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Nano Biochar for Sustainable Agriculture and Environmental Remediation: A Comprehensive Review

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Authors' contributions

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ABSTRACT

To safeguard soil, water, and air throughout intensive agricultural operations as well as significant industrial and transportation endeavors, it is imperative that the environment and agriculture are managed sustainably. Application of biochar might be a potential approach to solve these issues. The use of biochar (BC) in agricultural techniques and for environmental remediation has shown to offer a variety of benefits, despite certain drawbacks. Superior physicochemical characteristics of nanobiochar include strong catalytic activity, distinctive nanostructure, large specific surface area, and excellent mobility in soil environments. Nanobiochar is a prime contender for sustainable agriculture to pollution remediation and catalytic reactions. Despite growing interest in biochar research for agricultural and environmental uses, it is unclear how important nanobiochar is. So, in this study, we identified several fundamental uses of nanobiochar with an emphasis on its efficacy for environmentally and agriculturally sustainable practices.

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1. INTRODUCTION

The land and water supplies are threatened by environmental contamination, which requires prompt worldwide attention. Pollution has a significant negative impacts on the environment, these pollutants may include things like industrial emissions, sewage discharge from homes, heavy metals, and agricultural operations, etc. In recent years, biochar (BC) has become a popular soil amendment which has the potential to remediate polluted soil and water [1] and is now manufactured on a huge scale all over the world. According to studies, biochar may efficiently remove pollutants from wastewater [2], lower the bioavailability of contaminants in soil [3], and enhance ecosystem services. In oxygen-limited environments, biochar is produced by pyrolyzing biomass source materials at low to high temperatures (300-700°C) [4]. It is regarded as a possible sorbent for different toxins and pollutants including heavy metals [5], and the microbial oxidation of methane is supported by its soil stability, sorption characteristics, and microporosity [6].

“With the development of nanotechnology, studies have been done on the production of nano-biochar (nano-BC) for soil and agricultural use in a sustainable manner” [7]. The micro-sized BC, also known as "dissolved" and "nano-BC," is created during the carbonization process and has dimensions less than or equal to a micrometer (m) and up to a nanometer (nm). Nanobiochar is defined as biochar with particle sizes between 1 and 100 nm [8]. In general, there are two major approaches to obtain nanobiochar. One is produced intentionally, and the other is the physical breakdown of biochar caused by aging in the environment [9]. “The specific surface area (SSA), hydrodynamic radius, negative zeta potential, and number of oxygen-containing functional groups of nanobiochar are all much higher than those of bulk biochar” [10]. Nanobiochar has been researched and used in a variety of applications, such as pollution adsorbents, soil amendments, photocatalytic materials, and biosensors [8].

“Black carbon, activated carbon, and manufactured carbon nanoparticles have reportedly been shown to contain soluble organic material found in the natural environment” [11]. Additionally, nanobiochar outperforms bulk biochar in terms of stability and temperature-dependent dispersibility [12]. In the fields of environmental science and agriculture, the use of nano-BC is a key topic of research. The current review analyzes a brief biochar production methods, including physical, chemical, and biological methods, as well as the general (physical and chemical) properties of biochar. Additionally, the uses of nano-biochar for (i) sustainable environmental management, soil fertilizer, and soil greenhouse gas emission reducers, and (ii) remediation of organic and inorganic contaminants have been reviewed.

2. NANO-BIOCHAR (NANO-BC) PRODUCTION

The physiochemical parameters of nanobiochar are often influenced by its source material. According to Föhr et al. [13], “materials with high lignin often form nanobiochar with great aggregation ability”, “while biomass with high hemicellulose typically produces nanobiochar with low carbon content and high oxygen content” [16]. “Because of its nano-enabled properties, which include its extremely small size, varied mobilization, bioavailability, and consequent effect on soil and plant systems, nano-BC may be expected to have more attractive environmental management for intended purposes compared to bulk biochar materials” [15]. Top-down or bottom-up procedures can be used to create nanomaterials. While the bottom-up approach builds nanomaterial from the atomic level, the top-down approach reduces the size of the macro BC to the nanoscale.

Nano-BC is produced in an efficient manner using top-down techniques such grinding, cutting, centrifugation, and etching. The bottom-up approach involves carbonization, ball milling, and sonication for disintegration [16]. Without affecting the crystal structure, ball milling enables the manufacturing of nano-BC with enhanced characteristics [17]. Due to its low manufacturing costs, low energy requirements, eco-friendliness, and broad variety of applications, ball milling has drawn a lot of interest. By impacting it with metallic balls, the ball milling technique breaks down bulk-BC into nanoscale particles. Biochar may be ball milled at the nanoscale using either wet or dry methods. Due to the synthesis of nano-BC's improved dispersivity, increased surface functionality, eco-friendliness, and labor-saving benefits, the wet method is more preferable [18]. Another approach for fabricating nano-BCs is double-disc milling, however it has expensive operational expenses. Vibrating disc milling, one of the several ball milling techniques, generates more nano-BC with stable size and shape in larger numbers [19]. According to several research, nano-BC has been manufactured under controlled conditions utilizing parameters including a milling time of 120–1200 minutes, a number of balls ranging from 25 to 800, a ball weight of 0.5–100 g, and a ball size of 3/4–15 mm. Ma et al. [20] adjusted the grinding duration, rotating speed, and ball-to-powder mass ratio to optimize the process parameters for the production of ball-milled nano-BC. To enhance particle dispersion prior to separation, the BC mixes must be further disseminated in various solvents after milling [21]. However, the pre-treatment at 80°C makes it possible to reduce size aggregation, but it is a costly procedure, limiting its ability to be scaled up. By minimizing the use of risky chemical-assisted processes, ball milling is a high atom economy approach that produces nano-scale biodegradable goods utilizing renewable resources [16].

Sonication is one of the most effective physical techniques for producing nano-BC because it uses high-energy ultrasonic radiation to break apart BC in suspension. Shock waves cause blocked pores to open and the carbon structure to exfoliate, increasing the microporous area in BC. After that, the tiny exfoliated particles of BC stick to its surface or become embedded in its pores, producing nano-BC [22]. Two of the main advantages of sonication are the homogeneity of the nano-BC surface and the unhindered growth of porosity [23]. In a few studies, nano-BC was also produced from waste lignin carbonization as a post- or pre-treatment with milling to improve the surface characteristics and size of nano-BC with the removal of impregnating salts in the next step [24].

3. NANO-BC'S INHERENT FEATURES AND THEIR CHARACTERIZATION

Nano-BC is used for several applications in large part due to its inherent characteristics. Higher affinity and coordination binding of organic contaminants and heavy metals are produced by plant-derived nano-BC due to their large aromatic cluster size and high oxygen surface functionality. The abundant carbonate, sulfate, and aluminosilicate groups in nano-BC made from urban wastes allow for heavy metal complexation and co-precipitation [21]. The degree and kind of functional groups as well as porosity have an impact on the effectiveness of nano-BC as a nano-adsorbent and nano-catalyst. The production, characteristics, and morphological and physiological variety of nano-BC can be influenced by the graphitic and amorphous nature of BC (hardness and abrasion resistance) [34]. According to Nath et al. [27], nano-BC produced from bulk-BC that was created at high temperatures has a greater carbon content, bulk density, and extractable cations including Ca, Fe, K, Mg, Mn, P, and Zn. Nano-BC made from coconut fibers had a higher carbon content (90–94%) than nano-BC made from sewage sludge (4%). According to Wang et al. [35], the nano-BC typically contains more ash and less aromatic and carbonized carbon than the macro-BC. The qualities of the manufactured nano-BC are influenced by the pyrolysis's duration and operation temperature. Due to the enhanced solid density of micro-BC, an increase in pyrolysis temperature causes a rise in nano-BC size, which leads to the synthesis of big particles [36]. The transformation of less dense disordered carbon into microscopic particles that create denser mass fractal patterns is also made possible by lengthening the pyrolysis process [27].

4. NANO-BC IN SUSTAINABLE AGRICULTURE

Climate change appears to have a greater detrimental influence in the future, which have exacerbated to the negative effects in real-time leading to poor agricultural output and environmental pollution [37]. “Climate change and technological issues, which include aggregated unbalanced resource use and environmental issues like eutrophication, surface runoff, use of conventional fertilizers, and industrial waste emissions, have recently had a significant impact on the agricultural sector” [38]. “Nano-BC has the potential to reduce the biological availability of environmental toxins and regenerate damaged soils, which might help with these problems, particularly in agriculture or soil” [39]. “By altering the chemical, biological, and physical characteristics of the soil, biochar, a substance that is currently used as a soil supplement, has a significant effect on soil fertility” [40]. Nano-BC treatment raises soil quality, which increases the compatibility of the soil for plant growth and development (Fig. 1).

Table 1. Methods for synthesis of nano-BC and their applications [15]

Materials	Method for synthesis	Product	Application	Performance	References
Wheat straw	Ball-miilling at 700 °C	Ball-milled megnatic nano-BC	Removal of tetracycline and Hg from aquoues solutions through absorption	Maximum absorption of tetracycline and Hg was 268.3 and 127.4 mg/g, respectively	Li et al. [25]
Woody biochar, a by-product of *Gliricidia sepium* (Jacq.) Walp. gasification	Disc milling of preconditioned biochar (at -80 °C for three days) in ethanol media	Graphitic nano-BC	Removal of oxytetracycline, glyphosate, hexavalent chromium, and cadmium (Cd (II))	High partition coefficient for the removal of contaminants showed high efficiency of graphitic nano-BC over other adsorbents	Ramanayaka et al. [10]
Pine wood	Planetary ball milling	Green synthesized nano-BC	Removal of micropollutants such as carbamazepine from aqueous media	Upto 95% removing efficiency	Naghdi et al. [26]
Rice-husk	Chemically amended pyrolytic approach at 600 °C	Iron oxide Permeated Mesoporous rice-husk nano-BC (IPMN)	Adsorption based removal of arsenic from aquoues media	More than 90% uptake of dissolved arsenic by IPMN	Nath et al. [27]
Pine wood biochar	Planetary ball milling	Nano-BC having size of 60±20 nm	Removal of carbamazepine	Upto 95% removal of carbamazepine (74 µg carbamazepine/g nano-BC)	Naghdi et al. [28]
Oil palm empty fruit bunches	Pyrolysis-carbonization of $FeCl_3$ pre-treated biomass at 500 °C	Sulphonated magnetic nano-BC in amorphous phase with crystallite Fe_3O_4	Catalyst activity	Superior catalyst activity over commercialized catalysts, good activity of magnetic nano-BC loaded with $-SO_3H$ groups as catalyst for esterification	Jenie et al. [29]
Artichoke leaves	Pyrolysis in a muffle oven at 350 °C for 2h	Nano-BC with surface loaded with NaOH	Removal of anti-diabetic drug metformin	Adsorption of 20 mg/L metformin hydrochloride onto prepared nano-BC	Mahmoud et al. [30]

Materials	Method for synthesis	Product	Application	Performance	References
			hydrochloride	(R^2 = 0.996)	
Cynara scolymus L. leaves	Pyrolysis at 350 °C for 1 h	Ecofriendly nano-BC	Adsorption of cadmium and samarium through microwave sorption	Uptake efficiency of Cd(II) and Sm(III) were 1150 and 650 μmol/g, respectively	Mahmoud et al. [31]
Corncob bares	Pyrolysis at low oxygen atmosphere at 400 °C and modification of nano-BC by triethylenetetramine	Nano-BC or nano-BC-modified triethylenetetramine	Removal of tartrazine and sunset yellow dyes from aqueous media	More than 90% elimination percentage was observed for tartrazine and sunset yellow dyes removal from actual, tap, and industrial water	Mahmoud et al. [32]
Cynodon dactylon (L.) Pers. residues	Hydrothermal and coprecipitation method	Tri-metallic surface engineered superparamagnetic nano-BC coated with cobalt/ferrous silica and specific amine group	Removal of copper and lead ions from aqueous media	Sorption capacity of 220.4 mg/g for copper and 180.5 mg/g for lead ions	Vishnu et al. [33]

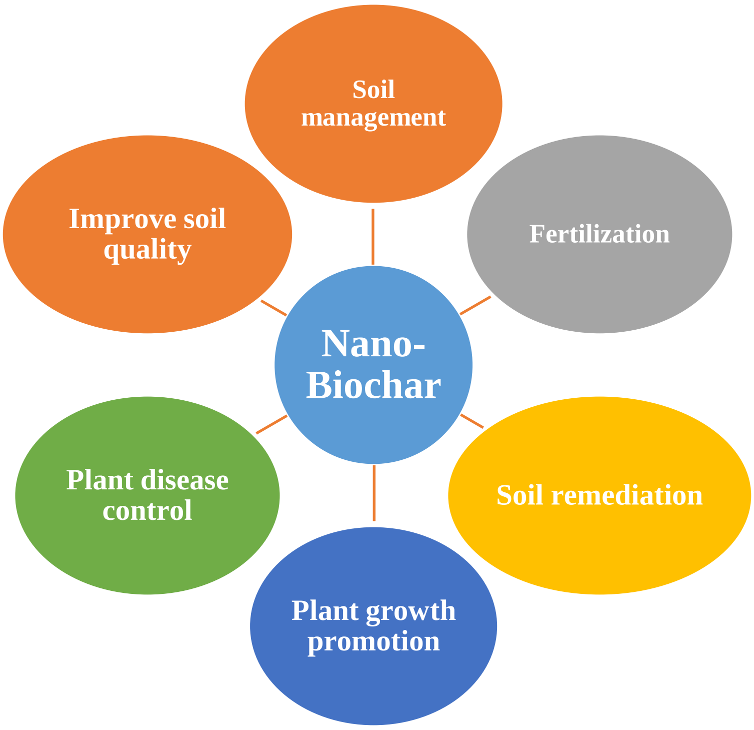

Fig. 1. Application of nano-biochar in agriculture

By improving soil porosity, soil tensile strength, and water retention capabilities, which are necessary for maintaining soil activities, nano-BC provides bacteria with the right soil habitat [41]. According to reports, the nano-BC significantly increases microbial diversity, improving soil fertility as a result [42] and also soil physicochemical, enhances soil-plant relationship, phytotoxicity management, removal of potentially toxic metals and enhancement in bioavailable soil phosphorus (Table 2).

5. NANO-BC FOR ENVIRONMENTAL REMEDIATION

Biochar's strong adsorption capacity and porous structure make it a potential sorbent for a variety of organic and inorganic contaminants in soil and water. These qualities may be used especially to the elimination of a certain environmental contaminant. As of right now, nano-remediation techniques have shown to be a major help in preventing pollution and protecting the environment [47]. The effectiveness of nano-BC in environmental remediation is significantly influenced by a number of environmental parameters, principally pH, coexisting ions, dissolved organic matter (DOM), organisms, and root exudates (soil system). Nano-BC has the potential to stabilize high concentrations of contaminants which significantly lessen the harm that pollutants pose to ecosystems and public health by reducing their movement and bioavailability and different environmental consequences, such as stability, mobilization in porous environments, reaction features, and hazardous nature [48], due to their advanced shape and properties.

The addition of nano-BC to the soil can be very helpful in enhancing and/or upgrading the soil quality and reducing the availability of harmful ions in the soil [49]. With few exceptions, nano-BC generally helps degraded and low-nutrient soils become more fertile, which increases agricultural yield. Numerous variables, including nutrient cycling, pH, soil N concentration, microbial population, cation exchange capacity, water retention, and C sequestration, are associated to soil fertility. Nano-BC amendment has been shown to have a number of applications and substantial effects, making it a useful tool for recovering unfertilized soil and maximizing crop yield [50]. Furthermore, even when sprayed excessively, nano-BC can be free of environmental contamination and does not harm crops, depending on the method of application. In addition to C, H, and O, silicon-rich biomass such as rice husk and maize straw is a key source of biochar [51].

Table 2. Nano-biochar for sustainable agriculture

Sl. No.	Properties	Role of Nano-Biochar
1.	Soil microbial diversity and fertility	By introducing nano-BC into the soil, actinobacteria and bacteroidetes' microbial biomass, availability, and community diversity increased whereas proteobacteria's diversity decreased. It controls several microbial activities, which affects how well the soil works. The mobilization of macronutrients like phosphorus is characterized as being amplified by the interactions of nano-BC with soil minerals; these changes in soil nutrients may be the cause of fluctuations in the number of soil microorganisms [30].
2.	Soil physico-chemical	The use of nano-BC as a soil amendment affects soil functions that rely on the physical, chemical, and biological characteristics of the soil. There is evidence that biochar improves soil nutrient conditions, carbon capture capacity, microbial traits, and soil organisms [43]. Following the application of biochar amendment, the emission of N_2O typically falls by approximately 83%. Reduced soil pollution, improve soil bulk density (BD), and water holding capacity (WHC), increased productivity, microbial activities, and nutrient cycling characteristics are also seen [44].
3.	Soil-plant relationship	Plant roots and other vital minerals quickly absorb nano-BC that has been suspended or disseminated in water. Morphological changes and seedlings recovery are improved, and they exhibited healthy growth, normalization in chlorophyll content, superoxide dismutase activity and malondialdehyde concentration were both decreased by the application of nano-BC [45]. Increase in phosphorus translocation in plants and improved mycorrhizal connection was attributed to the properties of biochar-mineral complexes.
4.	Soil remediation and phytotoxicity management	In addition to improving soil fertility and nutrient availability, biochar has showed promise in lowering the bioavailability of soil pollutants such potentially harmful heavy metals [46]. Increased mobilization of soil phosphorus due to surface adsorption on potentially hazardous metals like Cd on nano-BC. Additionally, laccase-mediated immobilization of carbamazepime, destruction of antimicrobial resistance genes present on eDNA by generation of free radicals on the surface of nano-BC, and cleanup of polluted waterways using nano-BC technology are also examples [7].
5.	Removal of potentially toxic metals	Conversion of biochar to nano-BC (a pyrogenic solid) and its utilization for the removal of three toxic metals have been reported as nano-BC reduced the availability of Cd in soil due to its stabilization by nano-BC. Additionally, it improved microbial biomass, diversity, and plant growth which are the important indicators of improved soil health. Arsenic from aqueous solutions was separated by using iron oxide impregnated rice-husk nano-BC fabricated through chemically assisted pyrolysis [27]. With the maximum Hg2+ absorption value of 127.4 mg nano-BC/g, wheat straw nano-BC produced at 700 °C was employed to remove Hg2+ [46]. The surface complexation of Hg with nano-BC, electrostatic interactions, and creation of the Hg-C bond were suggested as the causes of

Sl. No.	Properties	Role of Nano-Biochar
		the Hg adsorption by nano-BC. A graphitic nano-BC was used to extract hexavalent chromium Cr(VI) and Cd2+ [10]. Based on these findings, it can be inferred and underlined that nano-BC amendments of soils and other nutrients may also successfully separate other potentially dangerous metals, such as chromium (Cr), lead (Pb), copper (Cu), and zinc (Zn).
6.	Bioavailability of soil phosphorus	By causing osmotic stress or an ion imbalance, the poor availability and low plant absorption of phosphorus prevent plants from growing. Phosphorus deficit caused by soil salinity is therefore more detrimental to crop productivity. Nano-BC adaptations might be used to prevent this. According to batch sorption tests, adding nano-BC to salt-amended soil increased the amount of phosphorus that could be absorbed by the soil. Through spectroscopic investigations such FT-IR and X-ray diffraction, it was possible to see the mechanism of adsorption. These analyses revealed the presence of oxygenated functional moieties on the surface of nano-BC that were involved in the adsorption of P ions. The improved P adsorption was attributed, according to X-ray diffraction (XRD) data, to precipitation of P with nano-BC's K^+ ($KMgPO_46H_2O$), Al^{3+} ($AlPO_4$), Mg^{2+} ($MgPO^4$ and $MgHPO^4$), and Ca^{2+} ($Ca_5(PO_4)_3OH$, $Ca_3Mg_3(PO_4)_4$ and $CaHPO_4$). Additionally, it was discovered that surface precipitation contributed to the adsorption in soil that had been modified with salt [30].

6. NANO-BC FOR MITIGATION OF GREENHOUSE GAS (GHG)

The oxidation and amination changes in the surface chemistry of biochar provide an ideal active site. Many different types of pollutants can be adsorbed by biochar, including gases [52], organic molecules [53], harmful metal ions [54], mineral nutrients [55], and microorganisms [56]. While limited data is currently available, it appears that the external redox reactive portions are the main factor influencing the redox status of biochar. Nano-BC not only promotes the breakdown of organic contaminants by directing the shifting of electrons like a catalyst, but it may also interact directly with toxic contaminants, thereby exerting a positive impact on environmental variables or issues [57]. By eliminating nitrate, phosphate, and ammonia from the natural ecosystem, biochar helps avoid eutrophication—the excessive proliferation of photosynthetic organisms in response to a high concentration of inorganic nutrients in an aqueous environment.

The addition of biochar may alter the physico-chemical characteristics of the soil, which may have an effect on greenhouse gas emissions from the soil [46]. The pace at which biochar is applied may potentially have an impact on soil CO_2 emissions. As per Johnson et al. [58], there was a greater increase in CO_2 emission when biochar amendment was applied at high rates (10%) as opposed to low rates (1%). Overall, four processes can be used to explain how applying biochar affects CO_2 flux: (i) biochar application can change the amount of CO_2 released from soil by "priming effects" on the mineralization of the soil's organic C pool; (ii) biochar application can change the amount of CO_2 released from soil by adsorbing CO2 molecules on its surface; (iii) biochar application can change the physico-chemical properties of soil, which indirectly affects CO_2 emission; and (iv) biochar application can have a significant impact on soil microbial activities and diversity that are involved in CO_2 metabolism. One may anticipate a shift in soil CH_4 emissions after adding biochar. As demonstrated by the CH_4 flow from wet rice fields [59] and the CH_4 emission from anaerobic and forest soils (Karhu et al., 2011), the influence may be either inductive or suppressive. The five processes listed below could lead to an increase in CH_4 mechanisms after adding biochar [60]. These processes include: (i) raising the soil's carbon content, which methanogens (bacteria and archaea) could assimilate into CH_4; (ii) suppressing CH_4 oxidation by methanotrophic activity; (iii) increasing CH_4 emission due to off-gassing from surface and/or pore desorption; (iv) raising soil pH, which affects the activities of methanogens and methanotrophs; and (v) enhancing CH_4 production and emission by adding anaerobic microsites to the soil. Numerous agriculture soils and forest habitats have been demonstrated to emit less N_2O when biochar is used [61]. According to Sun and Lu [62], 25.5% less N_2O was released into the atmosphere when 30 t/ha of biochar was applied to forest soil. Recent meta-analysis research revealed that the average reduction in N_2O emissions by biochar is 32%, with the highest reduction occurring at biochar addition rates exceeding 40 t/ha [63]. Reduced soil N_2O emission is caused by two main mechanisms: (i) it increases soil aeration and O content, which prevents soil denitrification by denitrifying bacteria, which happens in conditions where O_2 is limited; and (ii) it has a high adsorption capacity that can adsorb NH_4^+ and NO_3^-. By immobilizing N compounds, lowering NH_3 volatilization, and increasing plant growth, this strategy lowers the inorganic N pool available to N_2O^-producing bacteria through the denitrification process [64].

In addition to serving as a detoxicant, nano-BC is essential for managing waste, reducing soil erosion, and retaining soil nutrients. The immobilizing of enzymes, biocatalysts, and microorganisms is made possible by the surface characteristics of nano-BC. In addition, nano-BC has the potential to replace chemical electrodes, acting as a biosensor for the identification and tracking of hazardous substances. Further study is necessary, though, as the large surface area also serves as a home for microbes on nano-BC. By comprehending these interactions at the molecular and genetic levels, new avenues for hybrid remediation solutions can be identified for environmental sustainability.

7. CHALLENGES FOR APPLICABILITY OF NANO-BC

Nano-BC has a number of drawbacks when it comes to direct environmental applications, including low stability and difficulty isolating nanoparticles, easy mobilization, uptake, and accumulation, and toxicity toward very fine particles (nano to micron) [35]. Numerous variables, including the size of the source material, the physical grinding or milling process, and the aging mechanism, may affect the distribution of nano-BC sizes [65]. Many roles and methods can lessen the restrictions and potential risks associated with nano-BC particles [66-69].

8. CONCLUSION

Agricultural activities can benefit greatly from the use of nano-BC as opposed to its bulk equivalent. Thus far, several investigations have demonstrated the significant alterations in soil physical-chemical and biological properties subsequent to the incorporation of nano-BC into the soil. Because of their minuscule size, nano-BC has the ability to remediate both organic and inorganic pollutants in the environment, improve soil quality, and ultimately enhance crop performance. Native soil plants and microorganisms may get the nutrients linked with nano-BC, which would promote plant development, microbial diversity, and soil biological activities. While there is no denying that nano-BC has more benefits for agricultural use, its tiny size may also pose certain negative impact to human health and soil organisms. Therefore, in order to suggest nano-BC for agricultural uses, further field research would be needed. To limit the negative effects, methods for quickly assessing nano-BC and mobilizing them to various soil profile regions must be evaluated. An additional area of focus is the optimization of nano-BC, which depends on the properties of the feedstock material, to maximize the benefits to soil and plants. Research on nano-BC in agriculture and the environment is very welcome, however studies on the longer-term adsorption-desorption of plant nutrients or environmental contaminants on nano-BC are needed for field applications.

COMPETING INTERESTS

Author has declared that no competing interests exist.

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