to 900 °C in an oxygen-deficient environment [4]. During thermal conversion, the complex organic compounds such as lignin, cellulose, and hemicellulose undergo various types of degradation reactions including fragmentation, depolymerization, and cross-linking at different temperatures to produce char, bio-oil, and a mixture of gases containing CO_2, H_2, and CO. However, the products of pyrolysis reactions are highly influenced by temperature, residence time, and heating rate. Depending on the temperature and residence time, pyrolysis is categorized into slow, intermediate, and fast pyrolysis (Fig. 2) [101]. During slow and intermediate pyrolysis, the feedstock is subjected to prolonged residence time from few hours to days with a low heating rate [97]. The biochar yield under slow pyrolysis is between 25 and 35%, and it has been reported that biochar production through slow pyrolysis is of high surface polarity and acidity along with low aromaticity and hydrophobicity. However, the yield and functional groups (i.e., hydroxyl (–OH) and carboxyl (–COOH)) are decreased with increasing pyrolysis temperature with an increase of ash content and basic functional groups (Table 1). Fast pyrolysis is the treatment of biomass at a high temperature for a short residence time (~ 1000 $°C\ s^{-1}$) Zhang et al. [166–168]. It is commonly used for producing bio-oil from biomass as the biochar yield is about 20% along with bio-oil yield of up to 75% of the total biomass [101]. The higher bio-oil at a higher temperature (above 500 °C) is due to the cracking process [113]. The research findings of Al-Wabel et al. [10] and Zhang et al. [166–168] indicated that increasing the pyrolysis temperature decreased the acidic functional groups and biochar yield, whereas the pH, ash content, C stability, and basic functional groups were increased. The main reason behind the pH increase with increasing the pyrolysis temperature was the reduction of various organic functional groups including –OH and –COOH.

Waqas et al. [150] produced biochar at different temperatures from various types of green waste. The feedstock, including waste leaves of date plant, branches, and leaves of ornamental plants, trimmed grass waste, and coconut plant leaves and branches, were subjected to pyrolysis for 3 h in the absence of oxygen (O_2) using a pyrolysis reactor at three different temperatures (250, 350, and 450 °C). They observed that increasing the pyrolysis temperature resulted in a decline in the volatile content of the resultant biochar. The volatile content of biochar produced at 250 °C was 13.5%, which was reduced to 10 and 7.6% in biochar produced at 350 and 450 °C, respectively. They explained that the reasons for the reduction in the volatile content with rising temperature were the volatilization of lignocellulosic matters and mineral deposition. In addition, they also found a reduction in the yield of biochar with increasing pyrolysis temperature. The biochar yield at 250, 350, and 450 °C was reduced from 51.1 to 33.5 and 24.3%, respectively. The primary reason behind the high yield of biochar at lower temperatures was the minimum loss of H- and O-containing surface functional groups and aliphatic concentration. While increasing the pyrolysis temperature

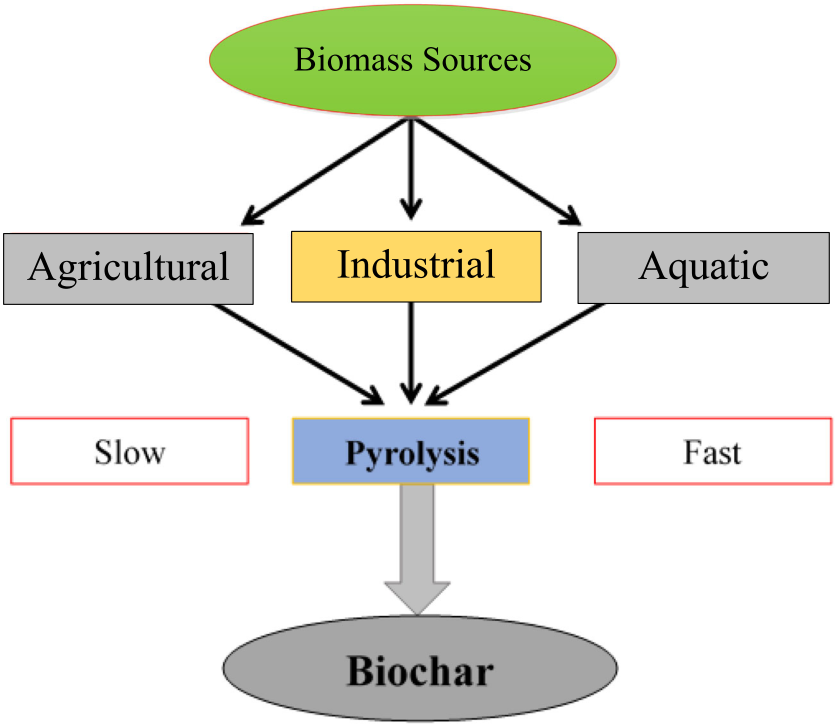


Fig. 2 Biomass to biochar conversion

resulted in the loss of –OH groups because of dehydration and formation of various gases and low molecular organic compounds due to the thermal degradation of various complex compounds, which resulted in lower biochar yields. Furthermore, they also studied the mineralogical composition of biochar produced at 250, 350, and 450 °C. The x-ray diffraction (XRD) spectral analysis presented several peaks depicting the development of various mineral crystals. The XRD analysis for biochar produced at 250 °C showed strong peaks at various degrees that could probably be associated with the presence of various minerals, including fluorite, chlorapatite, and graphite minerals. However, with the pyrolysis temperature increasing from 250 to 350 °C, an additional peak with a higher intensity was observed, which indicated the presence of gibbsite mineral. Furthermore, at 450 °C, the sharp peaks observed at 350 °C disappeared; while new peaks at a certain intensity were observed. They stated that this variation in peaks with increasing temperature revealed the mineral disintegration and formation of new components at higher temperatures. Moreover, the scanning electron microscope (SEM) images of biochar produced at different temperatures also confirmed that the surface variation in biochar with an increase in pyrolysis temperature was due to the high volatilization process. At 250 °C, the biochar showed

Table 1 Characteristics of biochar produced at different temperatures and feedstocks

Study	Feedstock	Pyrolysis temperature (C)	Yield (%)	Ash content (%)	C (%)	H (%)	pH	Surface area (m^2 g^{-1})
Ahmad et al. [3]	Peanut shell	700	21.8	8.9	83.6	1.6	10.6	448.2
Mullen et al. [104]	Corn stover	500	17.0	32.8	57.3	2.9	7.2	3.1
Keiluweit et al. [68]	Fescue straw	700	28.8	19.3	94.2	1.5	–	139.0
Chen and Chen [29]	Orange peel	500	26.9	4.3	71.4	2.25	–	42.4
Kloss et al. [69]	Poplar wood	525	–	6.8	77.9	2.7	8.7	55.7
Ahmad et al. [3]	Soybean stover	700	21.6	17.2	81.9	1.8	11.3	420.3
Kloss et al. [69]	Wheat straw	400	34.3	9.7	65.7	4.1	9.1	4.8
Liu et al. [87]	Rice husk	500	–	42.2	42.1	2.2	–	34.4
Lin et al. (2012)	Saw dust	550	–	2.8	85.0	1.0	5.9	–
Mullen et al. [104]	Corn cob	500	18.9	13.3	77.6	3.1	7.8	–

a slightly porous surface that was changed to flake-like structure by increasing the pyrolysis temperature from 250 to 350 and 450 °C. They reported that at higher temperatures, the flake structure of biochar surface was due to the partially blockage of micropores by condensed volatiles (tars) and other decomposed products.

2.3 Biochar development through hydrothermal carbonization

Various types of biomass contain high moisture contents, and hence to reduce the energy requirement and obtain high yields, an additional drying step is required to remove the extra moisture. The shortcoming is the hydrothermal treatment of such biomass to produce valuable products. During this process, the biomass is placed in a closed container, and the temperature is increased after a certain time. In addition, the pressure is increased to maintain the liquid state (above 100 °C). Based on the specific temperature and pressure used, biochar, bio-oil, and various gases are produced [28, 153]. However, the characteristics of the products are determined by the water-biomass ratio, pressure, temperature, and residence time. The char produced from hydrothermal carbonization (HTC) process is often called hydrochar. The produced char as a result of HTC contains high C compared with the char produced through the pyrolysis process [26].

2.4 Other technologies for biochar development

In addition to pyrolysis and HTC, there are other technologies for biochar preparation such as torrefaction and flash carbonization. In torrefaction, the biomass is slowly heated within a specific temperature range (200 to 300 °C) in O_2-deficient environment and retained for a particular period of time to remove moisture, O_2, and CO_2 present in feedstocks [144]. The biomass obtained after torrefaction has the characteristics between biochar and feedstock as this process is just like the initial stage of pyrolysis and therefore, the torrefied biomass still contains volatile organic compounds [65]. Likewise, in the flash carbonization, the solid and gas products are obtained by igniting the packed bed of biomass through flash fire at high pressures (1–2 MPa). For flash carbonization, the temperature for biomass conversion is about 300~600°C with a reaction time of ≤ 30 min. However, the carbonization time is decreased by increasing the pressure, and it has been reported that at 1-MPa pressure, about 40% of biomass is converted to biochar [26].

3 Characteristics of biochar

3.1 Structural and chemical characteristics of biochar

3.1.1 Surface chemistry

Generally, the structure of biochar is like a honeybee comb supported by the hexagonal arrangement of C without O and hydrogen (H) [81, 82]. However, the surface chemistry is much complex and heterogeneous, depending on the type of feedstock used for biochar production. Biochar surface exhibit both acidity and basicity in conjunction with hydrophobic and hydrophilic characteristics [73]. The acidity of biochar surface is mainly due to the presence of –OH and –COOH groups. In contrast, basicity is due to nitrogen (N) and O functional groups and some minerals like calcium carbonate ($CaCO_3$), magnesium oxide (MgO), and calcium oxide (CaO) [154]. During pyrolysis, some elements such as chlorine (Cl) and potassium (K) are vaporized easily at a lower temperature (below 300 °C), whereas some heteroatoms such as sulfur (S), phosphorous (P), O, and N are often present. Other minerals like sodium (Na), calcium (Ca), magnesium (Mg), and silicon (Si) and some toxic elements such as cadmium (Cd), lead (Pb), and arsenic (As) may also present in trace amounts [45]. Similarly, elements like S, Mg, Ca, P, and N tend to be covalently bonded with organic compounds that could be vaporized only at elevated temperatures (above 500 °C) [73]. Moreover, biochars obtained from fast pyrolysis (about 700 °C) have abundant –COOH and –OH functional groups, whereas the slow pyrolysis (250 to 900 °C) biochars are rich in C–H groups [138]. Other functional groups present on the surface of biochar are comprised of pyrenes, nitriles, phenols, carbonyls, quinones, and lactones [74, 89].

3.1.2 Surface area and pore volume

Brunauer–Emmett–Teller (BET) surface area of biochar range from several hundred to several thousand $m^2 g^{-1}$ [124]. However, the surface area is highly influenced by feedstock, pyrolysis temperature, the presence of active reagents (CO_2, O_2, and steam) and residence time (Table 1). Day et al. [36] reported that for most of the feedstock, the surface area of biochar increased with increasing the pyrolysis temperature. They observed that by increasing the temperature from 400 to 900 °C, the surface area was increased from 120 to 460 $m^2 g^{-1}$. The main reason behind the high surface area was the development of micropores. However, there is still a gap in understanding the role of micropores in soil due to the additional surface area provided by biochar. Therefore, it would be beneficial to produce biochar with a very high surface area in the macropore range. There exists the possibility to produce high-surface-area biochar in a well-defined macropore range, but the structure is likely to be highly influenced by feedstock and crushing the feedstock before pyrolysis [124]. Lik surface area, the porosity of biochar, is also highly affected by pyrolysis temperature, the presence of gases, and gas flow [78]. Mukherjee et al. [103] reported that increasing the pyrolysis temperature results in the release of volatile matter present in the biochar pore-infillings, thus producing biochar with high porosity. The relative distribution of micro, meso, and macropores has a high impact on interactions between biochar and its environmental application, such as nutrients flow and contaminant remediation. For instance, high adsorptive capacities towards small molecules have been observed for micropores in biochar [80].

3.1.3 pH and cation exchange capacity

In the literature, most of the biochars are reported to have an alkaline pH; however, as like other properties, pH is also dependent on feedstock and pyrolysis conditions [75, 161]. Laghari et al. [75] reported that biochar made from black locust wood and pinewood had neutral to slightly acidic pH. In addition, pH is also related to the ash content, where high ash contents led to higher pH values of the produced biochar [81, 82]. Typically, pH is also related to the temperature used (Table 1). The pH of the biochar increases with increasing the pyrolysis temperature. This could be mainly due to alkali salt separation from organic compounds that results in the reduction of acidic functional groups with enhancement in basic functional groups [142].

Furthermore, during pyrolysis, most of the volatiles compounds escape out while the exchangeable cations such as Mg^{2+}, Ca^{2+}, Na^{+}, and other recalcitrant cationic species remain in the biochar resulting in higher pH values [5]. It should be noted that the pH of biochar also has an impact on cation exchange capacity (CEC), where high pH values increase CEC and low pH values decrease the CEC of biochar [124]. The CEC of freshly produced biochar is low that increases with time in the presence of water and O_2 [31]. However, in comparison with pyrolysis temperature, the CEC of biochar is highly affected by the feedstock characteristics. Laghari et al. [75] reported that the CEC of biochar decreased by increasing the pyrolysis temperature. In contrast, for the feedstock, Agrafioti et al. [2] observed that the biochar prepared from straw showed a higher CEC than the biochar derived from manure. The reason behind this was the composition of the feedstock, where the presence of P, Mg, K, Ca, and Na increased the formation of O-containing functional groups resulting in the higher CEC of the biochar [2].

3.1.4 Redox potential of biochar

Redox reactions are the processes of accepting and donating electrons in a chemical reaction [116]. In the soil, redox reactions play an essential role in nutrient cycling, removal of free radicals, as well as in formation and decomposition of several chemical compounds Liu et al. [89]. In this context, biochar can also transfer, donate, or accept an electron to the surrounding environments through both various biotic and abiotic pathways [120]. The redox capacity of biochar varies with types of feedstock used and pyrolysis temperature applied. Notably, the high pyrolysis temperature, in combination with high residence time, results in high redox potentials in the resultant biochars [114]. At neutral pH, the reducing potential of biochar increased with increasing the pyrolysis temperature using grass or wood as feedstock [70]. Klüpfel et al. [70] studied the redox potential of different biochars produced from different feedstocks at different temperatures (200 to 700 °C). They observed that biochar could donate and accept electrons up to 2 mmol g^{-1}. Moreover, the biochar prepared from grass showed high electron exchange capacities compared to the wood-based biochar that was due to high mineral ash content in the grass-based biochar. Ishihara [60] carbonized wood at three different temperatures, i.e., < 300, 300, and 800 °C, and reported them as an insulator, a semiconductor, and a conductor, respectively. They further added that above 600 °C, the char produced was highly conductive but contained a lattice structure with a considerable amount of stable radicals and micropores within the structure. However, the concentration of O_2 functional groups and water-soluble organics were found very low. The redox potential of biochar is thought to be due to the products formed during the thermal decomposition of cellulose and lignin [114]. The O_2-containing functional groups form the redox pool within a soil-biochar system. For biochar, the reducing agents are phenolic species, whereas the oxidizing agents comprised polycondensed aromatic compounds and quinones [120].

4 Applications of biochar

4.1 Biochar as sorbent for organic pollutant remediation

The potential use of carbonaceous materials as a sorbent for the pollutant remediation from soil and water has been well reported in the literature (Fig. 1) [4, 35]. The most common carbonaceous materials are activated carbon; it is a material when charcoal is treated with O_2 to enhance its surface area and porosity. In contrast to activated carbon, biochar is a product of pyrolysis with a higher surface area and contains a non-carbonized fraction that interacts with the contaminants [19, 20, 106] (Fig. 3). The effective binding of soil pollutants to biochar is because of the presence of a wide range of –OH, O-containing –COOH, and phenolic functional groups on biochar surface [4]. Hence, due to these multi-functional characteristics, biochar has been proved as an effective sorbent for pollutant remediation from the environment (Fig. 4).

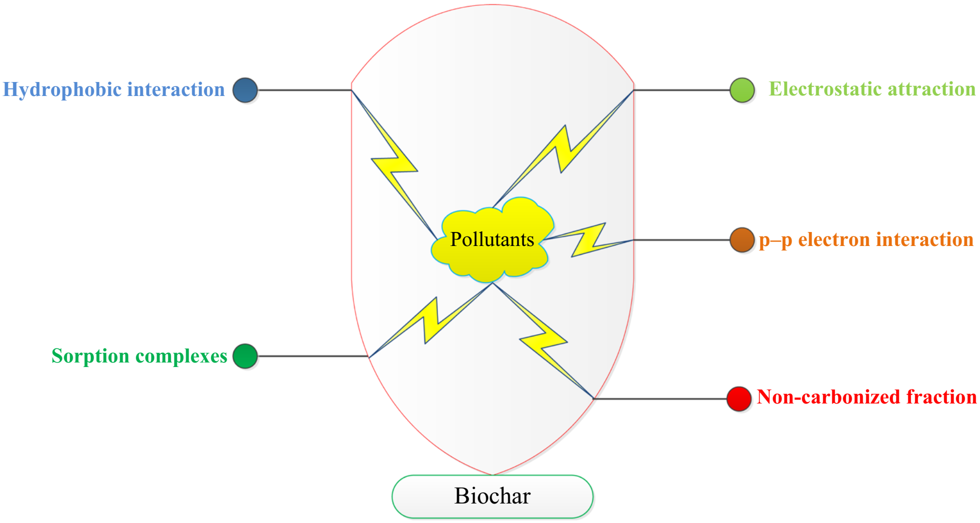


Fig. 3 Mechanisms of pollutants removal by biochar

4.1.1 Remediation of wastewater

Several characteristics of biochar help the sorption of the organic pollutants from water onto biochar, including particularly its microporosity and high surface area [92]. Ahmad et al. [3] reported that the biochar produced at a higher temperature (above 400 °C) showed high sorptive capacity towards organic pollutants because of their high microporosity and surface area. Chen et al. [30] observed that at lower temperatures (100–300 °C), the primary sorption mechanism was the splitting of the materials into non-carbonized fractions of biochar, while, for high temperatures (400–700 °C), the dominant mechanism was the adsorption onto porous carbonized fractions. However, aromaticity and surface polarity of biochar are also critical as they affect the sorption of organic contaminants from the aqueous medium [30]. For instance, the biochar produced at a higher temperature (above 500 °C) becomes more aromatic and less polar due to the loss of H- and O-containing functional groups, which may affect the adsorption of organic pollutants. The research findings of Uchimiya et al. [140] revealed that biochar produced from broiler litter at elevated temperature (700 °C) showed higher sorption capacity towards deisopropylatrazine because of higher aromaticity. Similar studies were carried out for the sorption of trichloroethylene on biochar derived from peanut shells and soybean stover at 300 and 700 °C. The high sorption by the biochar at 700 °C is attributed to low polarity and high aromaticity of the biochar surface [3]. On the other side, Sun et al. [132] stated biochar was produced at lower temperatures (400 °C) with high polarities for the effective sorption

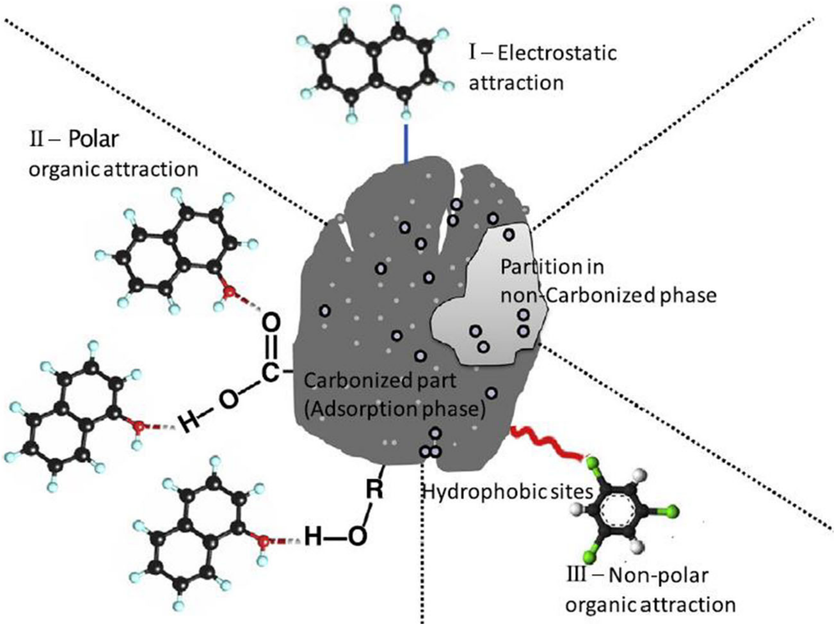


Fig. 4 Postulated mechanisms of the interactions of biochar with organic contaminants. Circles on biochar particle show partition or adsorption. I—electrostatic interaction between biochar and organic contaminant; II—electrostatic attraction between biochar and polar organic contaminant; and III—electrostatic attraction between biochar and non-polar organic contaminant [4]. Reprinted figure with permission from Elsevier. Copyright©2014. License Number: 4867180410300

of organic compounds such as fluridone and norflurazon. However, the mechanism of different types of organic compounds sorbed at various types of biochar is mainly attributed to the nature of the organic compounds. For instance, on biochar surface, the non-polar compounds such as trichloroethylene are adsorbed on the hydrophobic sites between water and O-containing functional groups in the absence of H-bonding, whereas polar compounds including fluridone and norflurazon are adsorbed through H-bonding among the O-containing functional groups on biochar and compound [3]. Therefore, it is proved that the adsorption capacity of biochar is directly affected by the functionality of the organic pollutant.

Another mechanism of pollutant adsorption is electrostatic attraction and repulsion (Fig. 3). The surface of biochar is negatively charged that could attract positively charged cations. Qiu et al. [115] and Xu et al. [155] reported an adsorption study of cationic dyes such as rhodamine and methyl violet from water using biochar. Generally, the biochar produced at 400 °C is highly polar due to aromatic p-systems, which are rich in electron drawing functional groups [68]. Hence, towards electron donors, they may act as p-acceptors. However, biochar produced at high temperatures are rich in both electron-poor and electron-rich functional groups; accordingly, they can interact with both electron acceptors and donors [133]. This interaction of electron donor-acceptor has enhanced between the p-electron-rich surface of biochar and positively charged p-electron-deficient organic compounds [133, 135]. Likewise, the electrostatic repulsion between biochar and anionic organic compounds could promote adsorption through H-bonding, as reported by Teixidó et al. [135] in their adsorption study of sulfamethazine on hardwood-derived biochar produced at 600 °C.

The solution chemistry, such as ionic strength and pH also affect the sorption potential of biochar towards organic compounds. Xu et al. [155] reported high electrostatic attraction between methyl violet and biochar at high pH. The reason behind the high attraction was the high net negative charge on the biochar surface because of the dissociation of phenolic $^{-}$OH groups. Likewise, the adsorption of organic compounds on biochar was positively affected by the ionic strength of the solution [4]. For instance, the adsorption of anionic blue dye on the biochar surface was due to neutralization of Na^+ with the negatively charged surface of biochar. Moreover, the attraction between the biochar and anionic dye was due to the compression of the electrical double layer near the biochar surface that reduces electrostatic repulsion [115].

4.1.2 Remediation of soil

In soil, the contaminants bind with biochar through O-containing hydroxyl, phenolic, and –COOH surface functional groups [141]. In addition, the unique characteristics of biochar make it a good sorbent material for the environmental remediation of organic and inorganic pollutants (Table 2). These characteristics include surface area, pH, porosity, surface functional groups, CEC, mineral composition, hydrophobicity, polarity, and molecular structure [159]. In addition to these properties, the suitability of biochar as a sorbent is also due to its low-cost availability with high resistance to decomposition [52].

Jones et al. [63] conducted a soil experiment to assess the effect of biochar on the sorption of simazine. They stated that leaching and biodegradation of simazine were reduced due to the sorption of simazine into the micropores of biochar. Among different particle sizes and application rates, they noted that small particle size of less than 2 mm and high application rate of 25 t ha^{-1} were proved effective for the adsorption of simazine. Similarly, in other studies, Yu et al. [160] and Yang et al. [158] reported low leaching of fipronil, chlorpyrifos, and carbofuran from the soil due to the high sorption capacity of biochar that reduces the bioavailability of these compounds. In comparison, the biochar produced at lower temperatures (below 450 °C) showed less efficiency towards the sorption of organic pollutants. Zhang et al. [163] explained this phenomenon that the lower adsorption of organic pollutants from the soil is due to the association of dissolved organic matter between the soil and biochar, which block the micropores in biochars, and hence reduce the availability of sorption sites for the organic compounds to adsorb. In another study, Cao et al. [19, 20] tested the sorption of atrazine on biochar produced at a lower temperature (450 °C). They reported that the higher content of dissolved organic carbon in the soil blocks the pores of biochar that reduce the sorption of atrazine on the surface of biochar.

However, along with the chemical and structural composition, the sorption capacity of biochar is highly affected by pyrolysis temperature during its production. Yavari et al. [159] reported that the pyrolysis of biomass enhances the sorption capacity of produced biochar by up to 1000 times. Biochar produced at higher temperatures (above 400 °C) shows high sorption capacity towards organic pollutants due to their high porosity and surface area [4, 141]. Moreover, at high temperature (500 °C), the biochar surface is more aromatic and less polar because of the loss of H- and O-containing functional groups that affect the adsorption of organic pollutants. Zhu et al. [172] have given proposed mechanisms of biochar-microbe interactions and the environmental effects of biochar (Fig. 5).

4.1.3 Redox reactions for pollutants degradation

Depending on the chemical structure, the organic pollutant transformation, either through substitution or through reduction, is highly facilitated by the redox potential of biochar [57, 161]. Yu et al. [160] reported the presence of redox-mediated

Table 2 Potential of biochar for remediation of organic and inorganic pollutants

	Study	Biochar feedstock	Pyrolysis temp (°C)	App: medium	Pollutant	Results
Organic contaminants	Zhang et al. [167]	Green biomass	450	Water	Atrazine	Partitioning and adsorption of the pollutant
	Yang et al. [158]	Cotton straw	850	Water	Chlorpyrifos and fipronil	Adsorption due to porosity and high surface area
	Lou et al. [92]	Rice straw	700	Soil	Pentachlorophenol	Adsorption due to porosity and high surface area
	Zhang et al. [163]	Pine wood	350 and 700	Soil	Phenanthrene	Trapping in the meso and micropores of biochar
	Jeong et al. [61]	Hard wood	850	Soil	Tylosin	Sorption
Inorganic contaminants	Hartley et al. [54]	Hard wood	400	Soil	Arsenic	Mobilization due to high DOC and pH
	Dong et al. [39]	Sugar beet waste	300	Water	Chromium	Complexation and electrostatic attraction; reduction of Cr(VI) to Cr(III)
	Tong et al. [136]	Crops straw	400	Water	Copper	Surface complexation result in adsorption
	Ahmad et al. [3]	Oak wood	400	Soil	Lead	Immobilization by rise in soil pH and adsorption onto biochar
	Kong et al. [72]	Soybean	700	Water	Mercury	Surface complexation precipitation and reduction

functional groups on biochar. Xu et al. [157] also observed the higher degradation of different organic pollutants due to the presence of sulfide on the surface of biochar. Likewise, using biochar in another study, Oh et al. [110] reported the chemical reduction of organic compounds of explosives and herbicides through electron shuttling between organic contaminants and reductants. Recently, it has also been reported that the catalyzing potential of biochar also degrades toxic organic contaminants (pesticides, antibiotics, and explosives) through biological or chemical transformation reactions. However, few research findings also revealed the enhanced chemical transformation reactions of biochar due to its electrical conductivity (p–p electron network with conductive graphite surface) in addition to surface functional groups (Fig. 2) [156]. In such a case, a direct transfer of electron occurs from electron donor's graphite regions in biochar to electron acceptor of the pollutant. Zhu et al. [172] have given the schematic diagram showing the roles of biochar functional groups (Fig. 6).

Similarly, using biochar, the biological transformation of organic contaminants occurs due to the extracellular electron transfer [57]. For instance, biochar added in the soil stimulates the microbial growth and metabolism that increases the extracellular electron transfer for the biotransformation of pentachlorophenol (PCP) [137]. Tong et al. [137] also reported that the efficiency of biochar to degrade PCP is due to both electron exchange capacity and electrical conductivity. Using biochar, they explain three pathways for the PCP degradation that is (i) PCP reduction by *Geobactor sulfurreducens*, (ii) transfer of electrons through its redox-active surface groups, and (iii) transfer of electrons through its conductive graphite framework. Correspondingly, the immobilization of inorganic contaminants (heavy metals) is also highly influenced by the redox potential of biochar. The dissolved organic matter (DOM) of biochar can act both as an electron acceptor and as a donor and hence had great influence biogeochemistry of metals in soil [161]. Dong et al. [40] proved this phenomenon by using DOM extracted from biochar and reported that the extracted DOM successfully reduced the Cr (VI) and oxidized the As (III). However, they suggest that in comparison to the oxidizing potential, the DOM had a higher reducing potential by reducing Cr (IV). The reducing potential was confirmed by the X-ray photoelectron spectroscopy (XPS) analysis, which revealed that surface functional groups of biochar were rich in p-electrons that act as electron donors.

4.2 Biochar as sorbent for inorganic pollutant remediation

In comparison with organic pollutants, the most critical are metals that are non-biodegradable with high toxicity to living organisms [165]. For inorganic pollutant remediation from soil and water systems, many carbonaceous materials have been extensively used (Fig. 1) [113]. Recently, biochar is termed as a novel material for metal sorption from soil and water (Figs. 2 and 3). Generally, the sorption of organic contaminants by biochars is more favored than that of the inorganic contaminants due to their high surface area and microporosity. The main mechanisms for sorption of inorganic contaminants by biochar are ion exchange, electrostatic attraction, and precipitation (Fig. 7).

4.2.1 Remediation of wastewater

Removal of heavy metals from aqueous medium using biochar has been reported recently to explain the binding mechanisms and adsorption [59]. Lima et al. [83] studied the ability of different types of biochar produced from various feedstocks to adsorb heavy metals from water. Among the heavy metals, copper (Cu^{2+}) showed higher affinity, which could be credited to the surface complexes between $^{-}$OH and $^{-}$COOH biochar functional groups and Cu^{2+} [136]. However, an x-ray absorption fine structure (XAFS) spectroscopic analysis showed that

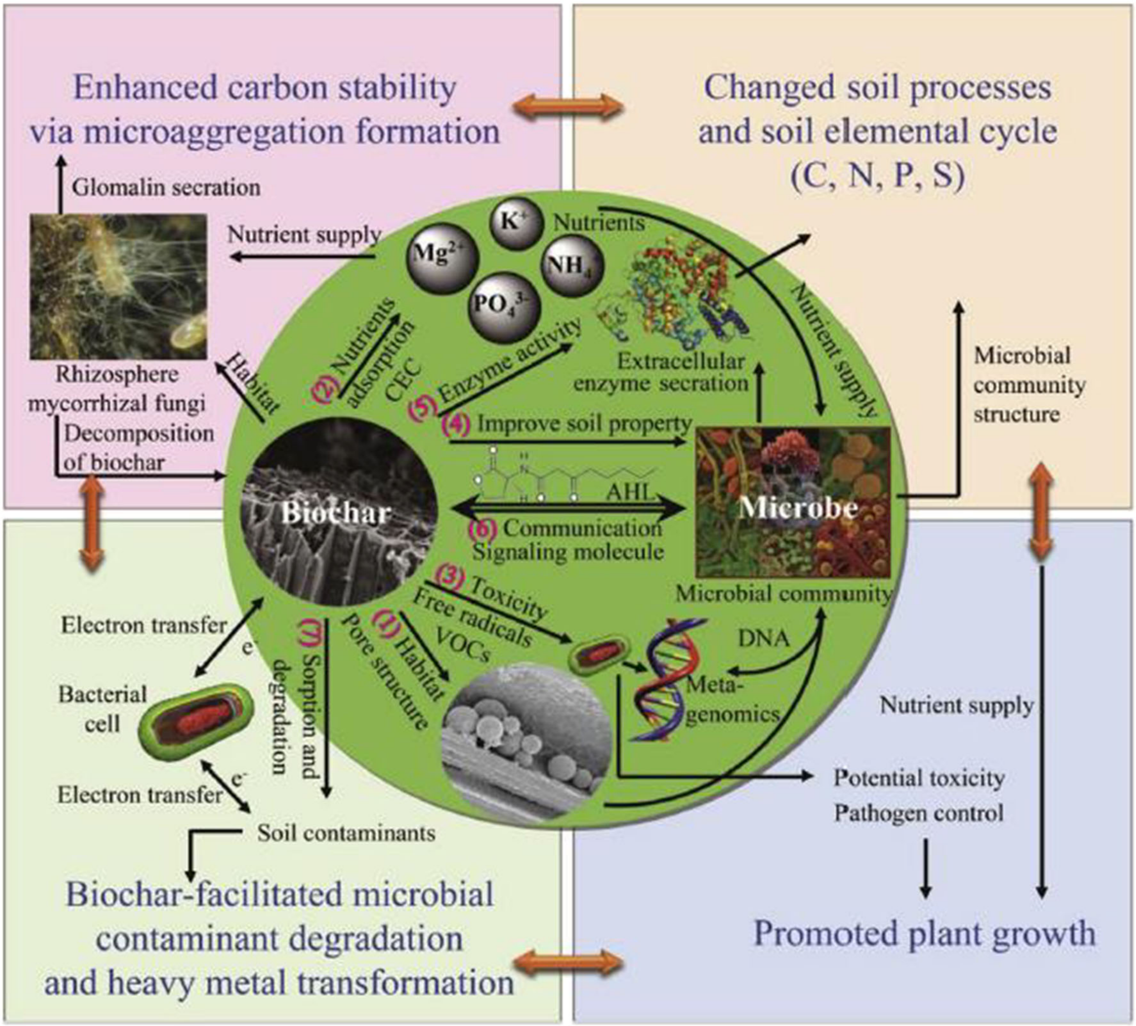


Fig. 5 Proposed mechanisms of biochar-microbe interactions and the environmental effects of biochar. The central circular area illustrates the interaction between biochar and microbes, while the enclosing four boxes represent the effects of their interaction on carbon sequestration, soil processes (elemental cycling), contaminant degradation, and plant growth. Interactions between the biochar and the microbes and its effects include the following: (1) biochar can act as a microbial shelter with its pore structure; (2) through sorption of nutrient cations via functional groups, biochar can improve soil cation exchange capacity and maintain nutrients for microbial growth; (3) free radicals and volatile organic compounds on biochar can be toxic to some soil microbes, inhibit soilborne pathogens, and favor plant growth; (4) biochar can improve soil properties (e.g., pH, water content, and aeration conditions), and change the growth pattern of soil microbes; (5) biochar can adsorb enzyme molecules, influence soil enzyme activities and elemental cycles; (6) biochar can adsorb and enhance the hydrolysis of signaling molecules, and consequently interrupt microbial communication and alter microbial community structure; (7) biochar can enhance the sorption (via biochar surface functional groups) and degradation of soil contaminants (facilitated through electron transfer between biochar, microbes, and contaminants), which can reduce the toxicity of contaminants to soil microbes. The interactions between biochar and soil microbes can alter the microbial community and their metabolic pathways (which can be revealed by metagenomics analysis of microbial DNA sequencing), resulting in changed soil processes. There are interactions among different environmental effects as well [172]. Reprinted figure with permission from Elsevier. Copyright©2017. License Number: 4867200697003

sorption of Cu^{2+} was affected by the pH of the solution [59]. They stated that higher sorption of Cu^{2+} on biochar was at pH 6 and 7. In addition, another parameter concerning adsorption of metals on biochar was the atomic size, where the small atomic radius could easily penetrate the pores of biochar and resulted in higher adsorption [105].

Lu et al. [93] explained the mechanisms of lead (Pb^{2+}) sorbed on the surface of biochar derived from sludge. They proposed four various possible mechanisms, i.e., (a) electrostatic outer-sphere surface complexation between Na^+ and K^+ available on biochar with metal exchange from the outer medium, (b) inner-sphere complexation and co-precipitation of metals from the medium with mineral oxides and organic matter of biochar, (c) surface complexation with –OH and –COOH functional groups of the biochar, and (d) metal precipitation in the form of lead–phosphate silicate ($5PbO–P_2O_5–SiO_2$). As like Pb and Cu, the alkaline biochar surfaces comprised of high chloride content could also precipitate the water-soluble mercury (Hg) in the form

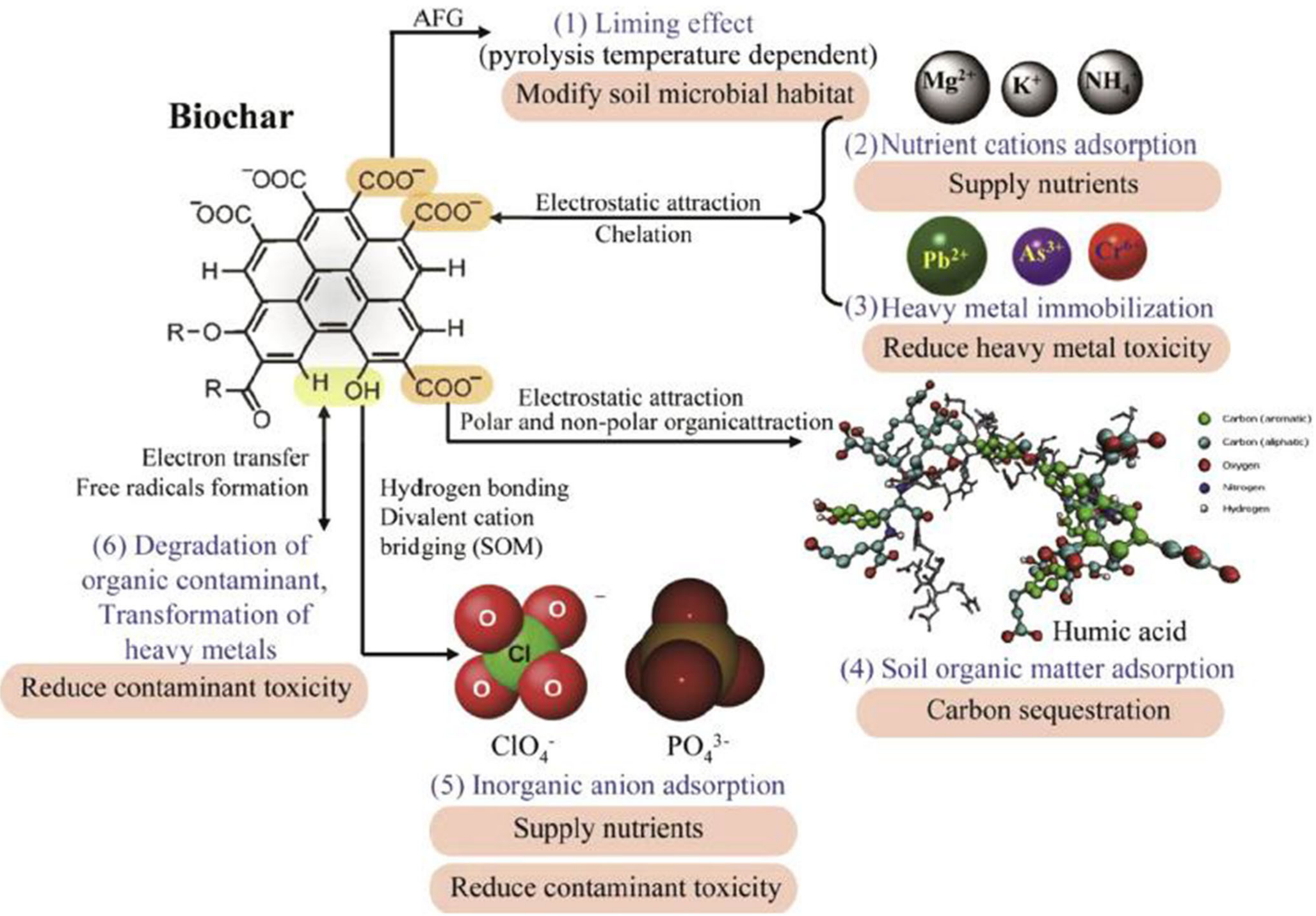


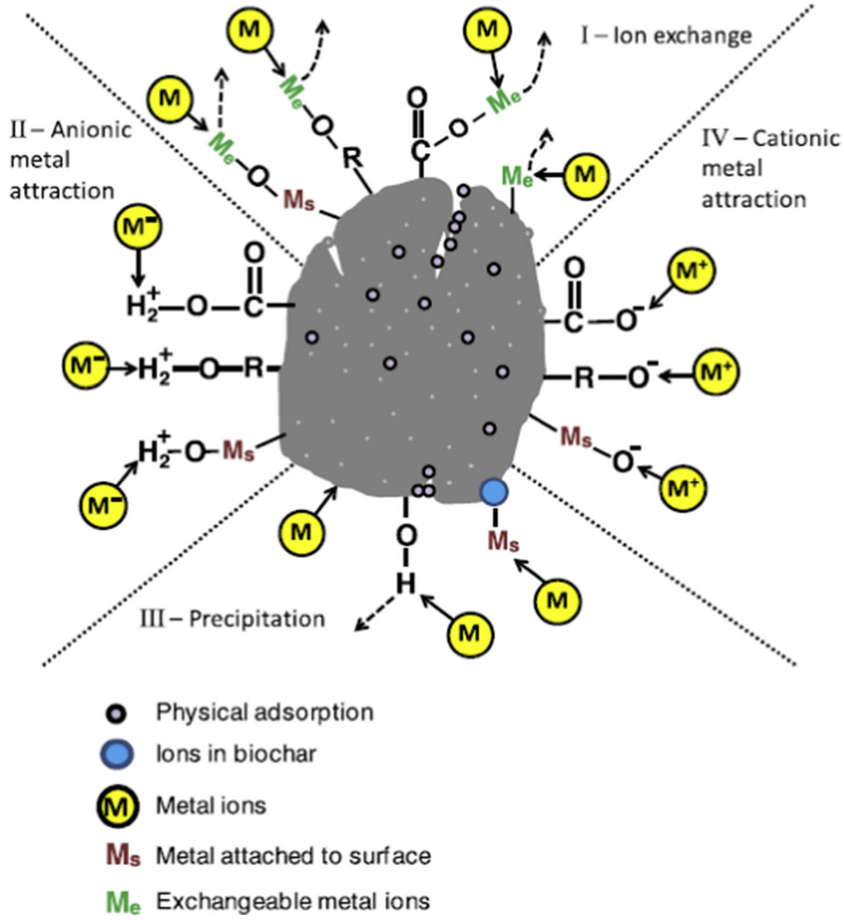
Fig. 6 Schematic diagram showing the roles of biochar functional groups (AFG = acidic functional groups, SOM = soil organic matter): (1) The AFG are responsible for the liming effect of biochar which modifies the soil microbial habitat; (2) the electrostatic attraction between the carboxyl groups of biochar with the nutrient cations effectively retains nutrients to ensure a nutrient supply to soil microbes and (3) to immobilize heavy metals, thus reducing heavy metal toxicity to microbial cells; (4) electrostatic attraction, as well as polar and non-polar organic attraction, of humic acid molecules can result in the adsorption of soil organic matter that is beneficial for carbon sequestration (further discussed in later chapter); (5) hydrogen bonding between –OH groups on biochar with oxygenated anions can adsorb inorganic anions to supply nutrients or reduce anion contaminant toxicity; (6) electron transfer to form free radicals on the biochar surface can facilitate organic contaminant degradation and heavy metal transformation and can reduce contaminant toxicity to microbes [172]. Reprinted figure with permission from Elsevier. Copyright©2017. License Number: 4867200697003

$HgCl_2$ or $Hg(OH)_2$ [72]. Similarly, the sorption mechanism of chromium (Cr) on biochar was credited to the negatively charged biochar active sites due to O-containing functional groups [15]. The high adsorption potential towards Cr (VI) of biochar produced from oak bark and wood at higher temperature was swelling behavior. This swelling of biochar opened the closed pores and hence enhanced the adsorption capacity by providing more internal surfaces.

4.2.2 Remediation of soil

In comparison with water, biochar has a different effect on metal mobility in the soil. Nevertheless, metal mobility is highly affected by soil pH. Biochar exerts a liming effect in the soil, for its alkaline nature, and causes mobilization of various oxyanions and immobilization of metals [9]. Ahmad et al. [4] stated that the soil blended with biochar enhanced the sorption of Pb on to kaolinite due to an increase in the soil pH. At higher pH values (above 5), kaolinite in biochar forms a strong inner-sphere surface complex with Pb [49]. Furthermore, biochar could also remediate Cr from the soil due to the ability to donate electrons and the presence of reactive sites with many functional groups [33]. The proton supply for Cr (VI) reduction is due to the presence of many acidic functional groups such as phenol, lactonic, –COOH, carbonyl, and hydroxyl and basic functional groups, including pyrone, ketone, and chromene [4]. As a result, the reduced Cr (III) either participates or adsorbs by forming surface complexes with biochar [58]. However, in some cases, the dissociation and oxidation of –OH and phenolic groups were inhibited due to the high alkalinity of biochar, which limited the proton supply and hence inhibited the Cr (IV) reduction [33]. Cao et al. [19, 20] also investigated the effect of biochar on Pb immobilization in the soil. They reported that due to the presence of phosphorus (P)

Fig. 7 Postulated mechanisms of biochar interactions with inorganic contaminants. Circles on biochar particle show physical adsorption. I—ion exchange between target metal and exchangeable metal in biochar; II—electrostatic attraction of anionic metal; III—precipitation of target metal; and IV—electrostatic attraction of cationic metal [4]. Reprinted figure with permission from Elsevier. Copyright©2014. License Number: 4867180410300



in the biochar, Pb was immobilized because of the formation of insoluble hydroxypyromorphite precipitates.

Kong et al. [72] reported 86.4% removal of Hg (II) and 99.5% removal of phenanthrene by biochar derived from soybean stalk. They stated that the high sorption capability of biochar towards organic compounds was due to their high microporosity and surface area. Likewise, for inorganic pollutant remediation, the prevailing mechanisms of biochar were precipitation, electrostatic attraction, and ion exchange. However, the physicochemical characteristics of biochar are greatly affected by the pyrolysis temperature and hence greatly influence their sorption potential towards organic and inorganic pollutants. For instance, the high surface area and pore structures of biochar produced at high temperature possess higher efficiencies towards organic pollutants, whereas the high cations release and O-containing functional groups on the biochar produced at a lower temperature are efficient towards inorganic pollutants [4].

4.3 Agricultural application of biochar

It is essential to understand the mechanism and impact of biochar on improving agricultural soil (Fig. 5). It has been well reported that for agricultural soils, biochar has been proved as an optimum conditioner. Biochar improves the stability of soil aggregate and increases the water holding capacity by enhancing water retention using its pore characteristics [67]. Moreover, the inorganic minerals and organic matter contents of biochar provide essential nutrients to the plants (Fig. 5). Biochar also affects other characteristics of the soil, such as tensile strength, swelling/shrinkage, and density of cracking [173]. In addition to these benefits, the key feature of biochar is the stability with very low decomposition rates in the soil. The estimated mean residence time of biochar in the soil is above 3000 years.

4.3.1 Nutrients source

Organic compounds such as fulvic-like and humic-like substances and inorganic compounds such as salts of N, P, and K present in biochar serve as fertilizer and can be assimilated by microbes and plants [37]. Lin et al. [84, 85] demonstrated that the biochar derived from sawdust and *Acacia saligna* at 450 and 380 °C contained humic materials up to 17.7% and fulvic-like materials up to 16.2%. Similarly, Masto et al. [98, 99] reported that the biochar produced from *Lantana camara* contained Ca (5880 mg kg^{-1}), Na (1145 mg kg^{-1}), Mg (1010 mg kg^{-1}), K (711 mg kg^{-1}), and P (0.64 mg kg^{-1}).

Likewise, Mukherjee and Zimmerman [102] also stated that freshly produced biochar had a high nutrients availability potential and could release large amounts of P (46–1664 mg kg^{-1}) and N (23–635 mg kg^{-1}). However, the nutrient contents of biochar is greatly affected by the feedstock and pyrolysis temperature. The biochar derived from different feedstocks showed various nutrients and elemental composition. For example, the biochar produced at 400 °C from swine manure contains P (6.1%) and N (3.2%), whereas at the same temperature the biochar produced from *Arundo donax* possessed P (0.13%) and N (0.69%) [139, 170]. Likewise, the ash content of biochar derived from poultry litter at 350 °C was 30.7%, whereas a lower ash content (1.5%) was recorded for the biochar produced at 350 °C from pine wood [18, 130].

The nutrient contents of biochar also considerably fluctuate with changing the pyrolysis temperature. For instance, above 400 °C, the N content began to lose, and at 750 °C, half of N was lost in different herbaceous and wood-derived biochar [76]. As reported by Zheng et al. [170] that increasing the pyrolysis temperatures from 350 to 600 °C, the available water-soluble N content in biochar was reduced from 39 to 8 mg kg^{-1}, which was due to the heterocyclization of N during pyrolysis. Furthermore, increasing the pyrolysis temperature from 300 to 600 °C, the total and available K concentration in biochar also increased from 3.7 to 5.02% and 37 to 47%, respectively [170]. In contrast, the total P concentration was considerably increased from 0.12 to 0.17% with increasing the pyrolysis temperature from 300 to 600 °C, which was due to the carbon loss and relative stability of P in plant biomass in response to heating [37, 170]. However, it has been found that the biochar produced at lower temperature contained a higher concentration of P than the biochar produced at elevated temperature.

4.3.2 Soil reclamation

Continuous cropping degrades most of the agricultural soils with several problems such as organic matter (OM) reduction, loss of water and nutrients, compaction, waterlogging, and erosion [75]. Soil with low OM, high compaction, and clayey nature has a high tensile strength, which directly affects soil processes, seed emergence and growth, and soil tillability. Hence, the tensile strength could be reduced through the addition of carbonaceous material such as biochar [14]. The changes in the tensile strength as a result of biochar addition is due to the ability of biochar that reduces the density, and cohesiveness of the soil through weakening the inter-particles bonding [174]. Zong et al. [174] reported that the tensile strength of soil was significantly reduced by applying higher rates of biochar (> 50 Mg ha^{-1}). However, at a lower application rate, biochar may have no or minute effect on soil tensile strength Chan et al. [27]. Regardless of the soil texture, biochar could significantly reduce the tensile strength by up to 42%. Moreover, biochar also contributes to soil flexibility against external forces as well as microstructural development [6]. Similarly, soil porosity is also highly affected by biochar addition through changes in soil bulk and particle density because the particle density has a direct effect on the porosity of the soil. Variation in C concentration as a result of biochar addition (> 60% C) induces changes in soil and significantly reduces the particle density Blanco-Canqui [14]. Biochar has a particle density of up to 2 g cm^{-3}, whereas depending on the texture, the particle density of the soil ranges from 2.3 to 2.7 g cm^{-3} [17]. The field study results reported that the particle density of the soil reduced by 14% (from 2.55 to 2.20 g cm^{-3}) when biochar was applied at 30 Mg ha^{-1}.

In addition to the soil's physical properties, biochar also has a high impact on soil temperature due to its unique thermal and electrical characteristics. Soil temperature is a primary factor affecting biological, physical, and chemical processes, as well as the energy balance of the soil [14]. Variation in soil thermal properties as a result of biochar addition is the most critical factor for understanding the response of soil to climatic fluctuations. The field study in the North China Plain reported that the application of biochar up to 9.0 Mg ha^{-1} reduced the daytime soil temperature by 0.8 °C [165]. In addition, the other soil thermal properties, such as thermal diffusivity, volumetric heat capacity, and thermal conductivity, are also highly affected through biochar addition. These thermal properties affect the heat storage and transfer, as well as the overall energy balance of the soil. Zhang et al. [165] also found that the thermal conductivity of the soil was reduced by 3.5 and 7.5% under 4.5 and 7.5 Mg ha^{-1} biochar application, respectively. Correspondingly, Usowicz et al. [143] also reported that the use of biochar up to 30 Mg ha^{-1} reduced thermal diffusivity and conductivity up to 10-cm soil depth. In other studies, Zhao et al. [169] observed that the application of biochar at 4.5 and 9.0 Mg ha^{-1} reduced the thermal conductivity and diffusivity of the soil. All these studies concluded with their findings that biochar can regulate the fluctuations or extreme soil temperature. Biochar can significantly reduce the amount of heat transfer through the soil. In the end, the biochar amendment could be a strategy for managing climatic fluctuations such as droughts and heat stress conditions [14].

4.3.3 Soil enzymes

It has been reported that soil enzymes have a crucial role in soil health (Fig. 5). Soil enzymes decompose organic matters and make the ammonium (NH_4^+) and energy available to the plants. Soil application of biochar has been proved to affect the composition of soil enzymes positively. In this regard, Luo and Gu [94] experimented with biochar application on mangrove sediments and found that biochar application significantly improved the level of β-glucosidase and phenol oxidase in the soil. However, they found that the level of other enzymes such as acid phosphatase, N-acetyl-glucosaminidase, and peroxidase was considerably reduced. Due to these consequences, Kavitha et al. [67] recommended assessing the impact of biochar to improve the levels of some enzymes while decreasing the levels of other enzymes. However, behind these consequences, the main reasons could be various factors such as soil types and biochar interaction with other substrates that resulted in the unavailability to soil enzymes [67].

4.3.4 Soil microbial activities

In the soil, most of the carbon (C) present in biochar is not available to the microbes. However, there exist several evidences that biochar promotes the activities, growth, and biomass of microbes present in the soil as it provides suitable habitat to the soil microbes (Fig. 5). The better activity, diversity, and retention of microbes are facilitated due to the high surface area of biochar [171]. Domene et al. [38] stated that biochar application on sandy loam soil significantly improved the functions and activities of soil microbes. Furthermore, they stated that biochar with the application rate of 30 t ha^{-1} doubled the population of soil microbes. Similarly, in another study, Ducey et al. [41] found that biochar application to arid subsoil significantly enhanced the microbes involved in nutrient cycling. The authors also observed the higher denitrification and nitrogen fixation microbial genes for the biochar applied at 135 t ha^{-1}. From the study, they concluded that biochar could enhance plant growth and nutrient cycling by improving soil biological characteristics. However, depending on the soil types (pore size, pH, charge properties, and surface area), biochar behaves differently to soil biological activities [112]. For instance, the activities of microbes, particularly the autotrophic nitrifying bacteria, were increased in less acidic soil conditions [112].

4.3.5 Crop productivity

It has been well reported in the literature that the application of biochar significantly improves soil fertility and substantially enhances the crop performance and productivity under different types of agricultural soils (Table 3; Fig. 5) [81, 82]. Glaser et al. [48] reported that the application of biochar at the rate of 68 t ha^{-1} enhanced the rice biomass by 20% and cowpea by 50%, whereas when applied at 136.75 t ha^{-1} the cowpea biomass was increased by 100%. Likewise, the 3-year field study of Major et al. [95] reported that in comparison to control treatment, the maize yield was significantly increased when biochar was applied at the rate of 20 t ha^{-1}. They also reported that the yield of maize in three consecutive growing seasons was increased by 29%, 31%, and 143%. The reason behind the higher maize yield was the liming effect of biochar that increased the base cation retention and improved nutrient availability in the rooting zone [117]. Furthermore, other mechanisms attributed to higher crop yield were the soil water retention and inhibiting the leaching of important nutrients such as N, P, K, Mg, and other associated nutrients. Additionally, it has been reported that biochar application not only increased the grain yield but also enhanced the growth and development of rooted crops, as reported by Liu et al. [88]. They found maximum sweet potato yield with increasing the application rates of biochar.

The fresh fruit weight of tomatoes grown under sandy loam soil also significantly increases with the addition of biochar [8]. This improvement of higher yield as a result of biochar is also attributed to the enhancement of water holding capacity of the soil [8]. However, the impact of biochar to enhance the crop yield is dependent on feedstock materials and pyrolysis temperature. For instance, different feedstocks such as rice hull, weed, bamboo, wheat straw, and eucalyptus when treated at various temperatures (450 °C to 600 °C) enhanced the maize yield from 6 to 143%. In addition to these, the soil type also plays a critical role in crop yield. The loamy texture soil such as fine loamy sand, silty loam, sandy loam, and loamy resulted in higher crop yields up to 101%. The variations in increasing the crop yield under various soil textures were also due to changes in the soil properties that directly affected the plant growth and development (Table 3). This happens as the soil texture directly affects the formation of aggregates, nutrient retention, and water holding capacity of the soil [7]. In contrast, Güereña et al. [50] reported a non-significant increase in yield of maize crop as a result of biochar application. The null effect on crop yield might be due to phytotoxic compounds present in biochar that inhibited microbial activities and thereby stunted plant growth [107]. Furthermore, Rajkovich et al. [118] revealed that biochar with low C/N ratios, when applied to soil, resulted in N immobilization and hence reduced the plant growth and final yield. Therefore, it is critical to give special attention to the biochar when selecting for improving specific soil type.

4.4 Balancing greenhouse gas emissions and albedo feedback

A meta-analysis of biochar application for controlling greenhouse gas (GHG) emissions revealed that characteristics of biochar are critical in offsetting the emissions (Fig. 1) [11, 96]. However, it was found that the potential GHG mitigation is highly dependent on the type of feedstock used to produce biochar (Table 4). Cayuela et al. [23] reported that woody and crop residue biochar decrease the GHG emissions by 50% more than the biochar produced from other feedstock. Moreover, the quantity of biochar also affects the potential where above 2 w/w% biochar application enhances the mitigation potential. Cayuela et al. [24] stated that the mitigation potential of biochar for GHG emissions, especially for N_2O, is

Table 3 Impact of biochar on crop yield different types of soil

Study	Crop	Soil type	App: rate (t ha^{-1})	Yield increase (% relative to control)
Masto et al. [98, 99]	Maize	Sandy loam	04	11
Liu et al. [88]	Maize	Calcic	20	10.38
Akhtar et al. [8]	Tomato	Sandy loam	67.5	20
Schmidt et al. [121]	Grape	Haplic regosol	08	2
Liu et al. [89]	Rice	Sandy loam	2.4	6
Joseph et al. [64]	Wheat	Sandy loam	0.1	40
Agegnehu et al. [1]	Peanut	Ferralsol	10	21
Raboin et al. [117]	Bean	Acidic clayey	50	53
Sigua et al. [125]	Wheat	Fine loamy	40	28
Liu et al. [90, 91]	Soybean	–	20	7

due to the H:C molar ratio of biochar. Biochar with lower H:C molar ratio (< 0.3) is highly effective by lowering N_2O emissions up to 73% with a high degree of aromatic compound condensation. In comparison, the biochar with a high H:C molar ratio of > 0.5 reduces the emission up to 40% [96]. Likewise, it has also been explored that the adsorption potential of biochar inhibits the mineral N supply, and thus lowers the amount of substrate to denitrifiers that require a labile N and C and hence expected to reduce the emissions of N_2O [145]. Moreover, biochar also contains organic compounds such as polychlorinated compounds, polycyclic aromatic hydrocarbons (PAHs), ethylene, furans, and dibenzodioxins that affect the microbial soil toxicity [55]. For instance, PAHs have been reported to affect the nitrification processes and modify the soil bacterial communities [51]. Spokas [129] observed a direct impact on N_2O emission from the soil as a result of ethylene released from biochar. The possible reason was the introduction of specific compounds that affect both nitrification and denitrification reactions and N cycling in the soil. Similarly, in another study, Case et al. [22] conducted a field trial by applying biochar at 49 tons ha^{-1} and observed that CO_2 emission was reduced up to 53%. Further, they explain that the reason for reducing the emission was due to the negative PE where new C stabilized in the soil and unavailable to the microbes for degradation.

However, to improve the efficiency of catalytic reduction, biochar activation has been recommended to increase the oxygen functional groups further, and increase the quantity of active sites, surface area, and pore size on the char surface. Cha et al. [25] and Jo et al. [62] pyrolyzed rice straw and sewage sludge to produce biochar and their use as selective catalytic reduction (SCR) catalysts. During their studies, the produced biochar was chemically activated using ammonia (NH_3) as a reducing agent, and their efficiencies were examined for the removal of NOx. Their results depict that oxygen-containing functional groups and NH_3 adsorption sites on biochar surface play an essential role in the removal of NOx. Moreover, to further increase the NOx removal efficiency, Cha et al. also recommended the impregnation of 3 wt% manganese on chemically activated char. In other studies, Ko et al. [71] activated the char obtained from municipal waste and refuse-derived fuel through a physical method using steam and chemical methods using KOH and HCl. The activated char was used as low-temperature SCR catalysts. They noticed that the NOx removal efficiency of KOH-activated char was higher in comparison to other chars. From the study, they suggested that the high NH_3 adsorption ability of that char was due to the increased oxygen functional groups, high quantity of active sites, surface area, and pore size on the char surface.

Table 4 Application of biochar for mitigation of greenhouse gases emission

Study	Location	Soil type	Biochar type	App: rate (t ha^{-1})	GHG abatement
Zhang et al. [164]	China	Calcareous loamy soil	Wheat straw	20 to 40	Increase CO_2 by 12% and decrease N_2O up to 40%
Wang et al. [149]	China	Paddy soil	Rice husk	25 to 50	Reduce N_2O up to 50%
Case et al. [21]	UK	Sandy soil	Hardwood	22	Reduce N_2O up to 49%
Taghizadeh-Toosi et al. [134]	UK	Pasture soil	Pine	30	Reduce N_2O up to 70%
Karhu et al. [66]	Finland	–	Mixed commercial biochar	9	Reduced CH_4 up to 96%

The application of biochar might also change the balance of surface radiative energy [16]. Biochar being a C-based material hence has a very low reflectivity [109]. Soil application of biochar affects the background color of the treated land and thus affects the energy flux partitioning and surface albedo [47]. In the climate system, surface albedo is one of the critical geophysical drivers that reveal information about the land use and the consequences of anthropogenic surface activities on the climate system of the earth [131, 148]. In addition to the environmental benefits (negative radioactive forcing), the changes in surface albedo as a result of biochar application to cropland might be higher than its benefits of C-sequestration [47, 131]. The research findings of Meyer et al. [100] predicted that the application of biochar at the rate of 30 Mg ha^{-1} could possess the mitigation potential from 13 to 22%. Other studies reported variations in the effect (5–11 to 13–44%), however, that depends on biochar application technique either deep incorporation or superficial application and rates of application (120 or 10 Mg ha^{-1}) [148]. In addition, it has been estimated that the effect of biochar on soil albedo during the winter season is stronger, with dominant bare soil in snow-free areas [47]. Similarly, in dense vegetation land, the effect is supposed to be negligible. However, on the proper scale of land studies, these predictions have not been explored yet due to variations in plants/crops phenology and cropping systems [16].

5 Key constraints in biochar application

5.1 Contamination risk

Several studies like Hilber et al. [55], Yavari et al. [159], and Han et al. [53] reported that biochar itself could be a source of contamination in the soil due to several factors. For instance, during biomass pyrolysis, different compounds (dioxins, PAHs, and PCBs) and heavy metals (Al, Cd, Pb, Zn, and Cu) are produced from parent biomass [56]. These compounds and heavy metals are tightly bound to biochar matrices through π–π interactions hence unavailable for the microbial breakdown [159]. The concentrations of these toxins in biochar depend on the feedstock, and pyrolysis conditions such as temperature and retention time [162]. Fast pyrolysis and gasification are most likely to produce biochar with a high concentration of dioxin (~ 92 pg g^{-1}) and PAHs (~ 45 μg g^{-1}). Special consideration should be given for the use of such biochar for environmental applications [53]. There are two main guidelines, the International Biochar Initiative (IBI) and the European Biochar Certificate (EBC) guidelines, that signify the threshold values of inorganic and organic contaminant content in biochar (Table 5). However, there exists a difference between the maximum threshold values for organic and inorganic contaminants in both EBC and IBI. The difference is mainly due to the contaminant management in different countries as the EBC based their maximum threshold values accordingly to Switzerland and Germany regulations, whereas IBI is based on the US and Australian regulations. However, each country also exists national standards that need to be followed for the potential application of biochar. For instance, for quality control of pyrolysis feedstock, Austria regulates the heavy metal contents in plant biomass [111]. For agricultural application, the regulation stated that the biochar must not exceed certain concentrations by 3 mg kg$^{-1}{}_{dw}$ for Cd, 100 mg kg$^{-1}{}_{dw}$ for Pb, 150 mg kg$^{-1}{}_{dw}$ for Cu, 1 mg kg$^{-1}{}_{dw}$ for Hg, and 500 mg kg$^{-1}{}_{dw}$ for Zn. In addition, the standards also provide guidelines for analytical methods, quality assurance, and control for the producers concerning the properties of biochar.

5.2 Environmental impacts on biochar performance

It has been observed that in comparison with laboratory-scale or greenhouse trials, the sorption capacity for contamination removal is lower for field applications of biochar. This could be due to several factors such as temperature, soil moisture, pH, wind, soil microbes, and rainfall that are difficult to control [108]. Many laboratory scales and greenhouse studies successfully explored the effect of temperature on the sorption capacity of biochar. Liu et al. [90, 91] observed that at 25 °C, sorption capacity was 14.9 mg g^{-1} for As (V), whereas, at 45 °C, it reached 17.9 mg g^{-1} that clearly shows a direct relationship of sorption capacities with temperature. Likewise, under field conditions, soil moisture, wind, and rainfall also affect the sorption capacities of biochar. Leaching and percolation of tiny biochar particles into the soil occurs due to heavy rainfall with large floating particles and hence separates them from contaminants that reduce the chance of contact and sorption. Correspondingly, during application and spreading some biochar may also be lost due to wind. Major [95] estimated that during loading, about 2% biochar is lost, whereas, during transportation, the loss is about 3%. Similarly, about 30% is lost during spreading; hence, the total loss during application is above 30% along with the high cost.

5.3 Biochar impacts on plant-environment interaction

The long-term application of biochar for promoting plant growth and biomass development had raised several important mechanistic questions about the effect of biochar on plant survival and success [12]. Spokas [129] observed beneficial effects on plants due to biochar-derived plant hormone (ethylene). However, the amount of ethylene decreased with increasing the pyrolysis temperature, whereas, at high treatment, no ethylene is detectable. The reasons are that low amount of ethylene either is produced during high-temperature treatment

Table 5 Maximum threshold level of pollutants in biochar

Pollutants	Name	IBI (max limit) $gt^{-1}{}_{dw}$	EBC (max limit)
Heavy metals	Cd	39	< 1.5
	Pb	300	< 150
	Cu	6000	< 100
	Ni	420	< 50
	Cr	1200	< 90
Organics	Dioxins and furans	17 ng kg^{-1} TEQ	< 20 ng kg^{-1} TEQ
	PCB	1.0	< 0.2
	PAHs	300	< 12

TEQ: toxicity equivalent

or may be sorbed by biochar due to high surface area. Through this phenomenon of sorbing organic chemicals, it has been suggested that biochar can affect symbiosis and allelopathy. Activated carbon and biochar are able to sorb allelopathic compounds and hence have been successfully used for studying allelopathic interactions between plants [77]. However, it has also been observed that in addition to allelopathic potential, they can affect the plant by reducing mycorrhizal root colonization by sorbing signaling compounds between symbionts and plant roots [152]. Moreover, several essential signaling compounds, such as flavonoids secreted for rhizobia by a legume host, are most likely to be sorbed by biochar due to its similar log Koc values to the PAH (naphthalene) and make them unavailable [42]. Hence, the high sorbing potential of biochar towards organic compounds is most likely to harm the plant signaling compounds and symbiotic microorganisms. Such conditions harm plant growth with the lower success of revegetation with a lower resistance of plants to diseases.

5.4 Regulatory constraints

For ensuring consumer satisfaction, various certifications demonstrate guidelines for specifications and quality requirements of biochar [146, 147]. These include International Biochar Initiative (IBI), European Community Biochar Criteria (ECBC), Biochar Quality Mandate (BQM), and European Biochar Certificate (EBC) that proposed guidelines for the sustainable soil application of biochar [146]. These legislative agencies attempt to define the production criteria, quality, and properties of biochar. In addition to the labeling and technical description of the feedstock, the certification frameworks consider the socioeconomic and environmental context of the area where the biochar is applied. In this regard, a certification label of biochar should include information about the properties of biochar that make it applicable for specific ecotopes to grow certain crops at certain application rates (Mg ha^{-1} per year). Moreover, the certification procedure should perform socioeconomic impact assessments for the possible combinations of all these factors [122, 123]. However, in several cases, the available soil data is not much enough to satisfy the required information for the certification procedure of sustainable biochar. Hence, the certification procedure in such cases requires a comprehensive soil testing. However, for any specific site, the sampling design and soil testing parameters should be according to the range of potential properties of biochar [147]. For instance, if the feedstock materials are organic waste with a sufficient amount of salt content, hence, the precautions should be kept to identify those type of soil that is susceptible to modification or salinization. For sustainable biochar application, any regulation or certification requires solid scientific evidence and recommendations. Likewise, the scientific evidence should be provided to the policy and decision-makers in such a way that it reflects comprehensiveness, and a vigorous, clear objective, and is free from any conflict of interest. For achieving all these, the mechanism should be provided by the intergovernmental panel on biochar [146].

6 Practical implications of this study

Biochar has a vital role in soil improvement and pollutant remediation. The primary mechanism of pollutant remediation is sorption; however, the sorption potential of biochar in laboratory-scale or greenhouse experiments is higher than field conditions. That is mainly due to several environmental factors such as rainfall, temperature, soil pH, and wind that are difficult to control; hence, more studies are required with a focus on understanding the behavior of biochar under natural field conditions. Likewise, it is also critical to understand the complete sorption mechanism as well as the coordination of these mechanisms among the contaminant and biochar [162]. Moreover, there is also no solid evidence supporting best biochar application procedures for most of the toxic pollutants, requiring a significant deal of work to specify of biochar, preparation conditions, specific time, and rate of application. Furthermore, for enhancing the redox potential of donating or accepting electrons, a detailed biochar production technology, as well as post-treatments, should be adopted for introducing more redox functional groups onto biochar surface. Correspondingly, the redox-mediated potential and long-term stability of biochar should also be checked against real industrial wastewaters with a heterogeneous mixture of pollutants to promote remediation on a commercial scale. In addition, to further enhance the potential of biochar, several modification technologies should be adopted, such as oxidation, grafting, impregnation, and nanomaterial treatment. The modification will bring changes into reactive surfaces, pore structure, and sorption potential of biochar for its wide-range applications.

7 Conclusions

The thermal conversion of biomass into biochar has the dual benefit of managing waste, along with the production of carbonaceous material that has a wide range of soil and environmental applications. In addition to carbon sequestration and soil application, biochar affects both abiotic and biotic processes to reduce the emissions of methane (CH_4) and nitrous oxide (N_2O). Similarly, through biotic and abiotic pathways, biochar can also transfer, donate, or accept an electron to the surrounding environments through its redox potential. Through redox reaction, biochar can play its role in nutrient cycling in the soil, removal of free radicles and toxins, and formation and decomposition of several important chemical compounds. Furthermore, biochar has been proved as an effective sorbent due to the presence of a wide range of –OH, O-containing –COOH, and phenolic functional groups, which provide effective binding sites to the pollutants from the surrounding environment. However, the redox and sorption potential of biochar are highly affected by the type of feedstock used, residence time, and temperature during biochar production. Primarily, the high pyrolysis temperature, in combination with high residence time, results in high redox potentials in the resultant biochars. Similarly, at high temperatures, biochar surfaces are more aromatic and less polar due to loss of H- and O-containing functional groups that affect the electrostatic attraction and repulsion. Biochar has also been proved as an effective soil amendment for improving the physicochemical characteristics of the soil. The application of biochar positively affects the physical, chemical, and biological properties of the soil. Being a rich source of organic compounds such as fulvic-like and humic-like substances and inorganic compounds such as salts of N, P, and K present in biochar positively affect the nutrient dynamics of the soil. The application of biochar positively affects the composition of soil enzymes and promotes the activities of soil microbes by providing a suitable habitat to the beneficial soil microbes. However, the impact of biochar on soil mainly depends on the interactions between biochar and soil, including types of biochar, crop, and soil system. Thus far, there still remains a gap in understanding the critical controlling parameters for the production and application of biochar that could affect its agronomic and environmental uses. Hence, significant work is required to produce biochar with specific activity and long-term stability for its agronomic and environmental applications.

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