Engineered Biochar as Soil Fertilizer

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Abstract Biochar, a heterogeneous carbonaceous material, has multifaceted application potential for environmental management. Biochar has been commonly used for contaminant removal from soil and water systems, soil quality improvement, soil C-sequestration, inoculant carrier, etc. Surface area, pore space, surface functional groups, pH, cation exchange capacity (CEC), and nutrient contents are a few key properties that determine the potential of biochar application. Raw materials and pyrolysis conditions are the determining factors for these aforesaid properties of biochar. Biochar production from lignocellulosic biomass and biosolids at moderate pyrolysis temperatures (350–600 °C) are commonly recommended for waste management. Despite its multifaceted application potential, biochar utilization at widescale is limited due to certain incompatibilities with the environmental systems. To overcome the incompatibilities between biochar properties and environmental conditions, engineering of biochar by using different additives and modifications in pyrolysis conditions are getting wider attention nowadays. In this chapter, we have explored the potential of engineered biochar as soil fertilizer. A bibliometric analysis was performed to collate the literature and to see the research trend of engineered biochar as soil fertilizer. Studies reported that engineering of biochar leads to improvement in its surface and physicochemical properties. Engineered biochar with improved properties helps in enhancing soil physicochemical, nutrient, and biological properties after amelioration. Improvement in soil properties showed better crop productivity in some pot/laboratory experiments. Overall, we observed that the research on exploring engineered biochar as soil fertilizer is comparatively

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limited as compared to its exploration as contaminant adsorbent and source of energy production.

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1 Introduction

Land degradation due to desertification, acidification, salinization, nutrient depletion, erosion, pollution, etc., is the major issue impeding the severity to attain food security and agricultural sustainability. As per the United Nations Food and Agriculture Organization (FAO), about 25% of agricultural lands are "highly degraded," 44% are "slightly-to-moderately degraded", whereas about 10% land has been "recovered from degradation," globally (FAO 2011; Smith et al. 2015; Huang et al. 2017). Intensive agricultural practices such as irrational applications of agrochemicals and irrigation regimes for increasing productivity, land-use changes, industrial activities as well as changing climatic scenarios are considered the major causes of the land degradation (Guo et al. 2010; Carlson et al. 2015). Land degradation leads to the deterioration in soil quality by decrease in soil organic matter (SOM) level, poor hydrophysical properties (e.g., water-holding capacity and aggregate stability), and reduced microbial functioning leading to poor plant growth and declining food production (Ibrahim et al. 2013; Ding et al. 2016). Moreover, massive amount of crop residues (~998 MT yr^{-1}) are generated globally (Copley et al. 2015), out of which a major portion is openly burnt in the field which leads to several environmental issues such as gaseous and particulate emissions, and soil health deterioration (Singh et al. 2020a; Jeyasubramanian et al. 2021). Therefore, minimizing the sole dependence on chemical fertilizers, enhancing SOM levels and microbial functioning of degraded/low-fertility soils, crop residue management, and reducing atmospheric CO_2 levels are critically needed for improving soil fertility and sustainable crop productivity (El-Naggar et al. 2019; Dai et al. 2020; Dissanayake et al. 2020). The sustainable methods such as soil amendments, which are abundant and biodegradable, and have ability to overcome the above-mentioned problems with minimal/no side effects on the environment, are the need of the hour (Kuppusamy et al. 2016; Rinklebe et al. 2016). Biochar, a by-product of biomass pyrolysis, has been considered as a promising tool to address these challenges (Khajavi-Shojaei et al. 2020; Panahi et al. 2020).

Biochar production by using crop residue biomass via pyrolysis is a sustainable process and its application as soil ameliorant not only improves soil properties and SOM levels, but also helps in managing crop residue burning, and reducing environmental pollution and CO_2 emission (Chen et al. 2019; Das et al. 2020; Leng et al. 2021). Depending on the biomass source and pyrolysis conditions, biochar has been characterized as a heterogeneous material having partially or completely carbonized, crystallized or non-polyaromatic C-forms and mineral matters (Keiluweit et al. 2010;

Spokas et al. 2012; Das et al. 2020). Moreover, biochar has higher porosity and cation exchange capacity (CEC), larger surface area, and long-term stability in the soil (Chabi et al. 2020; Jeyasubramanian et al. 2021). These properties of biochar help in improving crop growth and productivity by enhancing soil fertility, microbial activity, SOM storage and nutrient retention, modulating soil pH and water conditions, and aggregate formation after soil amelioration (El-Naggar et al. 2018; Dai et al. 2020; Das et al. 2020). Overall, the multifaceted application of biochar in soil quality improvement, C-sequestration, contaminants sorption and removal from soil and water systems, mitigating the emission of greenhouse gases (GHGs), as energy source, and waste management has resulted in gaining wider attention by the scientific and industrial communities (Lehmann and Joseph 2015; Singh et al. 2015; Dissanayake et al. 2020).

Though, biochar has multifaceted benefits as soil ameliorant; however, the sole application of traditionally produced biochar has been reported to have several challenges, viz. low nutrient contents as compared to the inorganic fertilizers, nutrient immobilization and slow-release, poor sorption/adsorption potential for contaminants, etc., which reduces its wider adoption by farmers (Mohamed et al. 2016a). For example, application of biochar with less porosity in hard soils may not result in improved crop productivity, and even application of inappropriate biochar in soil may lead to increased GHG emissions by modulating the soil physicochemical and biological properties (Panahi et al. 2020). Therefore, combined/blended application of biochar with other organic/inorganic materials such as compost, inorganic fertilizers, clay minerals, nanocomposites, etc., has also been suggested nowadays for improving soil fertility and crop performance, particularly in degraded soils (Agegnehu et al. 2017; El-Naggar et al. 2019; Singh et al. 2019, 2020b; Das et al. 2020). The conventional biochar production systems have little potential to be scaled-up at industrial production level due to low productivity and high production cost (Crombie et al. 2014; Mohamed et al. 2016b). Therefore, researches on biochar production by using different additives during the production or post-production upgradation of biochar properties and minimizing the production costs have been getting wider attention (Abdeljaoued et al. 2020).

1.1 Engineered Biochar: Definition and Need

Though biochar preparation from waste biomass is a sustainable approach; however, the properties of conventionally prepared biochar (viz. pristine biochar) can be further improved for its multifaceted applications (Akhil et al. 2021). For example, pristine biochar has low pore size and surface area which limits its potential to be used for the removal/remediation of several contaminants and nutrients which are smaller in size (Khajavi-Shojaei et al. 2020; Akhil et al. 2021). Improved pore size and surface area help in improving contaminant removal/nutrient retention potential after soil amelioration (Weber and Quicker 2018; Leng et al. 2021). For such improvements in biochar structural (surface and physical) and chemical properties, several novel methods and modifications have been evolved. The modification at the molecular or micromolecular levels to enhance the surface, physical and chemical properties (e.g., surface area and surface functional groups, porosity, pH, and CEC) of biochar with desired properties for specific applications in the fields of environment, energy, agriculture, and chemistry is referred to as biochar engineering (Wang et al. 2017; Abdeljaoued et al. 2020; Panahi et al. 2020).

Details about biochar engineering and the physicochemical properties of engineered biochar have been elaborated in different chapters of this book. In this chapter, a detailed insight has been given on exploration of the role of engineered biochar as a soil fertilizer. To observe the research trend on engineered biochar as soil fertilizer, a bibliometric analysis was performed using popular literature databases. Moreover, a brief account on the limitations of engineered biochar application as soil amendment has also been presented at the end of the chapter.

2 Bibliometric Analysis for Research on Engineered Biochar as Soil Fertilizer

Biochar has received greater attention of research communities in the last two decades due to its multifaceted application potential. Recently, engineered biochar with improved (surface/physicochemical) properties as compared to their pristine biochar counterparts are getting wider attention. In order to observe the trends in research concerned with engineered biochar and soil fertilizer or soil amendment during the last 20 years (2001–2021), we performed a bibliometric analysis on 27th July, 2021, using different search queries in the Scopus and Web of Science databases. These two databases are the largest indexing and regularly updated databases covering a wide range of peer-reviewed journals (Abdeljaoued et al. 2020; Singh et al. 2021). The initial search query was: (TITLE-ABS-KEY (“engineered biochar”) AND PUBYEAR > 2000). The query results in a total number of 182 and 190 documents published during the last 20 years (from 2001 to present, 27th July, 2021) in Scopus and Web of Science databases, respectively. Results were further refined by (“soil fertility” OR “soil amendment”) by searching within the first search query which resulted in total 68 and 19 documents in the Scopus and Web of Science databases, respectively.

The year-wise growth of the research on the topic was considered along with country-specific research outputs. Though, we searched from 2000 onwards, but we found research publications on this topic since 2013 only. Starting with merely one paper on the topic in the year 2013, the year 2020 observed a total number of 26 documents published within a single year (Fig. 1a). Interestingly, a total of 18 documents have already been published in the year 2021 (till 27th July). The results signified that the field is still emerging and recently getting much attention from the scientific community. Further, country/territory-, institute/affiliation-, subject/research area-, source/journal-, author- and publication type-wise distribution of research on the

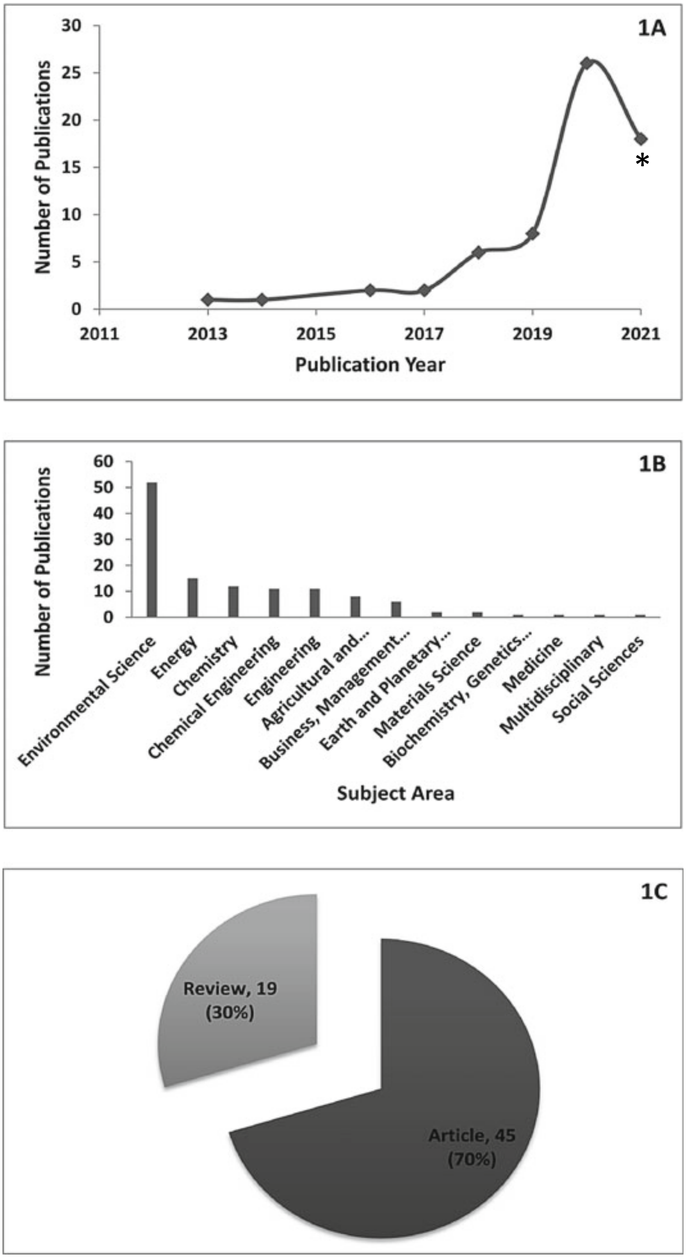

Fig. 1 Bibliometric analysis results showing **a** year-wise publication growth, **b** subject area-wise distribution, and **c** article type-wise publications for the search query "engineered biochar AND soil fertility" (*Source* Scopus database, 2021). *denotes incomplete dataset for the year 2021

topic was also analyzed. China emerged as the largest contributors of papers under country/territory-wise publication category with 33 documents. South Korea and Hong Kong ranked second and third by producing 25 and 19 papers each, while India stood at 6th rank with 7 papers published during the same period (Table 1). These observations revealed that research on engineered biochar as soil fertilizer is getting wider attention in Asian countries as compared to other countries/continents. Since most of the Asian countries are agrarian and facing the problem of massive waste management, such research trends hold crucial importance for future agricultural development. Among the research institutes and universities globally, Hong Kong Polytechnic University produced the maximum number of papers (19), followed by Korea University with 18 papers published during the last 10 years (Table 1). Out of the total 64 publications (Fig. 1b), more than 43% fall under the research areas of environmental sciences followed by engineering (18%), energy (12%), chemistry (10%), and agriculture (8%). This signified that the interdisciplinary researches are increasing on the topic and focus on environmental and engineering research is given optimal importance. Author-wise analysis results revealed Ok YS, Tsang DCW, Hou D, Gao B, and Rinklebe J, as the five most productive authors publishing 20, 19, 8, 7, and 6 papers during the last 10 years on the topic (Table 1).

Science of the Total Environment (7), Journal of Cleaner Production (6), Journal of Hazardous Materials (5), Chemical Engineering Journal (4), and Chemosphere (4) were observed as the major sources which published researches on the topic during the last 10 years (Table 1). These journals have started with the aim to manage and improve the ecosystems health and sustainability by promoting contaminants removal strategies and waste management approaches. Among 64 papers, research and review papers contributed about 70 and 30%, respectively, whereas conference papers, books, and book chapters were not identified (Fig. 1c). The ratio of <3:1 in research and review articles signifies that the topic is getting considerable attention by the research communities in different research dimensions; however, there is ample scope for writing a book chapter (and book) on this topic to reach the graduate and post-graduate reader groups. Based on the Web of Science Keyword-plus datasets, Fig. 2 depicts the focus areas of engineered biochar research in the field of environmental management. It can be seen that removal, adsorption/sorption, aqueous solution/water, pyrolysis, soil/calcareous soil, activated carbon, nitrogen/ammonium, raw material, stability, and low-cost are the top 10 areas of research related to engineered biochar which has been considerably explored in the recent years. In the next section, details about the role of engineered biochar as soil fertilizer have been provided.

Table 1 Bibliometric analysis results showing top 20 countries, top 10 research institutes/affiliations, top 20 authors, and top 10 research journals for the search query "engineered biochar AND soil fertility" (*Source* Scopus database, 2021)

Source category	No. of publications	Source category	No. of publications
Country-wise		*Country-wise*	
China	33	Australia	5
South Korea	25	Canada	5
Hong Kong	19	Taiwan	5
United States	17	Saudi Arabia	4
Germany	7	Finland	3
India	7	Iran	3
Sri Lanka	7	Singapore	3
United Kingdom	7	Belgium	2
Egypt	6	Czech Republic	2
Pakistan	6	Malaysia	2
Affiliation-wise		*Affiliation-wise*	
Hong Kong Polytechnic University	19	Ministry of Education China	7
Korea University	18	Bergische UniversitÃ¤t Wuppertal	6
Tsinghua University	9	China Agricultural University	5
University of Florida	8	Foshan University	4
Sejong University	8	The University of Newcastle, Australia	4
Author-wise		*Author-wise*	
Ok, YS	20	Bhatnagar, A	3
Tsang, DCW	19	Chen, Q	3
Hou, D	8	Chen, SS	3
Gao, B	7	Dissanayake, PD	3
Rinklebe, J	6	Fang, J	3
Sun, Y	6	Kwon, EE	3
Igalavithana, AD	5	Peng, Y	3
Shang, J	4	Sarkar, B	3
Vithanage, M	4	Shen, Z	3
Alessi, DS	3	Wang, H	3
Source-wise		*Source-wise*	
Science of the Total Environment	7	Bioresource Technology	3

(continued)

Table 1 (continued)

Source category	No. of publications	Source category	No. of publications
Journal of Cleaner Production	6	Environment International	3
Journal of Hazardous Materials	5	Biomass Conversion And Biorefinery	2
Chemical Engineering Journal	4	Clean Technologies And Environmental Policy	2
Chemosphere	4	Critical Reviews In Environmental Science And Technology	2

Fig. 2 Representation of application/research focus of engineered biochar for environmental management via word map (size of a word depicts the occurrence frequency in the literature) (*Source* Web of Science database, 2021)

3 Engineered Biochar as Soil Fertilizer

The ability of soil to sustain the crop productivity by providing essential nutrients and water supply to the plants for their survival and growth is referred as soil fertility (El-Naggar et al. 2019). Soil fertility is governed by different physicochemical (e.g., pH, soil N, P, K contents, CEC, and C-sequestration) and biological (e.g., microbial community composition and nutrient cycling) properties (Igalavithana et al. 2016; Panahi et al. 2020). After soil amelioration (Fig. 3), biochar has been reported to improve the physical, chemical, and biological properties of soil as well as improve the nutrient uptake and reduce leaching (i.e., improve nutrient-use-efficiency) in the agro-ecosystems (Wang et al. 2017; Qayyum et al. 2017), particularly in the degraded

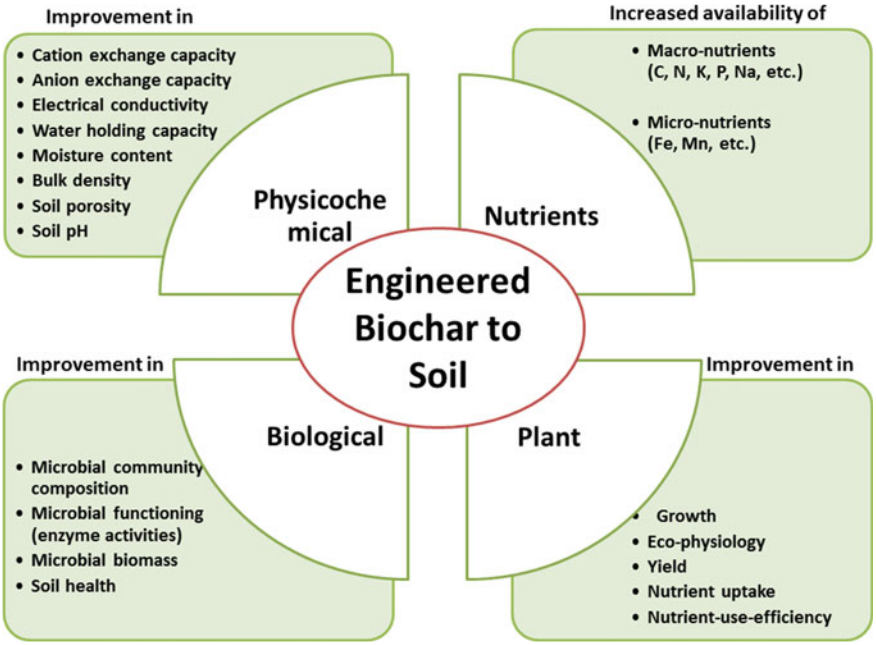

Fig. 3 Varying impacts of engineered biochar application on different soil physicochemical and biological properties as well as plant responses

and low fertility soils (Kuppusamy et al. 2016; Randolph et al. 2017; Panahi et al. 2020). Modifications observed in the soil properties after biochar application might be localized, initially (Quilliam et al. 2013). The impact of biochar amendment to soil could be direct or indirect. For example, application of nutrient-rich biochar directly improve the soil nutrient level, whereas in some cases biochar improve the soil nutrient availability indirectly by improving soil physicochemical properties (Fig. 3) such as water-holding capacity (WHC), soil porosity, water infiltration, pH, CEC, SOM level, etc. (Kuppusamy et al. 2016; El-Naggar et al. 2019; Panahi et al. 2020). Improvement in soil properties after biochar application resulted in enhanced crop production (Laghari et al. 2015; Zhang et al. 2017a). However, the impact of biochar amendment to soil properties and crop productivity mainly depends on biochar properties (e.g., pH, CEC, and C/N ratio) and its production conditions (e.g., raw material, pyrolysis temperature and other modifications), soil type and conditions, crop plant species, and management practices (Zhang et al. 2017a; Singh et al. 2019; Dai et al. 2020; Leng et al. 2021). For example, biochar derived from lignocellulosic biomass has better pore structure and help in improving soil hydro-physical properties after application (Singh et al. 2019), whereas biochar derived from nutrient-rich manure are more beneficial for improving nutrient content and crop productivity in low fertility soils (Jeffery et al. 2017; Dai et al. 2020). The combined/blended application of biochar with other nutrient sources like organic manure, fertilizer, clay minerals, etc., has shown better soil properties (e.g., nutrient availability) and crop productivity as compared to the sole application of biochar (El-Naggar et al. 2019; Singh et al. 2019). Moreover, engineered biochar has also been now produced for improving soil fertility (Li et al. 2016). Though, as highlighted in the bibliometric analysis section, the field is still emerging and more research attention is needed.

4 Enhanced Properties of Engineered Biochar and Its Impact on Soil Properties

The engineering process of biochar modifies its physicochemical properties making it suitable for industrial application. Engineered biochar differs from pristine biochar in terms of its morphological properties and chemical attributes (Table 2). Engineering of biochar improves its physical (density, particle size distribution, mechanical strength, pore size) and chemical characteristics (C and N content, pH, electrical conductivity, CEC) along with its surface (Fig. 3) properties (Das et al. 2020). The pH of biochar generally varies from 4 to 12; however, most of the biochar have alkaline pH range (von Gunten et al. 2019; Lehmann and Joseph 2021). Presence of different concentrations of oxides, hydroxides, and carbonates of alkali metals in the biochar resulted in higher pH ranges (Lehmann and Joseph 2021). Engineered biochar can enhance adsorption as it can hold both positive and negative charges on its surface. Biochar produced at lower pyrolysis temperature contains higher volatile matter content, low pH (prevents nutrient loss), and more nutrient exchange sites in the form of O-containing functional groups (El-Naggar et al. 2019). Microbial activity is enhanced due to the presence of aliphatic, cellulose-type structures in such biochar. Additionally, on raising the temperature from 350 to 600 °C, available N decreases whereas the content of P and K increases (Zhao et al. 2013). The amount of volatile matter and the residual C mass (ash) determine the stability of biochar in soil (Amonette et al. 2009). As a result, biochar has been reported to improve several soil physicochemical properties (Weber and Quicker 2018). Interestingly, improvement in soil physicochemical properties was more pronounced in the coarse-textured and low fertility soils as compared to the fine-textured and fertile soils (Laghari et al. 2015; Omondi et al. 2016). Biochar has been found to have a major environmental impact. Due to its recalcitrant/stable nature, biochar application has been reported to reduce GHG emissions by modulating soil C and N transformation processes (El-Naggar et al. 2019; Lehmann and Joseph 2021). In addition, biochar produced from lignocellulosic biomass has been reported as an effective agent for sorption of the organic contaminants (Wang et al. 2017). High surface area and pore spaces of the (mineral-treated) engineered biochar provide more adsorption sites for binding of the agrochemicals (Li et al. 2015). Improvement in key soil physicochemical properties after engineered biochar amelioration has been highlighted in the following subsections (also see Table 2).

Table 2 Comparative impact of pristine biochar and engineered biochar on different soil properties after application

S.n	Biomass source	Pyrolysis temperature	% Biochar used (w/w)	Modification	Soil system	Experiment type	Soil amendment by engineered biochar	Soil amendment by pristine biochar	References
1	Corn straw	500 °C	0.5%, 1%, 2%, and 4%	Chemical activation (Fe/Al hydroxides)	Calcareous soil	Laboratory (polyethylene containers)	(i) Increased soil pH (increased P precipitation and reduced soluble P) with high stability	Less stable pH compared with engineered system	Peng et al. (2021)
							(ii) Adsorption of excessive P from fertilizers was increased, thereby reducing P leaching while maintaining a saturated P content in soil	Poor P adsorption	Peng et al. (2021)
2	Cow dung	450–750 °C	2%	Chemical activation ($MgCl_2$ followed by P adsorption)	Acid sandy soil	Pots	(i) Considerably improved soil indexes (soil available P, pH, organic carbon, soil moisture)	Improvement seen to a lesser degree	Chen et al. (2018)

(continued)

Table 2 (continued)

S.n	Biomass source	Pyrolysis temperature	% Biochar used (w/w)	Modification	Soil system	Experiment type	Soil amendment by engineered biochar	Soil amendment by pristine biochar	References
							(ii) Basic characteristics of lettuce like plant height, fresh weight, and dry weight increased	More than control, but less than P laden engineered biochar	Chen et al. (2018)
3	*Eichhornia crassipes* (Water hyacinth)	450 ± 5.0 °C	NA	Chemical activation (Fe^{2+}, Mn^{2+}, Zn^{2+}, Cu^{2+})	Sandy soil	Samples from agricultural drain planted in pots	(i) Increased water-holding capacity (WHC, by 18.48–22.45%) was observed	Comparatively smaller increase (<18.45%)	Mosa et al. (2018)
							(ii) Higher anion exchange capacity (AEC, by 1.41–1.82%) and cation exchange capacity (CEC, by 3.73–6.35%)	Slight increase in AEC (0.77%) and CEC (3.53%) as compared to soils without biochar	Mosa et al. (2018)
							(iii) Available P and K contents increased upon engineered biochar application. But lesser increase in available N was observed	Higher increase in available N was observed as compared to engineered biochar	Mosa et al. (2018)

(continued)

Table 2 (continued)

S.n	Biomass source	Pyrolysis temperature	% Biochar used (w/w)	Modification	Soil system	Experiment type	Soil amendment by engineered biochar	Soil amendment by pristine biochar	References
							(iv) Improvement in biomass and nutrient concentration of early growth maize seedlings	Poor in comparison to engineered (activated) biochar	Mosa et al. (2018)
4	Switchgrass	300 and 400 °C	1% and 2%	Physical activation (microwave catalysis) + chemical activation (K_3PO_4, clinoptilolite and/or bentonite)	Loamy-sand soil	Laboratory	Biochar prepared by microwave heating showed higher porosity that caused an efficient increase in soil WHC	Conventional heating process is less efficient	Mohamed et al. (2016a)
5	90% beech + 10% oak wood	475 ± 25 °C	0.2%, 0.75%, and 1.5%	Physical activation (steam activated at 900 °C)	Haplic Luvisol (neutral sandy and slightly alkaline silty)	Pots	(i) Elevation in levels of soil available N, P, and C/N ratio with a decrease in nutrient leaching	Lower than the activated biochar	Borchard et al. (2012)
							(ii) Nutrient uptake by plant biomass decreased in case of sandy soil, increased in silty soil	Decrease in both soil types	Borchard et al. (2012)

4.1 Physicochemical Properties

Regardless of soil type, biochar application has been reported to improve soil–water interactions (Omondi et al. 2016; El-Naggar et al. 2019; Dai et al. 2020). Pore structure and volume, specific surface area and surface functional (hydrophilic) groups are the major factors which influence the biochar's ability to improve soil hydraulic parameters such as WHC (Wang et al. 2017; Panahi et al. 2020). However, the hydrophobicity of the biochar surfaces prevent the water adsorption/uptake in the pore spaces (El-Naggar et al. 2019). Altogether, engineered biochar has greater potential to improve soil hydraulic properties which will be beneficial to the plants in the drier or water-limited regions of the world (Mohamed et al. 2016a; Khajavi-Shojaei et al. 2020). In addition to water availability, application of biochar with varying pH range affects the soil pH which further regulates different soil biophysical properties and microbial communities (Palansooriya et al. 2019). Biochar application to soil generally increases soil pH (Dai et al. 2020). However, some (alkaline) soils have pH buffering capacity which did not show significant changes in soil pH after biochar application (Usman et al. 2016). Though application of acidic biochar may reduce the alkaline soil pH and improve the availability of some nutrients (e.g., K and micronutrients) in the soil matrix. Thus, application of engineered biochar (e.g., HCl-treated) has potential to improve the pH condition of alkaline or calcareous saline/sodic soils (Sadegh-Zadeh et al. 2018). Application of alkaline pH biochar is more suitable for acidic soils which improved nutrient bioavailability and crop productivity (von Gunten et al. 2019; Panahi et al. 2020). The changes in pH after biochar application have initial localized effects which further reflected in the whole soil matrix (Wang et al. 2017; Yu et al. 2019; Chen et al. 2021).

Biochar addition has been reported to improve the soil CEC due to high surface area and presence of negatively charged functional groups (e.g., –COOH) which increases the retention of cations on its surface and reduces nutrient leaching (Wong et al. 2016; Dai et al. 2020; Panahi et al. 2020). However, changes in soil CEC depend on biochar properties, soil types, and application rate (El-Naggar et al. 2019; Yuan et al. 2021). For example, biochar prepared at low pyrolysis temperature showed higher CEC as compared to the high-temperature biochar. Further, soil CEC increases with aging of biochar in the soil system (Wong et al. 2016). The improvement in soil CEC after biochar application has been found more pronounced in sandy/low fertility soils (El-Naggar et al. 2019). Overall, engineered biochar have potential to improve various soil physicochemical properties which may further lead to improvement in soil nutrient availability and biological properties (Fig. 3).

4.2 Improvement in Soil Nutrient Contents

Chemical properties of biochar are majorly determined by the amounts of mineral elements (C, H, N, S, O, etc.) present. These elements are found in the form of biomolecules including cellulose, hemicelluloses, and lignin. They consist of both organic and inorganic linkages. The elemental constitution of pristine and engineered biochar differs considerably. The amounts of C, H, and N in engineered biochar are lower than that in raw biochar. These elements are used to assess the chemical factors of biochar. High pyrolysis temperature leads to the crystallization of amorphous elements and organic salts as insoluble phases. Therefore, they have low nutrient contents (Ding et al. 2016; Zornoza et al. 2016). The content of water-soluble P is dependent on H/C and O/C ratios and negatively linked to pH of biochar and charosphere. Therefore, engineering of biochar increases its suitability as P fertilizer due to enhanced P availability (Chen et al. 2021).

Biochar application to soil has been reported to improve soil fertility by enhancing nutrient retention and use-efficiency by the plants (Randolph et al. 2017; Wu et al. 2020). It reduces the nutrient (NO_3^-–N, NH_4^+–N, and PO_4^{3-}–P) leaching after fertilizer application by adsorbing the nutrients on its surfaces (Brassard et al. 2019; Jeyasubramanian et al. 2021). The results are more pronounced in the low fertility sandy soils (Laghari et al. 2015; Lei et al. 2018; Yuan et al. 2019). Biochar being a rich source of exchangeable cations (such as Na, K, Ca, and Mg) increases their availability in soil matrix (Mohamed et al. 2016a, b; Moon et al. 2017). However, availability of micronutrients and soil P to the plants may reduce after biochar application to the alkaline soils due to changes in soil pH conditions (Gunes et al. 2014; Laghari et al. 2015). As P availability to plants has been found more pronounced at pH 5.5–7.5 range, application of biochar which increases the soil pH above or below this range may change the soil P availability (Andersson et al. 2015; Chen et al. 2021). Application of engineered biochar (e.g., $MgCl_2$-modified and steam activated) has been reported to further improve the nutrient adsorption properties and may act as slow-release fertilizers which reduces the nutrient leaching and increase crop productivity (Zhang et al. 2017b; Khajavi-Shojaei et al. 2020). The changes in soil pH conditions after biochar application affect the soil microbial activities which further modulate different soil biogeochemical processes (Yu et al. 2019). Thus, the impacts of biochar application to soil nutrient availability are governed by the complex interactions of soil–water–plant–microbe nexus in the agroecosystems (Singh et al. 2018, 2019).

Biochar application in soil system regulates the N dynamics by acting as either N-supplier through its own N content directly or as N-improver by increasing N retention after fertilizer application (Randolph et al. 2017; Mia et al. 2019). In general, biochar application mainly acts as N-improver in the soil system (Dai et al. 2020). Biochar properties, soil pH, fertilizer type, etc., regulate the soil microbial functioning related to the N-transformations such as N-fixation, nitrification, and denitrification processes (Panahi et al. 2020). Specifically, surface (e.g., surface area and acidic functional groups) and physicochemical (e.g., pH and CEC) properties of biochar predominantly regulate the N cycling in the soil (Nguyen et al. 2017). Biochar adsorbs the inorganic-N species (e.g., NH_4^+–N and NO_3^-–N) on its surface and release them slowly in the soil system, thus acting as slow-release fertilizers (Haider et al. 2017). In addition, biochar application induces the N-transforming microbial communities which further determine the soil N cycling (Nguyen et al.

2017; Zheng et al. 2013a). However, negatively charged biochar surfaces showed greater affinity to the NH_4^+–N as compared to the NO_3^-–N in soil system (Zheng et al. 2013a). Engineered biochar showed improved efficiency for N-transformations in the soil. For example, biochar prepared after chemical and ultrasonication treatment showed better N (particularly, NH_4^+–N) adsorption capacity as compared to the pristine biochar (Chen et al. 2017; Feng et al. 2019). Steam-activated biochar showed increased retention of NO_3^-–N as compared to pristine biochar (Borchard et al. 2012). The $MgCl_2$-modified biochar release soil nutrients (e.g., NH_4^+–N and NO_3^-–N) more slowly as compared to the pristine biochar and chemical fertilizers (Khajavi-Shojaei et al. 2020). High porosity and surface area with sufficient (O-containing) functional groups and improved soil physicochemical properties are responsible for increased adsorption capacity of nutrients released in the biochar applied soil systems (Panahi et al. 2020; Khajavi-Shojaei et al. 2020). The C/N ratios of soil and biochar and inorganic-N species availability in the soils determine overall N dynamics (Nguyen et al. 2017). For example, application of high (>20) C/N ratio biochar resulted in N-immobilization, whereas low (<20) C/N ratio resulted in N-mineralization (Jeffery et al. 2017; Nguyen et al. 2017; Lehmann and Joseph 2021). Thus, C/N ratio (ranging between 7 and 400) of biochar (and soil) should be taken into consideration, as it regulates the N-availability via mineralization and immobilization processes resulting in N-limitation and poor plant performance. To overcome the challenges related to N-availability, early application of biochar (one month before crop cultivation) and/or along with organic N-sources has been suggested (Dai et al. 2020; Panahi et al. 2020).

Improvement in soil physicochemical properties has been reported to improve P-availability and use-efficiency by plants (Qayyum et al. 2017; Bornø et al. 2018). Biochar application has been reported to improve the soil P-retention and availability (Copley et al. 2015; Glaser and Lehr 2019). Improvement in soil pH by biochar addition is mainly responsible for increased P-availability in soil (Panahi et al. 2020). Like P, biochar application to soil is also reported to improve the soil K-availability (Dai et al. 2020; Panahi et al. 2020). As mentioned earlier, biochar derived from biosolids (e.g., animal manure, poultry wastes, and sewage sludge) has more potential to improve soil P- and K-availability as compared to the lignocellulosic biochar (Zheng et al. 2013b; Igalavithana et al. 2016). For example, better P-availability was observed in neutral and acidic soils, whereas less or no improvement in P-availability was observed in alkaline soils after pristine biochar application (Glaser and Lehr 2019). Application of engineered biochar may help in improving P-availability in alkaline soils (Qayyum et al. 2017). For example, Mg- and Al-modified biochar showed high P adsorption potential which can be utilized as slow-release fertilizer (Wang et al. 2017). Addition of inorganic catalysts such as clinoptilolite, bentonite, and K_3PO_4 during the pyrolysis of biomass improves the physicochemical properties of biochar and their sorption capacity for the available nutrients (Mohamed et al. 2016a). Similarly, acidified biochar application also improved the P-availability in alkaline soils (Takaya et al. 2016; Qayyum et al. 2017). However, acidification of biochar should be adequately done, as higher acidification may not result in improving P-availability (Qayyum et al. 2017). Nanobiochar or MgO-biochar nanocomposites produced by pyrolyzing anaerobically digested or $MgCl_2$-pretreated lignocellulosic biomass showed considerably high P-sorption capacity as compared to other C-based adsorbents (Zhang et al. 2012; Yao et al. 2013). Moreover, addition of P-laden engineered biochar improved soil moisture, pH, SOM content, and available P content of soil, thus, enhances the soil fertility (Chen et al. 2018).

In addition to the effects on major soil nutrient availability, biochar application also affects the micronutrient (e.g., Fe and Mn) availability in soil matrix by several mechanisms (Das et al. 2020). For example, decrease in pH after biochar amendment in highly alkaline soils results in increased availability of Fe and Mn (Masto et al. 2013). Moreover, excess availability of K in soil after biochar addition has been reported to interfere with the uptake of Mg and Ca by plants, particularly in presence of chemical fertilizers (Das and Awasthe 2018). Overall, biochar has variable impacts on different nutrients in the soil which are majorly regulated by the biochar types and properties, soil conditions, and management practices.

4.3 Soil Biological Properties

Biochar application to soil influences the soil microbial community composition and structure by modulating soil physicochemical and nutrient parameters (Panahi et al. 2020). As described earlier, biochar has a large surface area with high (micro, meso, and macro) pore spaces, high (labile and stable) C content and other nutrients on its surface (Quilliam et al. 2013). These properties provide a suitable habitat conditions (and available nutrients) for the settlement and growth of soil microfaunal diversity such as bacteria, protozoa, fungi, etc. (Lehmann et al. 2011; Gul et al. 2015). Biochar's macropores provide suitable microenvironment for microbial colonization by protecting them from desiccation, predation and other adverse environmental conditions, whereas micro- and mesopores help in storing nutrients for microbial metabolism (Gul et al. 2015; Zhu et al. 2017; Awad et al. 2018; Das et al. 2020). In addition, biochar addition to soil improves soil aeration, water content, and reduces soil compaction which further helps in luxuriant microbial growth (Laghari et al. 2016). Organic C content, pH, and WHC of the biochar considerably affect the soil biological properties such as microbial biomass, N-mineralization/immobilization, and enzyme activities (Li et al. 2019; Das et al. 2020). Similarly, improved macro- and micronutrient availability induces symbiotic and free-living N-fixing bacterial growth, depending on soil–water conditions (Biederman and Harpole 2013; Nguyen et al. 2017). The macropore spaces of the biochar favor fungal (hyphae) growth, whereas alkaline pH range favors soil bacterial growth (Panahi et al. 2020). However, presence of different phenolic and polyphenolic compounds on the biochar surfaces pose negative effects on soil microbial growth (Das et al. 2020). Thus, the impact of biochar on soil biological diversity mainly depends on the soil and biochar properties and application rates.

Various extracellular and intracellular enzymes released from the soil microorganisms play significant role in different biochemical transformation processes

(Panahi et al. 2020). Biochar addition to soil has variable impacts on soil enzyme activities. Biochar application could induce the α-glucosidase, β-glucosidase, β-D-cellobiosidase, aminopeptidase, *N*-acetyl-β-glucosaminidase, and alkaline phosphatase enzyme activities which are involved in nutrient cycling in the soil matrix (Wang et al. 2015). Improved microenvironmental conditions after biochar application are the primary cause for improved enzyme activities (Nie et al. 2018). Biochar produced from animal manure increased the alkaline phosphomonoesterage activity, whereas reducing the acid phosphomonoesterase activity in different fine-textured soils (Batool et al. 2015). High surface area and surface functional groups bind the extracellular enzymes, thus interfere with their activities (Das et al. 2020). Teutscherova et al. (2018) reported decrease in some hydrolytic enzymes (viz. β-glucosidase, β-glucosaminidase, and phosphatase) activities after biochar application in the Acrisol, possibly due to inactivation of these enzymes after adsorption on the biochar surfaces (Panahi et al. 2020). In a pot experiment study, pristine biochar has been reported to increase the soil catalase and urease activity, whereas Fe-modified biochar decreased these enzyme activities (Wen et al. 2021). Changes in soil pH conditions and different ion/nutrient availability after different biochar application might be the primary cause of variation in enzyme activities (Wen et al. 2021). Moreover, biochar prepared at different pyrolysis temperatures also showed variable impacts on soil enzyme activities (Steinbeiss et al. 2009). Thus, depending on the biochar and soil conditions, the extent of different extracellular and intracellular enzyme activities may vary.

4.4 Crop Responses to Engineered Biochar Application

In general, improvement in soil physicochemical, nutrient, and biological properties (e.g., pH, CEC, hydraulic properties, nutrient availability, and use-efficiency) after biochar application enhances the nutrient uptake and plant growth conditions which further improve the crop productivity, in general (Das and Avasthe 2015; Dai et al. 2020; Panahi et al. 2020; Qayyum et al. 2017). However, crop responses to biochar application may be regulated by different factors such as biochar properties, soil conditions, climatic conditions, and experimental types (Hussain et al. 2017; Dai et al. 2020). Application of P-laden biochar considerably improved the plant growth (height and weight), ecophysiological (water use-efficiency) characteristics and productivity (Chen et al. 2018; Das et al. 2020). Biochar application (having high ash/mineral content) to sandy soils improve the plant productivity (Dai et al. 2020). Improvement in soil pH after biochar application is considered as the most important factor influencing the plant growth owing to the direct impact of pH on soil microbial functioning and nutrient cycling (Dai et al. 2017). Application of acid-treated biochar to the alkaline soils may improve crop productivity by modulating soil pH conditions (Sadegh-Zadeh et al. 2018). Fe-modified biochar application in continuously flooded soils showed more grain production as compared to alternative flooded system (Wen et al. 2021). Application of $MgCl_2$-modified biochar as slow-release fertilizer to maize crop grown in a pot experiment increased plant growth (height, shoot and root dry weight), eco-physiological (chlorophyll content and leaf area) properties, and plant N-use-efficiency (Khajavi-Shojaei et al. 2020). However, there is no conclusive remark on the impacts of engineered biochar on plant growth due to lack of understanding of the mechanisms operating in soil–plant system after biochar application to soils (Xiao et al. 2019; He et al. 2020; Akhil et al. 2021).

5 Limitations Related to Engineered Biochar Use as Soil Fertilizer

Although (engineered-)biochar has multifaceted application potential for environmental management, its application as soil fertilizer directly as well as after contaminant adsorption should be considered based on the following risk assessments:

1. Application of engineered biochar produced from contaminant-loaded raw material may lead to the distribution and movement of tiny contaminants and particles (e.g., nanobiochar) in the water and air systems (Ramanayaka et al. 2020; Huang et al. 2020)
2. Since the particle size of engineered biochar is very small (e.g., biochar-nanocomposite), their application to soil may result in bioaccumulation or biomagnification after some time (Panahi et al. 2020)
3. Application of nanobiochar as soil fertilizer may induce cytotoxic, genotoxic, or ecotoxic effects to crop plants (Cifuentes et al. 2010)
4. Nanobiochar showed higher activity in alkaline medium; thus, presence of nanobiochar to the water system may influence the humans and animals at different (e.g., ingestion, dermal contact to cell and tissue damage) levels (Chen et al. 2010; Ma et al. 2019)

6 Conclusion and Future Prospects

Biochar engineering leads to the enhanced surface area and pore structure, and nutrient retention capacity. Application of engineered biochar with improved properties modulates different soil properties such as pH, CEC, soil nutrient availability, and microbial activities (and enzyme activities) which resulted in improvement of soil fertility and crop productivity. Engineered biochar showed better potential to be used as soil ameliorant as compared to the pristine biochar. Surface area, pore spaces, surface functional groups, pH, and CEC of the biochar play a major role in determining their potential as soil fertilizer. However, most of the studies are limited to lab or pot scales. Further research should focus on:

1. Combined application of engineered biochar with other soil additives such as organic manure for further improvement in soil fertility and crop performance
2. Impact of engineered biochar application on changes in soil biological (micro- and macrofaunal) diversity and activity for achieving the sustainability in agriculture
3. Risks associated with engineered biochar application to soil should be thoroughly studied before its wider application to plot and field scales

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