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Modulating effects of biochar on phosphorus dynamics in soil–biota–plant system: a comprehensive review

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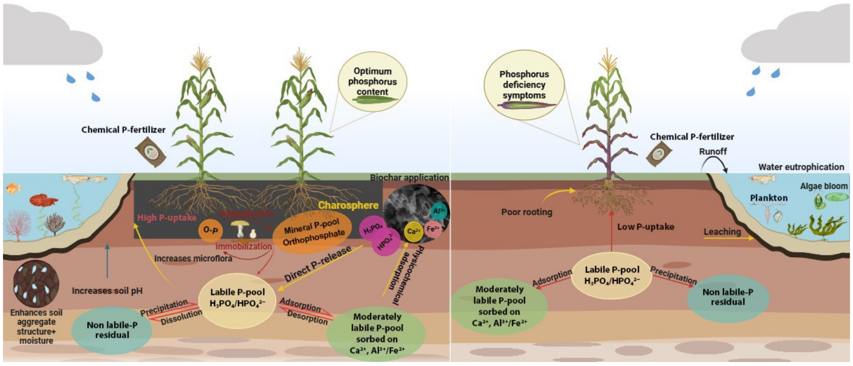
ABSTRACT

- Phosphorus dynamics in soil–biota–plant system of the charosphere was reviewed.
- Phosphorus content of biochar is a feedstock– and pyrolysis temperature–dependent.
- Biochar stimulates colonization of microorganisms mediating phosphorus availability.
- Modulating effects of biochar on phosphorus use efficiency was highlighted.
- Tailoring functionalized biochar to unlock phosphorus reserves was reviewed.



Phytoavailability of phosphorus (P) is limited in most soil orders due to insoluble precipitates formation in the rhizosphere with ions of calcium, iron, and aluminum. Therefore, biochar has been adopted as an eco-friendly soil amendment to unlock soil P reserves and modulate P dynamics in soil–biota–plant system. However, this hotspot area of research has not been critically reviewed up to now. This review delves into the specific mechanisms responsible for improving P phytoavailability in the charosphere, either directly by its inherent P content or indirectly *via* modulating soil physicochemical characteristics that would solubilize the legacy P. Data of this review were extracted from recent publications to evaluate the beneficial effects of biochar on mechanisms responsible for modulating P phytoavailability in the charosphere. Data analysis illustrated that inherent P content in biochar is a feedstock– and pyrolysis temperature–dependent, in which bones feedstock and the high pyrolysis temperature (>600 °C) could produce the highest P concentration (124216 and 31160 mg kg^{-1}, respectively). Biochar showed pivotal roles in stimulating the colonization of microorganisms mediating P phytoavailability involved in organic P mineralization and legacy P solubilization. The high functionality of biochar also showed a beneficial effect in minimizing the vulnerability of P losses through surface runoff and percolation into groundwater. These modulating effects of biochar were responsible for maximizing P use efficiency (PUE) relative to the unamended soils (43.36% *vs.* 20.26%). %Average values of PUE varied widely according to biochar's feedstock (29.1%–38.5%), pyrolysis temperature (9.4–60.1) and application rate (29.9%–88.1%). Nonetheless, this data showed contradictory results with obvious significant effects under lab investigations and only minimal effects under field-scale experimentations.

Keywords biochar, legacy phosphorus, mineralization, solubilization, phytoavailability

Contents

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1 Introduction

Phosphorus (P) is an essential macronutrient for optimal plant nutrition due to its pivotal roles in cell division, photosynthesis, sugars metabolism, energy transfer/storage, and transference of genetic information (Alshaal et al., 2017). Plants often uptake P from the soil pore water in forms of orthophosphate ions ($H_2PO_4^-$ and HPO_4^{2-}), which exist with only small portion of the total soil P (10–25%). For instance, concentrations of topsoil Olsen–P in both of EU and UK averaged as 32.3, 33.6 and 20.0 mg kg^{-1} in arable, pasture and forests, respectively (Panagos et al., 2022). The low concentration of orthophosphate ions is caused by multiple edaphic processes, and rapid fixation by several components either in alkaline or acidic soils (Frossard et al., 2000). The predominance of Ca^{2+} and Mg^{2+} ions in alkaline soils could fix orthophosphate ions in precipitated minerals (e.g., apatite); however, the prevalence of Fe and Al ions and oxides in acidic soils encourages precipitation of P in variscite ($Al(OH)_2.H_2PO_4$), strengite ($Fe(OH)_2.H_2PO_4$) and Fe/Al–oxide–rich minerals (e.g., gibbsite, hematite and goethite) (Mabagala and Mng'ong'o, 2022).

Due to its low kinetic mobility/solubility in soil, P often depleted form the rhizospheric soil layer by plant roots, leading to a gradient in P concentration in a radial direction away from the root zone. Accordingly, substantial amounts of mineral P fertilizers are annually added to sustain P requirements of plants. In this regard, the future global market of P fertilizer forecasts a yearly 22–27 and 4–2 million tons by the year 2050 to meet cropland and grassland demands, respectively (Mogollón et al., 2018). Nevertheless, most applied phosphatic fertilizers accumulate in soil matrix as a legacy P. This legacy P store has a low phytoavailability potential and might cause several environmental hazards if not appropriately managed.

Legacy P could be subjected to substantial losses *via* erosion and vertical runoff to cause significant deteriorations in surface and groundwater bodies (Ngatia et al., 2017). The literature pointed to high levels of P concentration in groundwater samples worldwide (> 0.1 mg L^{-1} as an average value): 78% in China, 66% in Brazil, 47% in Wales, 38% in Mexico, 24% in USA, and 19% in Canada with a high potential of contamination hazard (Warrack et al., 2022). These high levels of P in groundwater (shallow resources in particular) might be a significant source of P flux into surface water with the re-exposure of groundwater runoff to surface water bodies (Yu et al., 2018). Numerous reports highlighted P non-point source pollution as a main reason of eutrophication in water bodies, including Lake Huron and Detroit River in North America (Scavia, 2023), tropical rivers in Côte d'Ivoire (Soro et al., 2023), and Fuxian Lake in China (Duan et al., 2023). More terribly, excessive P fertilization might have unforeseen effects on crop susceptibility to pest and pathogen infections. For instance, Rashid and coworkers illustrated that the excessive application of phosphate fertilizers to rice basins favored the population of *Nilaparvata lugens*, which is a major pest of rice worldwide (Rashid et al., 2017). In addition, the overuse of phosphate fertilizers could enhance rice susceptibility to the infection of *Magnaporthe oryzae*, which is the causal agent of the blast disease (Campos-Soriano et al., 2020).

On the other hand, an intensive increase has occurred in the international prices of phosphate rocks/minerals, including hydroxyapatite (10 000 \$ t^{-1}), struvite (533 \$ t^{-1}) and phosphate rock (120 \$ t^{-1}) due to the over mining activities, which further starved raw materials of phosphate (Zhang et al., 2023a). Accordingly, several soil amendments are added to unlock soil P reserves, involving (i) inorganic amendments (e.g., sulfur in alkaline soils (Daer et al., 2024), and lime in acidic soils (Azeez et al., 2020)), (ii) organic amendments, such as biochar (Mosa et al., 2018), humic substances (Zhao et al., 2024), compost (Estrada-Bonilla et al., 2021) and sewage sludge (Jalali et al., 2021), and (iii) biological amendments such as phosphate–solubilizing bacteria/fungi (Doilom et al., 2020; Beltran-Medina et al., 2023), and vesicular arbuscular mycorrhizae (Hou et al., 2021). Among, biochar (a carbonaceous material derived from the thermochemical treatment of organic feedstock under cut-off or limited O_2 supply) has become the focal point of research in several agro-environmental applications (including soil P dynamics) taking into consideration its unique functionality, cost-effectiveness, and renewability potential.

Biochar application can serve as a considerable source of phytoavailable P to meet agricultural P demands (Mosa et al., 2018, 2020). Besides, the amending effect of biochar could indirectly modulate P chemical cycling (adsorption/desorption, precipitation/dissolution, leaching and runoff), biological cycling (mineralization/immobilization) and other biochemical processes that could regulate P phytoavailability in the charosphere (microbial solubilization, plant symbioses and root exudate-derived compounds). For example, P phytoavailability in the charosphere is greatly regulated by multiple modulations in soil physicochemical properties responsible for P availability in soil (e.g., soil pH–Eh, calcium carbonate, organic matter and Fe/Al (oxyhydr)oxides) (Islam et al., 2024). Besides, biochar application has pivotal implications on various biotic and abiotic factors that would govern P mineralization and immobilization in the charosphere. Phosphorus mineralization involves conversion of organic P such as inositol phosphates (e.g., phytic acids), phytate phosphomonoesters (e.g., nucleotides and sugar phosphates), and phosphodiesters (e.g., nucleic acids and phospholipids) into labile mineral orthophosphate by phosphatase enzymes (e.g., acid/alkaline phosphatase and phytase) (Jarosch et al., 2019). Phosphorus immobilization, however, describes the transformation of mineral P forms into microbially-synthesized organic P compounds including monoesters/diesters orthophosphate, organic polyphosphates and phosphonates (Arenberg and Arai, 2019).

Despite the plethora of publications that have been focused on the effect of biochar on soil P dynamics (Fig. 1), few have reviewed these dynamics in the charosphere. Consequently, a comprehensive review on this hotspot area of research is crucial to shed the light onto the current and state–of–the–art knowledge to sustain the future agricultural P demands in a sustainable manner. In this article, we are seeking to contextualize a comprehensive, authoritative, and decipherable review to meet the global needs of academic/research communities, environmental agencies, industrial entities, and decision makers.

2 Bibliographic data collection

Literature search was carried out using the key words of "biochar", "soil amendment", "soil phosphorus dynamics", "phosphorus availability", and "phosphorus fractions". Data were extracted from recent publications (during the last decade) comprising incubation, pot, and field experimentations, which reported data of P in soil, plant, and biochar. These publications, including research articles, review articles, books, book chapters and proceedings were written in English, and included in reputable sources (e.g., Scopus, Web of Science, Springer Link, Wiley-Blackwell, ProQuest, JSTOR and EBSCO). The extracted data were presented in box and whisker plots using OriginPro 2021. Box chart includes mean (dot), median (centerline), lower quartile (the

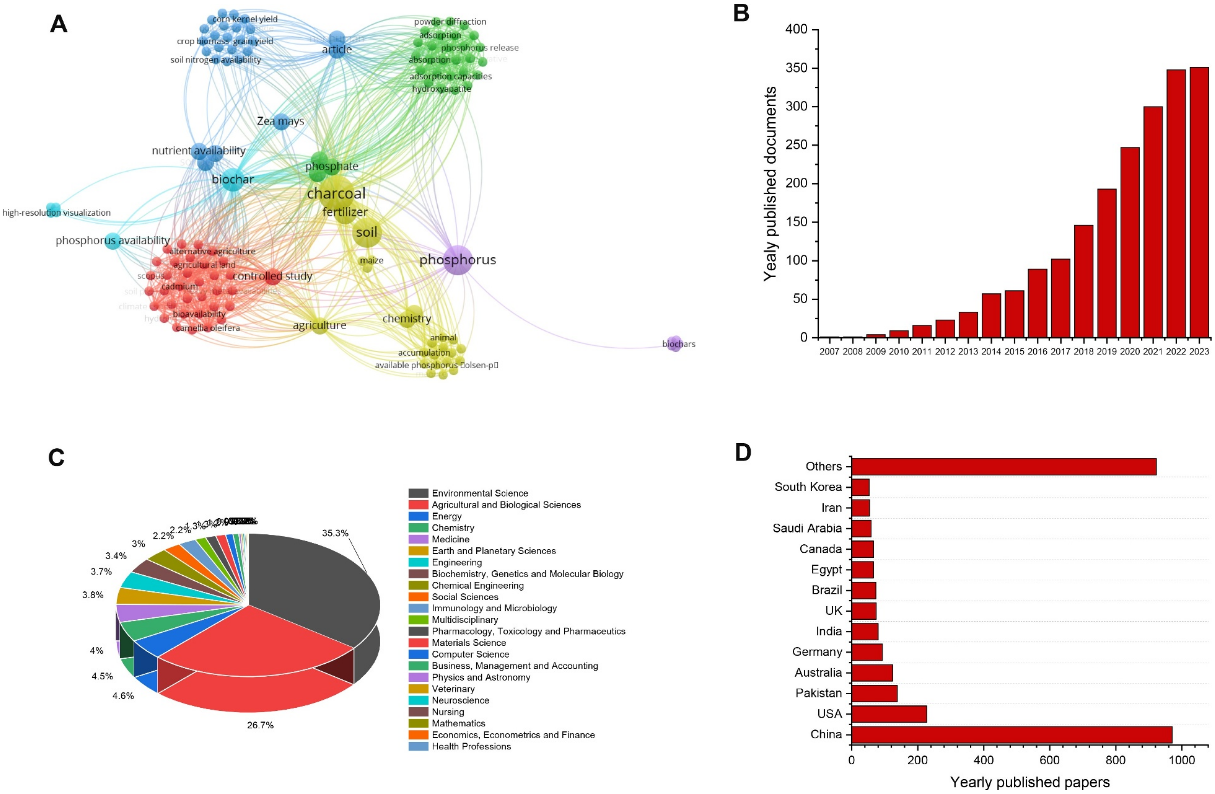

Fig. 1 Yearly published documents in the Scopus database between 2007 and 2023 based on a query that employed the keywords of "biochar", "soil" and "phosphorus": (A) VOSviewer co-occurrence map combined with unit analysis, (B) total number of yearly published articles, (C) published articles (%) according to the subject area, and (D) published articles (%) in different countries/territories.

lower border of the box), upper quartile (the upper border of the box), and whiskers-error bars (the minimum and maximum observations). Findings of meta-analysis studies published in peer-reviewed journals were further considered to contextualize a coherent judgment of the current state of potential utilization of biochar to modulate soil P dynamics in soil and terrestrial ecosystems. The graphical abstract was prepared using BioRender software. Data in Fig. 1 were extracted from Scopus database based on yearly published documents between 2007 and 2023 according to query that employed the keywords of "biochar", "soil" and "phosphorus". Data published in figures were converted into corresponding numerical values using Data Graph Digitizer (ver. 2.22, Russian Federation). Constructing/visualizing of bibliometric data was carried out using VOSviewer software. Phosphorus use efficiency was calculated based on total P uptake by plants amended with biochar relative to those grown in control treatments using the following equation:

$$\mathrm{PUE} = \frac{\mathrm{P\ uptake}_{\mathrm{treatment}} - \mathrm{P\ uptake}_{\mathrm{control}}}{\mathrm{Amount\ of\ P\ fertilizer\ application}} \times 100$$

3 Inherent phosphorus content of engineered biochars

Phosphorus content varied widely in feedstocks (200–18000 mg kg^{-1}), wherein phytate is the major organic constitution; however, polyphosphates and orthophosphates are the dominant inorganic P-containing species (Frank, 2013). The high P content in the feedstock might increase the produced biochar yield during the thermochemical conversion process. As such, the high organic and inorganic P contents in the feedstock maximized biochar yield by more than three folds due to the enhanced crosslinking by phosphate-containing structures in the carbonaceous matrix (Chen and Wu, 2021). Another investigation also illustrated that P enrichment by different sources during the thermochemical conversion increased carbon retention in biochar (47.8–73.6%) as well as its aromaticity and graphitization (Bai et al., 2023).

Biochar contains considerable amounts of P, which retained in its carbonaceous material against volatilization at temperatures below 700 °C. Phosphorus concentration in biochar is a feedstock–dependent, in which its concentration is typically around 2–3 folds of that in the raw material given the sublimation of organic C during pyrolysis (Ghodszad et al., 2021). In this regard, P concentration in biochar varies between 130 and 42790 mg kg^{-1} according to the feedstock material (Gul et al., 2015). In the current study, data extracted from literature (88 recent investigations comprising 193 values) illustrated that average concentration of P in biochars derived from several feedstock origins ranks as follows: bones (124216 mg kg^{-1}) > manures and sludges (68941 mg kg^{-1}) > crustacean shell wastes (17846 mg kg^{-1}) > crop residuals (4701 mg kg^{-1}) > woody wastes (1410 mg kg^{-1}) (Fig. 2). Biochar derived from animal bones has been utilized as an organic fertilizer source due to its high P content and hydroxyapatite composition (Azeem et al., 2021a). In addition, P recovery from sludges and manures could be considered as a win–win strategy to prolong limited P resources, and fulfil significant amounts of plant nutrient requirements in some countries (e.g., about 50% of the mineral P requirements in Germany) (Krüger and Adam, 2017). In view of this, an earlier study reported a high proportion of P in sludge-derived biochar that could be released speedily (within 24 h) into the rhizospheric layer of soil (He et al., 2016). Available P, however, comprises of about 45–60% of the total P in poultry litter biochars compared with only 10% of total P in biosolids-derived biochar (Freitas et al., 2020).

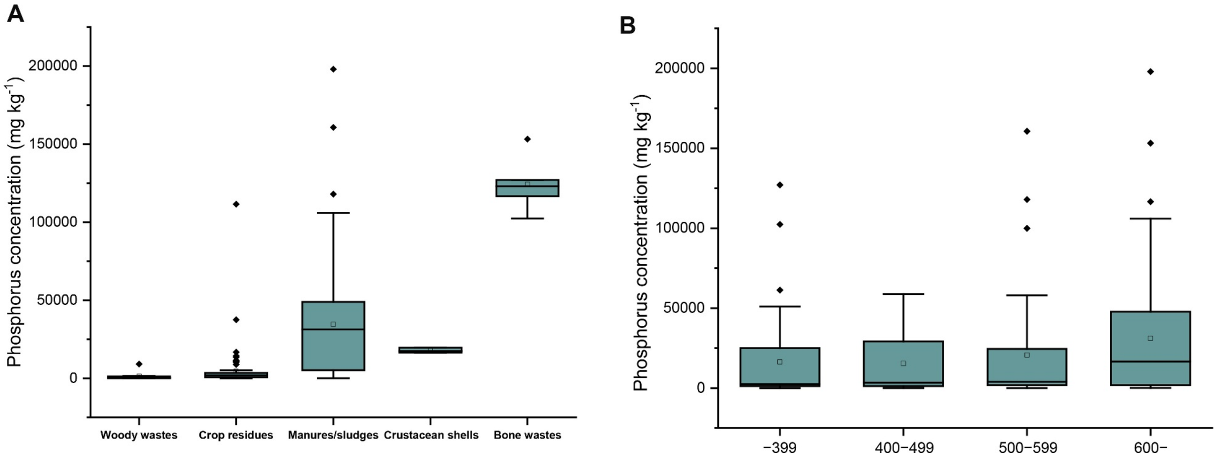

Fig. 2 The inherent P concentration of the produced biochar: (A) effect of feedstock type, and (B) effect of pyrolysis temperature. Data were extracted from 88 recent investigations comprising 193 values. Box charts are presented by mean (dot), median (center line), lower quartile (the lower borders of the box), upper quartile (the upper borders of the box), and whiskers-error bars (the minimum and maximum observations).

Unlike organic elements (i.e., carbon, nitrogen, hydrogen and sulfur), which might volatile during thermochemical conversion process, P do not volatile under pyrolysis temperatures below 700 °C (Atkinson et al., 2010). The inherent pyrophosphate ($P_2O_7^{4-}$) in plant biomass is persisted in biochars pyrolyzed below 650 °C (Ghodake et al., 2021). Consequently, it is hypothesized that increasing pyrolysis temperature might increase total P content in biochar. We extracted data from 88 recent studies to elaborate the effect of pyrolysis temperature on P concentration in the engineered biochar. Based on analyzing data generated from these studies (177 values), it could be concluded that increasing pyrolysis temperature causes a significant increment in total P concentration in the produced biochar: –300 °C (16375 mg kg^{-1}), 400–499 °C (15396 mg kg^{-1}), 500–599 °C (20719 mg kg^{-1}), and 600–°C (31160 mg kg^{-1}). Phosphorus transformation during the thermochemical conversion of biochar is also a temperature dependent. In view of the study carried out by Xu and coworkers, increasing pyrolysis temperature tend to convert water soluble P into labile and semi–labile pools ($NaHCO_3$–P_i and NaOH–$P_{i,}$ respectively) as well as stable pools (Dil. HCl P and residual –P) due to the formation of less soluble compounds such as crandallite ($CaAl_3(OH)_5(PO_4)_2$), wavellite ($Al_3(OH)_3(PO_4)_2 \cdot 5H_2O$) and poly–P (Xu et al., 2016a). This finding was supported by a meta-analysis of 108 pairwise comparisons, which illustrated that biochars derived from temperatures below 600 °C exhibited high P phytoavailability relative to those pyrolyzed above 600 °C (Glaser and Lehr, 2019).

The high content of Ca^{2+} in the feedstock material might significantly minimize P availability in biochar pyrolyzed at low temperatures since Ca^{2+} ions facilitate the adsorption/precipitation of orthophosphates/pyrophosphates; however, the high pyrolysis temperature motivates complexation rather than precipitation of released soluble poly–P with Ca^{2+} ions (Qian et al., 2019). In a recent study, the thermochemical transformation of cottonseed meal at different pyrolysis temperatures (300–600 °C) tend to transform organic P into inorganic forms (initially polyphosphates and subsequently orthophosphates) as promoted by a higher pyrolysis temperature (Guo et al., 2024). This study also demonstrated that total P content in biochars comprised 9.3%–17.9% of readily labile P, 10.3%–24.1% of generally labile P, 0.5%–2.8% of moderately labile P, 17.0%–53.8% of low labile P, and 17.8%–47.5% of residual P.

4 Effect of biochar on soil microorganisms mediating phosphorus phytoavailability

4.1 Vesicular arbuscular mycorrhizae

The symbiotic effect of vesicular arbuscular mycorrhizae (AM) on improving root architecture to reach phytoavailable P by root-external mycelium in large area of soil matrix is well documented (Tarraf et al., 2017; Abd El-Fattah et al., 2023; Wahab et al., 2024). The community composition of AM varies greatly according to edaphic properties of soils as well as common agricultural practices (e.g., fertilization) (Neuberger et al., 2024). Several research inquiries, however, need to be clarified regarding mutual interactions among biochar and plant-promoting AM for maximizing phosphate solubilization in soil. Hammer and coworkers introduced the first evidence that AM fungi are able to exploit biochar as a physical growth media, and as a source of nutrition (Hammer et al., 2014). Authors also demonstrated that fungal hyphae penetration into the carbonaceous lattice of biochar improved the translocation potential of P into the hosting root by about six times greater than treatments without biochar (Fig. 3).

According to Mickan et al., the presence of biochar might help in enabling extraradical mycorrhizal hyphae to access microsites of P that are difficult to be accessible to plant roots given their larger diameter (Mickan et al., 2016). In a work by Chen et al. (Chen et al., 2024), biochar application (rice husks pyrolyzed at 500 °C) enhanced spore germination of *Rhizophagus irregularis* (32%), its hyphal length (662%), most probable number (70%) and mycorrhizal colonization rate (28%), which maximized the content of available P up to 48%. Interestingly, the higher the inherent P concentration in biochar, the lower the AM colonization (Solaiman et al., 2019). Biochar can also facilitate the accessibility of mycorrhizae to limited P locations in soil matrix, since the fungal hyphae could access microsites within the organo-mineral complexes of soil-biochar aggregates that were not accessible before biochar application (Liu et al., 2020).

The abundance of nutrients in biochar might also stimulate the efficiency of AM fungi, and their efficiency (Javeed et al., 2023). In a recent study, gene expression analyses were performed in order to acquire mechanistic insights into synergies between different types of biochar (chicken manure and wheat straw @ 450 °C) and AM fungi (Figueira-Galán et al., 2023). Results of this study demonstrated that the synergy between biochar and AM is feedstock-dependent, which controls the release of phytoavailable P and its uptake potentials (Figueira-Galán et al., 2023). Specifically, the slow release of P from wheat straw biochar reinforces the symbiosis with AM greater than other high–P biochar (chicken manure biochar), which showed less symbiotic and colonization levels.

4.2 Bacteria

There is a close correlation between edapho-climatic conditions (e.g. soil physicochemical properties, nutrients status, temperature and precipitation) and communities/densities of

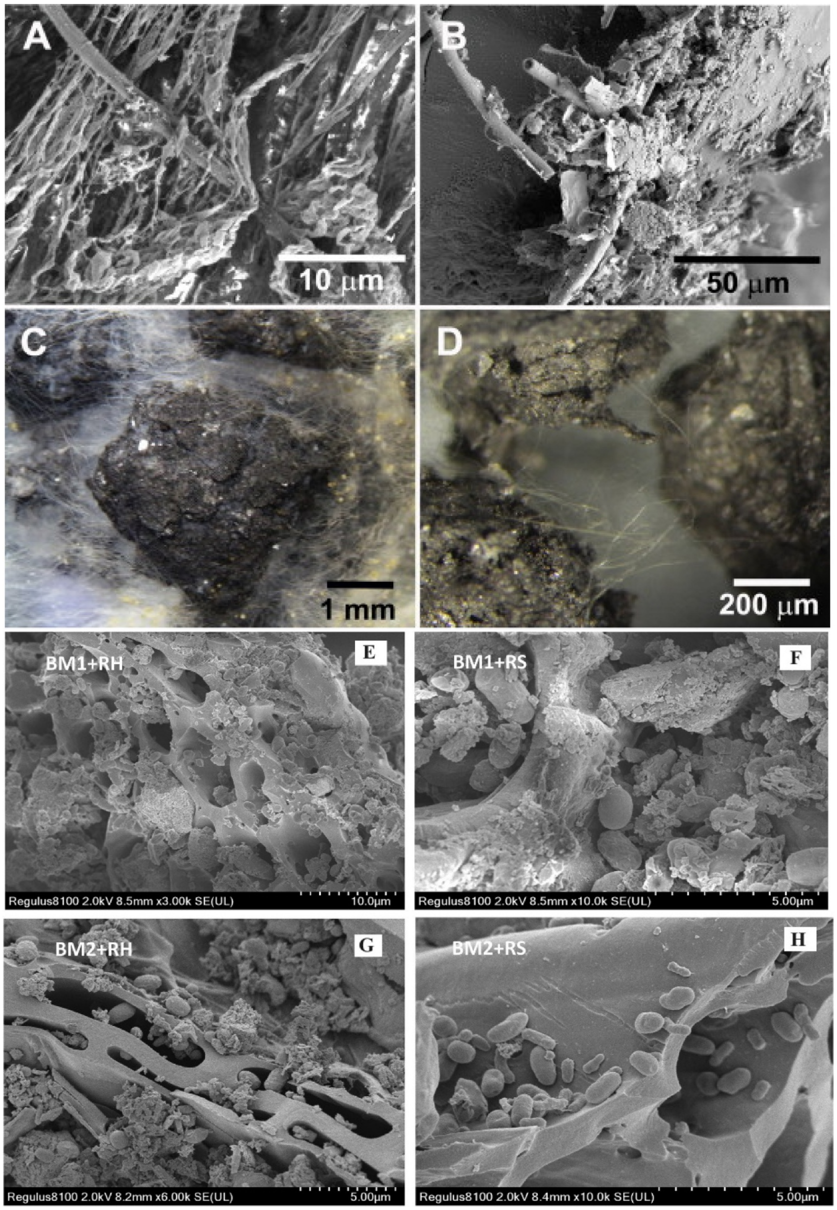

Fig. 3 Microscopy images illustrating the colonization of AM fungus (*Rhizophagus irregularis* AM fungal hyphae) and bacteria (*Bacillus megatherium* and *Bacillus mucilaginosus*) into the carbonaceous lattice of biochar derived from chicken manure. (A) cryoSEM of surface shot, (B) cryoSEM of inner part of the biochar, (C) *in situ* dissecting microscope image illustrating complete hyphal coverage a minimal nutrient medium, (D) *in situ* dissecting microscope image illustrating distinct hyphal connection of particles in MilliQ water, (E) *Bacillus megatherium* colonization into rice husk biochar, (F) *Bacillus megatherium* colonization into rice straw biochar, (G), *Bacillus mucilaginosus* colonization into rice husk biochar, and (H) *Bacillus mucilaginosus* colonization into rice straw biochar (reproduced from Hammer et al., 2014 and Lu et al., 2023, with permission from the publisher).

bacteria involved in phosphate solubilization (Janati et al., 2023). Consequently, the utilization of biochar as a soil amendment for modulating edapho-climatic conditions in the rhizosphere might provide the favorable zone to flourish phosphate solubilizing bacteria. Furthermore, the mutual interaction between biochar application and agricultural practices (e.g., deep tillage) could increase P phytoavailability and modulate bacterial structure in the deeper soil layer (Chen et al., 2022b). Biochar utilization as a soil amendment to promote soil P dynamics has received a recent increasing interest; however, much less information is available regarding its modulating effect on phosphate solubilizing bacteria. According to Fox et al.'s study, miscanthus biochar application to a non-fertilized gley soil since 1968 significantly increased the abundance of rhizospheric soil bacteria (Acidobacteria, Actinobacteria, Planctomycetes, Proteobacteria and Verrucomicrobia) capable of growing within the presence of phosphate-esters, tri-calcium phosphate and phosphonates as sole sources of P (Fox et al., 2016). Another investigation illustrated that rice husk and rice straw biochars as a bacterial shelter (Fig. 3) showed high efficacy in improving P solubilization capacity (43.9% greater than the unamended treatment) by affecting secretion of polysaccharides and organic acids as well as phosphatase activity secreted by phosphate solubilizing bacteria (*Bacillus megatherium* and *Bacillus mucilaginosus*) (Lu et al., 2023). The mutual relationships among biochar, phosphate solubilizing bacterial, secretion of phosphatase enzymes and P availability is demonstrated in Fig. 4.

Mechanisms involved in the stimulatory effect of biochar on functionality of phosphate solubilizing bacteria were rarely reported in literature and require additional investigations. It was reported that phosphate solubilizing bacteria (*Enterobacter hormaechei* Rs-198) are adhered to biochar surfaces, which marked with low aromaticity and radicals' content, due to the low total interaction energy between biochar and bacteria surfaces and the high negative secondary energy minimum (Liu et al., 2023b). In another study, Lu and coworkers stated that biochar enables stimulation of phosphate solubilizing bacteria by enhancing their organic acids, polysaccharide and phosphatase activity secretion necessarily for phosphate solubilization (Lu et al., 2023). In a study carried out by Heidari et al. (2020), biochar application (cow manure, wheat straw, wood biochar) improved the efficacy of phosphate solubilizing bacteria (*Bacillus lentus* and *Pseudomonas fluorescence*) through stimulating their microbial growth (expressed as microbial biomass carbon) and their enzymatic activity (alkaline phosphatase, acid phosphatase, urease and dehydrogenase). It is worth noting that pyrolyzed biomass might exhibit higher performance in improving the efficacy of phosphate solubilizing bacteria than the original form. In a thorough work by Fan et al. (2023), cow dung biochar pyrolyzed at 500 °C increased the biodiversity of rhizospheric and non-rhizospheric soil bacteria, maximized the abundance of phosphate-dissolving bacteria (*Sphingomonas* and *Lactobacillus*), and stimulated the copy number of the P functional genes *phoC* and *pqqc*. In yet another study, rice straw biochar pyrolyzed at 450 °C stimulated the activity of phosphate solubilizing bacteria due to providing a highly porous material for microbial colonization and reduced carbon as a source of nutrition (Ali et al., 2020). Biochar also showed high capacity to support phosphate solubilizing bacteria to survive under the stress of heavy metals contamination through stimulating acid secretion and extracellular electron transfer (Chen et al., 2023a).

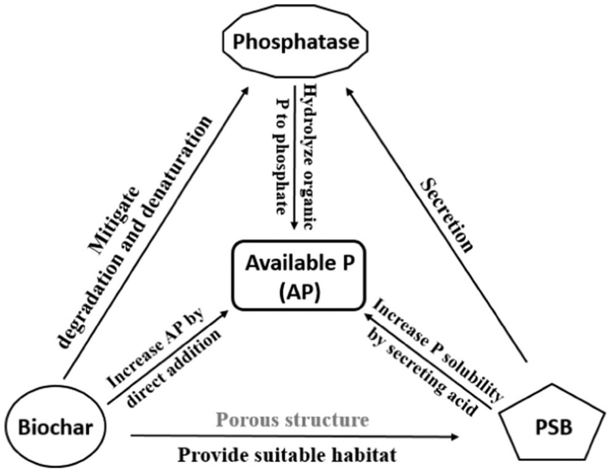

Fig. 4 Relationships among biochar, phosphate solubilizing bacteria, phosphatase enzymes, and phytoavailable phosphorus (reproduced from Zhang et al., 2019, with permission from the publisher).

4.3 Fungi

Despite the surplus investigations regarding synergistic effects of combined arbuscular mycorrhizal fungi inoculation and biochar application, little is known about the mutual interaction between biochar and other fungal genera. In a published study, biochar application (the high rate in particular) modulated the structure of fungal community in a yellow soil, southern China through inhibiting the growth of harmful pathogens, and stimulating the abundance of beneficial fungi (*Aspergillus, Mortierella, Spizellomyces, Penicillium and Fusarium*) (Zhang et al., 2022a). In a work by Sani et al. (2020), the high surface area of 400 °C timber waste biochar (1 045 m^2 g^{-1}) acted as a physical medium for stimulating hyphal growth and elongation of *Trichoderma* sp. toward colonization and proliferation in tomato roots for better uptake of P from Shallow Red Brown Terrace soil in Bangladesh (Sani et al., 2020). Besides, it was reported that holm oak-derived biochar (@480 °C) could enhance the activity of *Aspergillus niger* toward rock phosphate solubilization by increasing its capacity toward secretion of organic acids and immobilization of fluoride (F$^-$) released from rock phosphate during solubilization process (de Oliveira Mendes et al., 2014). This finding was also supported by a recent study, which concluded that biochar (derived from chicken feathers and corn straws) primarily motivated phosphate-solubilizing capacity of *Talaromyces pinophilus* fungi (by about 356%) through stimulating their ability to generate organic acids (citric acid in particular), rather than by enhancing strain biomass (Lu et al., 2025).

The combined interaction between biochar and P-solubilizing fungi to maximize the phytoavailability of P derived from biochar has been reported. The crucial effect of biochar on stimulating the performance of *Penicillium aculeatum* to improve P uptake by wheat grown under P limiting growth conditions (an acidic sandy loam soil with a 0.96 mg water-extractable P kg^{-1}) explained why this fungus had no significant effect without biochar application (Efthymiou et al., 2018). The mutual effect between *Penicillium aculeatum* and sewage sludge biochar (450 °C) relies on stimulating citrate production by the fungus strain, which chelated cations existed onto biochar (e.g., Ca, Fe and Al), and reduced P binding by these cations. Another report pointed out that sewage sludge biochar has a catalytic effect on P solubilization by *Aspergillus niger* through reducing the phytotoxic effect of potentially toxic elements derived from the rich P source ($AlPO_4$ and rock phosphate), and improving the fungus capability to produce organic acids (e.g., oxalic, citric, and gluconic acids) that can supply protons to react with phosphate minerals to liberate soluble phosphates (Rossati et al., 2023).

5 Biochar as a soil amendment for improving phytoavailability of legacy phosphorus

5.1 Inorganic phosphorus solubilization

The rhizospheric layer of soil contains a considerable amount of total P. Most of this P pool, however, is not readily available for uptake by plants since the concentration of phytoavailable orthophosphates (HPO_4^{2-} and $H_2PO_4^{-}$) is very low. Biochar has been adopted as an eco-friendly soil amendment to mobilize soil legacy P and maximize its phytoavailability in both of alkaline and acidic soils. Sequential fractionation technique had been adopted by Hedley and coworkers to evaluate P bioavailability/readiness to plants and soil microorganisms into: (i) H_2O–P, $NaHCO_3$–Pi, and $NaHCO_3$–Po fractions (the labile P pools), (ii) NaOH–Pi and NaOH–Po (moderately labile P pools), and (iii) HCl–P and Res–P (non–labile P pools) (Hedley and Stewart, 1982). It is thus of great importance to contextualize a soil management toolkit for modulating soil physicochemical properties based on data of soil P fractionation following biochar application (Table 1). In view of this, there is a growing interest toward soil biochar application to promote the interconversion of labile P fractions (Adhikari et al., 2019; Sui et al., 2022; Cao et al., 2023). According to Hu et al., biochar application increased soil labile–P content, and decreased both of moderately labile– and stable–P contents suggesting its key–role in maximizing availability of legacy P by stimulating activities of acid and alkaline phosphatase (Hu et al., 2023). In an incubation trial, The application of biochar (4% corn straw @ 400 °C) could regulate P fractions and enhance P phytoavailability under freezing–thawing cycles (Sui et al., 2022). Several long-term experiments have been undertaken to assess the beneficial role of biochar on soil health and P phytoavailability. Another long-term study pointed to the safeguard effect of biochar application on reducing total and dissolved reactive P losses from paddy field by 6.77%–17.62% and 6.22%–10.28%, respectively (Qi et al., 2023). Another 9-year field experiment pointed to favorable impact of biochar on reducing diffusion and release of P from rice basin into soil pore water, thereby minimizing the hazardous release of P into the hydrosphere (Chen et al., 2022a).

In saline–alkali soil, the higher salinity value enhances the degree of P fixation, leading to minimize P availability and vigority of plants. In a meta-analysis study, biochar application could enhance P phytoavailability in saline–alkali soils by 39.9% although it showed a minimal impact on soil pH value (Yuan et al., 2023). A short-term pot experiment showed that the reuse of P–laden biochars (four types of feedstocks modified *via* co–treatment of ball milling and Fe/Mn oxide) as a soil amendment in a coastal salinized fluvo–aquic soil (pH = 8.6) offered sufficient P requirements to sustain optimal growth of lettuce (Che et al., 2024). Biochar also plays pivotal roles in modulating inorganic P dynamics in calcareous soils. In view of this, the long-term application of biochar (20 Mg ha^{-1}) to Fluvo-aquic (6 years) and Cinnamon (5 years) calcareous soils led to increase P phytoavailability by 13.1%–49.1% due to stimulating biological mechanisms involved in activating alkaline phosphatase and enhancing the copy numbers of the phosphatase genes (*phoD*, *phoX*, and *nifH*) (Yuan et al., 2025). In another calcareous soil in Iran (11.34% $CaCO_3$ equivalency), cow manure biochar application increased proportions of labile and semi–labile pools but decreased proportions of moderately and stable pools as well as the activity of alkaline phosphatase (Nahidan and Ghasemzadeh, 2022).

The beneficial effect of biochar on stimulating the phytoavailability of legacy P in soil could be also related to its modulating effect on soil physicochemical characteristics (e.g., water holding capacity, pH value, cation exchange capacity and extractable cations) that would change diversity of soil microbial taxa (Mosa et al., 2020; Ahmad et al., 2021). Biochar application (chicken litter @ 10 Mg ha^{-1}) into an acidic soil increased total P, available P, inorganic P (soluble, Fe/Al–bound, redundant soluble and Ca–bound), and organic P fractions due to increasing soil pH, and reducing exchangeable acidity, exchangeable Fe and exchangeable Al (Ch'ng et al., 2014). A recent study indicated also that biochar exhibited a essential role in decreasing the high affinity between phytoavailable P and active soil components responsible for P fixation (Wang et al., 2023).

The extent of biochar's potential to modulate legacy P dynamics depends upon its feedstock source and pyrolysis temperature. According to Alotaibi et al. (Alotaibi et al., 2021), biochars derived from sewage sludge and chicken manure increased the readily bioavailable inorganic P by about 77% and 206%, and $NaHCO_3$–inorganic P by 200 and 188%, respectively relative to biochar originated from date palm residues that showed insignificant effect. Authors also concluded that $NaHCO_3$–inorganic P was higher in biochars

Table 1 Effect of biochar application on phosphorus fractions in different soil orders.

Soil order	Country	Soil texture	pH_b	$CaCO_3$ (%)	Phosphorus fractions before biochar application			Biochar treatments			pH_a	Phosphorus fractions following biochar application				Underling mechanism	Refer-ences
					P_S	P_O	P_{FA}	Feedstock material	Pyrolysis Temp.	Application rate		P_S	P_O	P_A	P_F		
Aridisol	Iran	Clay loam	7.7	8.5	2.7	24.7	9.4	Walnut	400 °C	2.5% 5.0% 10.0%	7.71 7.65 7.38	5.8 5.67 7.1	25 31.5 24.1	20.8 21.8 28.4		M1	[1]
			7.7	8.5				Almond	500 °C	2.5.0% 5.0% 10.0%	7.61 7.58 7.51	3.84 4.91 6.89	26.3 28.1 31.2	11.8 14.8 16.7			
Aridisol	Iran	Sandy loam	7.9	5.6	7.3	24.7	9.1	Walnut	400 °C	2.5% 5.0% 10.0%	7.77 7.74 7.67	5.1 8.88 9.6	29.1 29.6 38.1	12.8 18.7 27.8			
			7.9	5.6				Almond	500 °C	2.5% 5.0% 10.0%	7.84 7.81 7.70	6.2 9.1 8.89	31.2 35 37.1	9.3 13.2 18.2			
Aridisol	Egypt	Clay	7.59	–	0.73	12.86	31.78	Corn stover	350 °C	0.65%=6.5 g kg^{-1} 1.9% =19 g kg^{-1} 3.8%=38 g kg^{-1}	7.59 7.55 7.57	0.70 0.87 0.98	13.53 15.72 17.1	33.22 29.21 34.25		M2	[2]
Aridisol	Iran	Calcareous Clay loam	8.0	34.0	–	20.0	–	Sugarcane residues	400 °C	1% =25 Mg ha^{-1}	–	–	33	–	–	M3	[3]
	Iran	Calcareous Clay loam	8.0	34.0	–	20.0	–	Sugarcane residues	400 °C	1% =25 Mg ha^{-1} + phosphorus fertilizers addition	–	–	43.2	–	–		
Aridisol	USA	Acid clayey	4.52	–	–	12.1	–	Corn stover	650 °C	40 g kg^{-1}	5.4	–	28.4	–	–	M4	[4]
								Switch grass	650 °C	40 g kg^{-1}	5.11	–	22.2	–	–		
								Ponderosa Pin wood chips	650 °C	40 g kg^{-1}	4.78	–	17.1	–	–		
Aridisol	USA	Fine loamy Calcareous	7.9	4.05	–	8.4	–	Corn stover	650 °C	40 g kg^{-1}	8.36	–	22.1	–	–	M5	[5]
								Switch grass	650 °C	40 g kg^{-1}	8.20	–	20.2	–	–		
								Ponderosa pin wood chips	650 °C	40 g kg^{-1}	7.62	–	24.5	–	–		
Aridisol	Pakistan	Silty loam	8.17	10	–	13	–	Sugarcane bagasse	450 °C	1.5%= 15 g kg^{-1}	8.56	–	19.5	–	–	M6	[6]
								Rice husk	450 °C	1.5%= 15 g kg^{-1}	8.48	–	19.2	–	–		
								Wheat straw	450 °C	1.5%= 15 g kg^{-1}	8.59	–	16.2	–	–		

(*Continued*)

Soil order	Country	Soil texture	pH_b	$CaCO_3$ (%)	Phosphorus fractions before biochar application			Biochar treatments			pH_a	Phosphorus fractions following biochar application				Underling mechanism	Refer-ences
					P_S	P_O	P_{FA}	Feedstock material	Pyrolysis Temp.	Application rate		P_S	P_O	P_A	P_F		
Aridisol	Pakistan	Silty loam	8.08	10	–	13	–	Acidified Sugarcane bagasse	450 °C	1.5%= 15 g kg^{-1}	8.1	–	14.1	–	–	M6	[6]
								Acidified rice husk	450 °C	1.5%= 15 g kg^{-1}	8.2	–	15.5	–	–		
								Acidified wheat straw	450 °C	1.5%= 15 g kg^{-1}	8.13	–	11.89	–	–		
Aridisol	Egypt	–	7.72	–	–	0.078	–	Citrus wood acidified biochar	–	5 t ha^{-1} 10 t ha^{-1}	7.52 7.83	–	598 670	–	–	M7	[7]
Aridisol	China	Clay loam	7.76	–	–	92.4	–	Maize straw	700 °C	2%= 5 g kg^{-1}	8.2	–	139.8	–	–	M8	[8]
Aridisol	China	Clay loam	7.76	–	–	92.4	–	Ball-milled maize straw biochar	700 °C	2%= 5 g kg^{-1}	8.4	–	172	–	–	M9	[9]
Aridisol	Pakistan	Silty loam	7.05		–	29.6	–	Tea camellia	350 °C	1%	7	–	31	–	–	M10	[10]
									600 °C		7	–	31	–	–		
								Tea camellia loaded with *Bacillus cereus*	350 °C	1%	6.9	–	37	–	–		
									600 °C		6.9	–	38	–	–		
Aridisol	Pakistan	Loamy	8.34	3.1	–	1.9	–	Woody sawdust	350 °C	1%	–	–	17.2	–	–	M11	[11]
								Biogass	350 °C	1%	–	–	15.5	–	–		
Aridisol								Woody sawdust +PSB	350 °C	1%	–	–	18.73	–	–		
								Biogass+PSB	350 °C	1%	–	–	16.41	–	–		
Aridisol	Multan	Fine silty	8.5	–	–	21.1	–	Rice straw Rice straw+PSB	450 °C	2%	8.57 8.69	–	24.2 26.1	–		M12	[12]
Oxisols	Brazile	Clay	4.8	–	2.19	4.67	27.3	Poultry litter	500 °C	–	–	12.9	24.4	96.1		M13	[13]
Ferralsols	China	Loamy	5.2	–	4.56	87.6	–	Corn stalk	500 °C	5 g kg^{-1} 20 g kg^{-1}	5.4 6.56	1.53 1.59	56 79	215 223	378 375	M14	[14]
Ferralsols	China	Loamy	5.2	–	4.56	87.6	–	Mg/Al modified Corn stalk Fe/Al modified corn stalk	500 °C	5 g kg^{-1} 20 g kg^{-1} 5 g kg^{-1} 20 g kg^{-1}	5.5 5.99 5.49 5.97	1.48 1.5 1.46 1.41	40.1 20.09 35.8 23.8	363 321 242 276	375 380 394 380		
Cambosol	China	–	7.4	–	–	15.9	–	Maize stover	500 °C	2.63 t ha^{-1}	–	–	27.26	56.7	87.4	M15	[15]

(*Continued*)

Soil order	Country	Soil texture	pH_b	$CaCO_3$ (%)	Phosphorus fractions before biochar application			Biochar treatments			pH_a	Phosphorus fractions following biochar application				Underling mechanism	Refer-ences
					P_S	P_O	P_{FA}	Feedstock material	Pyrolysis Temp.	Application rate		P_S	P_O	P_A	P_F		
Ultisol	China	–	4.61	–	–	8.2	–	Rice straw	350 °C	50 g kg^{-1}	4.67	–	11.1	29.9	101.1	M16	[16]
									550 °C		4.92	–	10.5	34.5	103.2		
								Canola straw	350 °C	50 g kg^{-1}	4.75	–	11.3	33.8	79.2		
									550 °C		4.70	–	11.7	38	71		
Ultisol	China	Silty clay	4.22	–	–	8.8	–	Chicken manure	400 °C	–	4.73	6.1	22.9	99.8	155.4	M17	[17]
Ultisol	Malysia	Sandy loam	4.29	–	–	4.2	–	Chicken litter	550 °C	20 t ha^{-1}	–	541.5	820	210.7	515.5	M18	[18]
Ultisol	China	Clay loam	5.4	–	0.56	8.68	–	Rice husk	450 °C	1% 2%	5.4 5.5	0.83 1.1	59 59.1	128 130	567 561.3	M19	[19]
								Bamboo	450 °C	1% 2%	5.48 5.5	1.1 1.8	59.09 59.1	162 171.3	574 560		
								Deciduous tree leaves	450 °C	1% 2%	5.79 6.2	2.5 2.81	49.2 47.5	205 235.4	540.07 599		
								Reeds	450 °C	1% 2%	5.6 5.7	0.97 1.4	68.89 70.04	223.4 271	549.98 550		
								Rice Straw	450 °C	1% 2%	5.6 5.8	1.09 2.12	77 87	242.6 263	567.7 560.07		
Alfisols	China	Silt loam	6.2	–	1.4	5.09	–	Rice husk	450 °C	1% 2%	6.2 6.62	1.91 3.15	82.4 82.3	239.9 247.3	383 388.5	M20	[20]
								Bamboo	450 °C	1% 2%	6.3 6.39	2.09 3	82.4 83.1	265 264.96	389 391		
								Deciduous tree leaves	450 °C	1% 2%	6.8 7.3	2.1 2.2	80.1 79.89	261 262	369 350.5		
								Reeds	450 °C	1% 2%	6.4 6.49	2.26 3.15	89.1 90	274.3 289.2	380.6 400		
								Rice Straw	450 °C	1% 2%	6.42 6.5	3.1 7.8	98.9 110.1	326 368	402.2 450.33		
Mollisols	China	–	6.82	–	7.1	19.51	74	Corn straw	400 °C	1% 2% 4%	7 7.4 7.6	21 47.2 100.1	43.07 84.51 161.43	79.1 88.6 92.8		M21	[21]

(*Continued*)

Soil order	Country	Soil texture	pH_b	$CaCO_3$ (%)	Phosphorus fractions before biochar application			Biochar treatments			pH_a	Phosphorus fractions following biochar application				Underling mechanism	References
					P_S	P_O	P_{FA}	Feedstock material	Pyrolysis Temp.	Application rate		P_S	P_O	P_A	P_F		
Anthrosols	China	Silty clay loam	6.58	–	–	16.7	–	Wheat straw	400 °C	20 t ha^{-1} 40 t ha^{-1}	5.63 6.14	–	22.4 28.9	–		M22	[22]

pH_b: pH before biochar application; **pH_a**: pH after biochar application; **P_S**: Soluble-P (mg kg^{-1}); **P_O**: Olsen-P (mg kg^{-1}); **P_{FA}**: Fe/Al-P (mg kg^{-1}); **P_A**: Al-P (mg kg^{-1}); **P_F**: Fe-P. **M1**: There was a noticeable reduction in soil pH values following biochar application; This pH reduction led to transform significant amounts of Ca-P fraction into exchangeable and Fe/Al fractions and maximized the release of phytoavailable P. **M2**: An obvious increase in phytoavailable P, which directly derived from biochar application; Biochar application increased soil organic matter content and microbial colonization. **M3**: Olsen-P increased due to the reduction of Ca^{2+} and Mg^{2+} cations via immobilization process; Biochar showed a stimulating effect on microbial community. **M4**: Biochar application caused an increase in soil acidic pH and point of zero net charge, which caused an increase in soil P availability; A significant increase was recorded in soil surface area, CEC and C/N ratio. **M5**: Biochar application caused a reduction in point of zero net charge as well as noticeable increases in CEC, surface area and available *P* values. **M6**: There was an increase in soil pH, which in turn modulated P availability in soil; The release of humic acid might compete with p ions for exchange soil sites; A stimulating effect on phosphate solubilizing bacteria, which showed a functional role in increasing P availability; Maintaining enzymatic activity via protecting soil enzymes from proteolysis and denaturation. **M7**: A reduction in soil pH, which led to enhance organic P mineralization and legacy P solubilization. **M8**: Increasing organic matter and CEC due to the high mineral ash content in biochar, O-functional groups, newly formed P-functional groups, which increased sorption capacity of biochar for metal ions and its stable organic carbon; Increasing soil pH value due to cations existed in biochar and the alkaline O-functional groups; The high P content derived from biochar. **M9**: Increasing organic matter and CEC of soil due to the high mineral ash content in biochar, O-functional groups, newly formed P-functional groups, which increased sorption capacity of biochar for metal ions and its stable organic carbon; Increasing soil pH value due to cations existed in biochar and the alkaline O-functional groups; The high P content derived from biochar. **M10**: Stimulating microbial colonization to the high porosity of biochar, which supported microbial colonization; The high porosity of biochar supported water retention and protected microorganisms in soil from desiccation; Increasing soil microbial biomass and microbial enzymatic activities, which catalyzed mineralization of organic P; Stimulating colonization of rhizobacteria, which increased phytohormones production and P phytoavailability. **M11**: Stimulating microbial community, which improved P availability via producing certain bioactive compounds (e.g., Indol-3 acetic acid (IAA), gibberellin and cytokinin). **M12**: Biochar stimulated the activity of phosphate solubilizing bacteria, which led to maximize P Phytoavailability via secretion of organic acids in soil. **M13**: The liming effect of biochar and the increment of CEC. Minimizing the affinity between available P and soil constitutions responsible for P fixation; The synergistic effect between loaded Mg and P. **M14**: Increasing soil pH of the acidic soil. Increasing soluble and Ca (hydro)oxides bounded P instead of Fe–P or Al–P through biotic pathways; Biochar's microporous structure favored P binding against leaching; Pristine biochar slightly reduced content of Al–P in lateritic red soil, while metal oxide biochar increased it; Stimulating phosphate solubilizing bacteria. **M15**: A reduction in soil acidity after biochar application due to biochar alkalinity. Consequently, a reduction in P precipitation with Fe/ Al and Ca. **M16**: Organo-mineral complexes formation following rising soil pH value participated in reduction of phosphorus fixation by acidic soil constitutions; Stimulating soil microorganisms' activity, which contributed in mineralization of organic P compounds. **M17**: Increasing soil pH value after biochar addition, which increased P availability; Increasing the abundance of negatively charged surfaces of soil, which increased repulsion forces of phosphate anions by soil particles. **M18**: An increase in soil pH, which led to reduce soil exchangeable acidity and transformed Fe and Al ions to insoluble hydroxides; Organic acids derived from biochar led to chelate Fe and Al ions into stable forms. **M19**: The slight increase in soil pH led to precipitation of free Al^{3+} and Fe^{3+} ions, and most of P trapped with Fe/Al oxides was released and redistributed in labial P pools. **M20**: A significant increase in soil pH to precipitation of free Al^{3+} and Fe^{3+} in soils and most of P trapped with Fe /Al was released and redistributed in labial P pools. **M21**: Increments in soil pH and soil organic matter content; Freezing-thawing cycle contributed in increasing P availability via soil aggregate fragmentation; Biochar accelerated transforming of different P fractions to the available form ($NaHCO_3$-P). **M22**: Phosphorus availability increased due to increasing soil pH; Enhancing soil microaggregate structure and stability; Accumulation of high amount of organic P in macro and microaggregates; Increasing microbial enzymes activity and mycorrhizal associations. **References**: [1] Hemati Matin et al., 2020; [2] Amin, 2018; [3] Motaghian et al., 2020; [4] Chintala et al., 2014; [5] Chintala et al., 2014; [6] Qayyum et al., 2021; [7] Abd El-Mageed et al., 2020; [8] Zhang et al., 2022; [9] Zhang et al., 2022; [10] Azeem et al., 2021; [11] Rafique et al., 2017; [12] Ali et al., 2020; [13] Lustosa Filho et al., 2020; [14] Peng et al., 2023; [15] Cao et al., 2020; [16] Yang and Lu, 2022; [17] Kamran et al., 2019; [18] Ch'ng et al., 2017; [19] Hong and Lu, 2018; [20] Hong and Lu, 2018; [21] Sui et al., 2022; [22] Zhang et al., 2020.

pyrolyzed at temperatures less than 700 °C. In Sui et al.'s work, raising pyrolysis temperature converts the labile P fraction into less labile forms since the high alkalinity and surface area values of high temperature-pyrolyzed biochar would increase precipitation/fixation of labile P forms (Sui et al., 2022). Other pyrolysis parameters (e.g., heating rate and residence time) would also affect the efficacy of biochar toward modulating soil P fractionation (Adhikari et al., 2019).

Biochar also exhibits an important role in reducing P losses from soil matrix and stimulating microbially driven P dynamics in paddy soil, and the application rate was crucial in this concern. In a study by Wang et al. (2022d), reed–biochar application (1%–8% w:w) diminished leaching losses of soil P due to enhancing the abundance and diversity of soil *phoD*–harboring microbes (Wang et al., 2022d). Authors also added that the application rate of 4% was the optimum application rate in this regard from an economic point of view. In another study, $NaHCO_3$−P pool increased, and the residual–pool decreased as the application rate of *Conocarpus* waste biochar (pyrolyzed at 400 °C) increased from 0 up to 5% (Akanji et al., 2022).

Despite the beneficial effects of biochar on improving P phytoavailability, it has also several drawbacks and cons that need to be considered prior to its widespread application. The literature pointed to significant declines in P availability in alkaline (Li et al., 2020), calcareous (Chintala et al., 2014) and saline–sodic soil (Xu et al., 2016b). In a field study carried out in Iowa, USA, hardwood biochar application alongside with composted manure caused a noticeable decline in P availability (Biederman et al., 2017). Another long–term investigation (10 years) pointed out that biochar application at different rates (4.5–45.0 Mg ha^{-1} yr^{-1}) led to increase orthophosphates fixation and reduction in fluxes of rhizospheric P by about 11.6%–79.0% (Yuan et al., 2024) .This is mainly associated the increase in soil pH value and the alteration in redox status of Fe and S due to the decline in dissolved oxygen contents in the rhizosphere.

5.2 Organic phosphorus mineralization

Phosphorus exists in soil in two broad chemical forms: (i) inorganic P comprising soluble, sorbed and precipitated orthophosphates; and (ii) organic P, wherein P atoms are covalently bonded to carbon in multiple forms, including direct linkage (P–C), and indirect linkage *via* phosphoester (P–O–C) and phosphodiester (C–O–P–O–C) (McLaren et al., 2020). The relative amount of organic P in soil varies greatly according to pedogenesis and land use (20%–80% of the total P content in soil) (Reusser et al., 2023). Ions of phosphate are released into the soil solution following the mineralization of organic P compounds by multiple ways, including phosphatases (e.g., phytate by phytase), hydrolysis of polyphosphates, biological/biochemical mineralization of soil organic matter and liberation of inorganic P existed in plant cells during organic matter decomposition (Raguet et al., 2023). The thermochemical conversion of organic biomass into biochars leads to convert less phytoavailable organic P compounds into higher phytoavailable inorganic forms (orthophosphates and potassium/calcium/magnesium pyrophosphates) (Mousavi et al., 2023) (Fig. 5).

Biochar has the potential to modulate soil P cycling in soil. To date, however, the impact of biochar application on organic P mineralization in the soil is still unclear. It was used as a soil amendment to mitigate losses of soil organic P and avoid water eutrophication. In view of this, lanthanum modified biochar showed a good sorptivity (2.836 mg g^{-1}) to organic P (Zhao et al., 2022a). Following organic fertilization, the *phnF* gene was dominant factor to promote the mineralization of Or-P, because it encodes Csingle bondP lyases that pyrolyzes the Csingle bondP bounds in organophosphate esters. Overall, organic fertilization decreased P release risk in soil aggregates, especially for the micro-aggregates that showed a higher capacity to activate non-available P and immobilize endogenous P in farmland soil. Besides, the capability of biochar to restructure the formation of soil matrix reinforces its potentiality to serve as a promising soil amendment to alleviate the high affinity between organic P and soil minerals that prevent the mineralization of soil organic P (Lizcano-Toledo et al., 2021). According to Tian et al.'s work, biochar application (derived from rice straw) could enhance the production of acid/alkaline phosphomonoesterase, phosphodiesterase and organic P mineralization (Tian et al., 2021). The study also concluded that biochar application under low inputs of P supports a more organized *phoD* gene community and stimulated the activity of microbial taxa (*Micromonosporaceae*, *Chitinophagaceae*, *Oxalobacteraceae*, *Nitrosomonadaceae* and *Streptomycetaceae*) linked in soil organic P mineralization. Another investigation highlighted the high efficiency of poultry litter biochar utilization as a soil amendment to phytate–utilizing bacteria in a grey brown podzolic soil (Deinert et al., 2024). Biochar exhibits less efficiency in organic P mineralization in saline–alkali soils. For example, raw rice straw (applied at 9.0 Mg ha^{-1}) was more efficient than its derived biochar (applied at 8.0 Mg ha^{-1}) in favoring the abundance of some *phoD*–harboring bacteria in a saline–alkali paddy soil (Fei et al., 2023). Likewise, the content of soil microbial biomass P was higher with the application of superphosphate or raw rice straw than that of the biochar application (rice straw pyrolyzed at 400–500 °C) in a Salic Fluvisol developed from Loess Plateau (Wu et al., 2021). In a 3-year field, however, available P content was greater with biochar application (particularly in its high application rate of 3.6 Mg carbon ha^{-1}) as compared with its

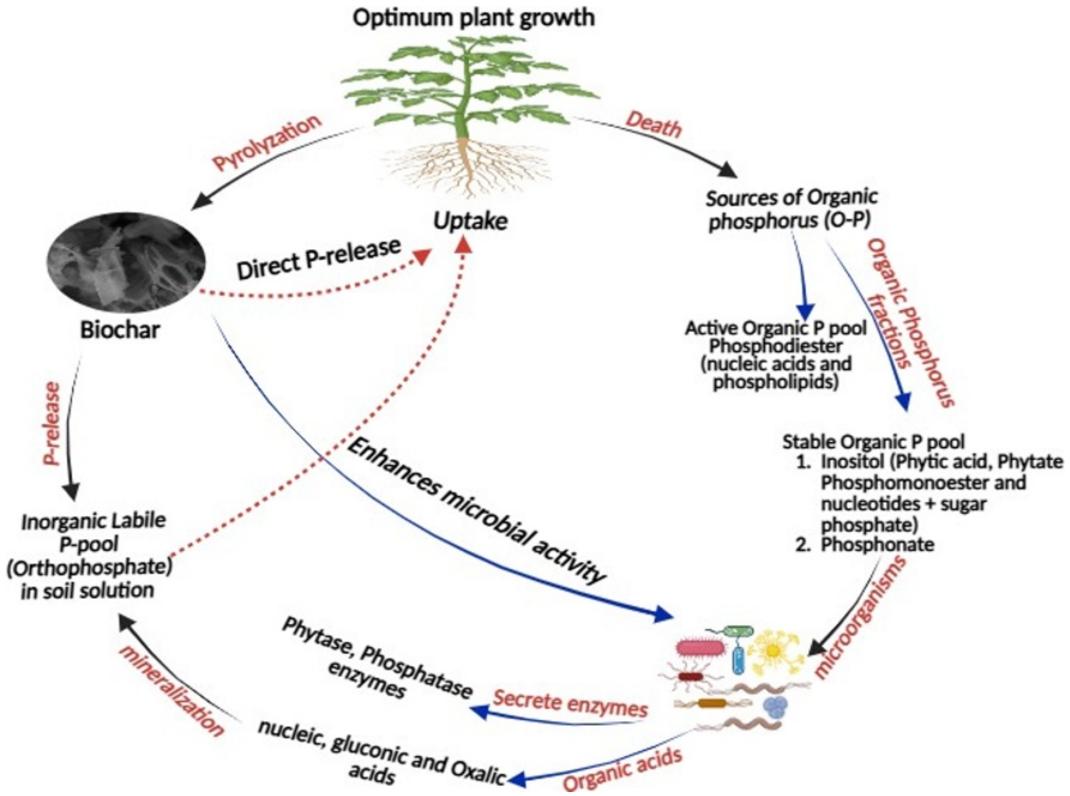

Fig. 5 Role of biochar in organic phosphorus forms transformations.

straw application. This finding highlights the relatively longer time required for organic P mineralization in saline–alkali soils. Functionalized biochar (Fe–doped 600 °C rice straw biochar), however, recorded higher efficiency in promoting organic P mineralization by *phoD*–harboring bacteria in saline–alkaline paddy soil (Liu et al., 2023a). In a saline–alkali in China, the effect of combining *Phragmites australis*-based biochar (@ 400 °C) with different P fertilizers forms (potassium dihydrogen phosphate, calcium phosphate and pig manure) was studied (Hou et al., 2024). Biochar application enhanced soil labile organic P content (phospholipids and nucleic acids), which poses high potential for mineralization and utilization by plants. Besides, the secretion of phosphatase by P–solubilizing microorganisms involved in mineralization of organic P. Biochar possesses less profound impacts on phytoavailability of P in alkaline and/or calcareous soil taking into consideration the alkaline nature of biochar. Therefore, biochar functionalization is urgently needed to be tailored to such soil conditions. For example, Ahmed et al. (2021) carried out a pot experiment to study the effect of acidified biochar application on soil P availability in a calcareous soil in Iran. Results show that the highest organic P content was recorded with green waste biochar with 75% P application and the lowest value was recorded with acidified corncob biochar with 100% P application rate.

6 Phosphorus–enriched biochar as a slow released phosphorus fertilizer

Excessive amounts of P fertilizers are added seasonally to replenish orthophosphates consumption. Nevertheless, after being applied, orthophosphate ions are transformed into insoluble forms following interaction with soil components (e.g., calcium compounds in alkaline soils and Fe/Al (oxyhydr)oxides in acidic soils), resulting in minimizing P use efficiency up to 10%–25% (Wang et al., 2024a). What is worst, excessive application of P fertilizers might suppress the activity of beneficial microorganisms, increase soil salinity values and cause eutrophication (Cui et al., 2020; Wang et al., 2021b).

Several investigations highlighted the potential utilization of biochar as a slow–released source of P. These methods depend upon using either pre– or post–loading methods for enhancing P content in biochar to sustain plant nutrients requirements upon its soil application. This section will summarize different techniques for developing P–enriched biochars to be used as a as a slow released P fertilizer.

6.1 Phosphate loading during the thermochemical conversion process

Phosphorus loading during the thermochemical conversion process can sustain plant's P requirements in P–deficient soils, especially those having low pH values. In Zimbabwe, nonreactive Dorowa phosphate rock was mixed with maize residuals and pyrolyzed at 450 °C to generate a suite of biochar–based fertilizer. The functionalized form yielded biochar with a 30% increment in its citric–soluble P relative to the original form. Besides, the functionalized biochar yield was greater by about 26% and retained more carbon by about 43% as compared with the original form. In another study, the co–pyrolysis of phosphatic fertilizer (triple superphosphate and bone meal) with organic biomass (sawdust and switchgrass) during the thermochemical conversion process produced an effective slow–released phosphatic fertilizer since the $Ca(H_2PO_4)_2$ reacted with carbonaceous materials to form $C–O–PO_3$ or C–P (Zhao et al., 2016). Another investigation suggested that the presence of bentonite with cotton straw during pyrolysis process could encourage the optimum interactions between phosphates and biochar for producing an efficient slow–released phosphatic fertilizer (An et al., 2020). Another acidified slow–release P fertilizer was developed by pyrolyzing (@ 300 °C) mixtures of low–grade phosphate rock, coffee husk, magnesium (Mg) and inorganic acids (H_2SO_4, HCl, and HNO_3) (de Morais et al., 2023). Acidulated fertilizers exhibited low pH value with a high potential to enhance solubilization of phosphate rock and the incorporation of Mg slowed the release of P from fertilizers. Besides, biochar incorporation maximized the wettability of the modified fertilizer allowing higher extraction of phytoavailable P. Hydrothermal carbonization technique was also tested to produce P–loaded hydrochar. In (Daer et al., 2024), co–hydrothermal carbonization of corn straw with phosphate rock @ 180–240 °C resulted in generation of acidic solution and humic acid–like substances which in turn reduced the crystallinity of rock phosphate to be more easily dissolved and maximized the abundance of $C–O–PO_3$, $C–PO_3$, C=O, and O=C–O chemical bonds. A 15%–15% N–P slow-release fertilizer was also produced and showed a slow–released supply of N and P for optimal nutrition of maize grown on Ultisol (Barbosa et al., 2022). To produce this N/P–slow-release fertilizer, P–enriched biochar was first generated through pyrolyzing phosphoric acid–impregnated poultry litter at 500 °C; thereafter, the generated P–enriched biochar was loaded with urea.

6.2 Biochar as a coating material for phosphorus fertilizers

Due to the high functionality of biochar, it has been utilized as a carbon–based coating material to mineral phosphatic fertilizers to control P diffusivity in the fertosphere zone (the fertilizer granule region). This technique provides a protective layer to avoid the direct interaction between phosphatic fertilizers and soil matrix leading to reduce orthophosphates fixation. Besides, this protective layer could enhance the use efficiency of phosphatic fertilizers through reducing the fast release of orthophosphates. Pogorzelski and coworkers carried out a kinetic test to assess P release rate from ordinary and biochar–coated fertilizer and found a significant decline with the coated form relative to the ordinary fertilizer (92% vs. 36%) (Pogorzelski et al., 2020). Besides, the agronomic study showed an enhancement by about 20% in P uptake with biochar–coated fertilizer given the improvement of its use efficiency. Cellulose/engineered biochar–coated triple superphosphate was developed by Kassem and coworkers and showed a reduction of P leaching by about 43.90% with a significant increase in its crushing strength (30.29%) relative the uncoated superphosphate (Kassem et al., 2022). As well, a recent study illustrated that triple superphosphate coated with biochar derived from olive pomace and macroalgal residues minimized P release up to 67% and 78% relative to 82% with the commercial biochar and 100% with the uncoated fertilizer (Poirier et al., 2025). In another study, slow released P fertilizers were prepared by either mixing or coating triple superphosphate with biochar (da Silva et al., 2024). Results of this study concluded that coating technique resulted in a lower values of P release and higher cumulative release at the end of the experiment relative to the mixing technique. A new class of slow–release P fertilizers was further developed by An and coworkers *via* co-pyrolysis and co-polymerization of cotton straw, $Mg_3(PO_4)_2$ bentonite and sodium alginate (An et al., 2021). This coated fertilizer exhibited a high P utilization efficiency (75.8%) and high water–retention capacity, which improved vegetative growth parameters of pepper seedlings.

6.3 Post-pyrolysis phosphate loading to produce phosphorus-enriched biochar

Phosphorus–laden biochar has been adopted in several lab-scale experimentations as a rich–P organic source (Mosa et al., 2018; Pei et al., 2021; Ai et al., 2023). Based on findings provided by Li et al., pristine biochar application (maize stalks produced at 350 and 600 °C) led to a decrease in P availability of soil due to the high binding of P onto organo–mineral complexes of soil–biochar; however, P–laden biochars (immersed into saturated solution of KH_2PO_4 for 24 h) showed excellent performance for maintaining soil available P as compared with mineral phosphatic fertilizers (Li et al., 2020). Another study indicated that P content in P–laden–ball–milled Ca–loaded biochar showed a high bioavailability (86.7%) and low leaching potential (3.3%) to be considered as a promising slow–released phosphatic fertilizer (Ai et al., 2023). Concentrated seawater (a byproduct generated from seawater desalination) was also exploited for biochar functionalization due to its rich inorganic salt resources. In (Wang et al., 2024b), peanut shells biochar (@ 600 °C) was functionalized using concentrated seawater and the engineered biochar was utilized for recovery of phosphate from aqueous solutions. Phosphate–laden biochar showed significant effect for improving germination and vegetative growth rate of wheat and proved a high potential as a slow–release P fertilizer. Recently, P−loaded biochar has been tested as a partial substation of P fertilizers (Luo et al., 2024). Results of this study illustrated that biochar incorporation with only two-thirds of recommended superphosphate was more efficient than the control treatment (full dose of superphosphate) for improving soil health and enhancing vegetative growth characters and productivity of peanut.

7 Effect of biochar application on reducing phosphate runoff from soil matrix

Agricultural runoff is an important pathway in P losses from soil matrix leading to release of excessive P amounts in the hydrosphere that often ends in local watersheds where it might cause water eutrophication (Barcellos et al., 2019). As such, P release from China's rural agriculture is three folds of that generated from industrial emissions, and it contributes by about 67.97% of P pollution sources in Yangtze River Basin (2.3 and 34 folds of that generated from domestic and industrial sources, respectively) (Hui et al., 2024). Another report pointed out that P emitted from agricultural nonpoint sources in China at the end of 2017 was 21.2 million tons, accounting of about 67.2% of the total P release (Ministry of Ecology and Environment of the People's Republic of China, 2019). Several studies reported the beneficial effects of biochar on reducing soil erosion and P runoff, due to its high porosity and water sorption capacity that would reduce runoff and soil losses (Table 2). Zhang et al. reported an increment of P retention in soil matrix by about 16% following the application of hardwood biochar (@ 5% w:w; pyrolyzed at 720 °C) (Zhang et al., 2016). In yet another column investigation, 1% application of 720 °C *Erythrina arborescens* biochar reduced the cumulative PO_4^{3-}—P in the leachate by about 12.9% relative to the control treatment (Nan and An, 2022). Corn straw biochar application proved also a high efficacy in modulating surface/underground erosion and reducing total P flow into groundwater through bedrock fissures (Yin et al., 2023). In a 30–min simulated rainfall experiment, runoff of field plots amended with biochar at 5 Mg ha^{-1} contained significantly less ortho–P relative to the unamended ones given the enhancement of microaggregate stability, water holding capacity, and water infiltration within soil matrix (Sachdeva et al., 2019). In another field experiment, 500 °C wheat straw biochar application @ 24.0 Mg ha^{-1} to an acidic soil under double–rice cropping system reduced runoff flow–weighted total P by about 42.1% due to the microbial regulation in the charosphere (Wang et al., 2021a). Biochar was also exploited to maximize stormwater retention and immobilize P against runoff. In the study of Goldschmidt and Buffam, commercial biochar application to extensive green roof substrate improved the quality of runoff water by decreasing the release of P (Goldschmidt and Buffam, 2023).

The release of P from engineered biochar was also taken into consideration in literature to avoid any potential release into the hydrosphere. In the study of Krishnamoorthy et al. (2023), phosphate leaching from biochars derived from canola straw, wheat straw, sawdust and manure pellets was negligible (<1 mg L^{-1}), in which manure pellets biochar was the highest and sawdust was the lowest in correspondence with their constitutions of ash content. Authors also clarified that the release of phosphate from biochar decreased as the pyrolysis temperature increased from 300 up to 500 °C given the transformation of labile P into more recalcitrant/stable forms. In view of that, an earlier study demonstrated that pyrolysis of manure and plant wastes at 350 °C resulted in conversion of phytate to inorganic P (Uchimiya and Hiradate, 2014). Meanwhile, inorganic orthophosphate (PO_4^{3-}) showed persistence in manure biochars when raising pyrolysis temperature above 500 °C; however, pyrophosphate ($P_2O_7^{4-}$) persisted at pyrolysis temperatures above 650 °C. Consequently, it seems that pyrolysis process could efficiently convert inherent P into bioavailable slow–released P fertilizers. For instance, the high pyrolysis temperature of sewage sludge could stimulate the transformation of non–apatite inorganic P into higher phytoavailable apatite inorganic P (Liu et al., 2021). This study also concluded that alterations of environmental conditions such as raising ionic strength, domination of SO_4^{2-} anions, and modulation of pH value could increase the release of inherent phosphate existed in biochar.

8 Role of biochar in maximizing phosphorus uptake and its use efficiency

Biochar has been emerged as an attractive amendment, especially in low fertile soils, to modulate soil physicochemical properties and maximize nutrients use efficiency (particularly phosphatic fertilizers) to meet food security. A meta-analysis of 108 pairwise comparisons concluded that biochar could act as a short-, mid-, and long-term source for P supply with a potentiality to maximize P availability in soil by about 4.6 folds depending upon the feedstock source (sludges in

Table 2 Effect of biochar application on minimizing phosphorus losses from soil.

Location	**Soil properties**		**Biochar engineering**			**Reduction in P losses**	**Mechanisms**	**References**
	Soil pH	**Soil available P (mg kg^{-1})**	**Feedstock**	**Pyrolysis Temp. (°C)**	**Application rate**			
Hunan Province, China	5.8	40.95	Rice straw	500	1.5 Mg ha^{-1}	39.9%−48.8%	-Enhancement of P retention in soil due to the high functionality of biochar.	Zhang et al., 2021
Zhejiang Province, China	7.31	16.25	Rice straw	350−500	1.0% (w:w)	21.92%−25.21%	-Enhancing enzymatic activity and microbial community composition leading to P reservation in soil. -Biochar aging increased its surface area, active functional groups and porosity.	Zhao et al., 2023
Xinjiang Uygur Autonomous Region, China.	7.8	3.27	Cotton straw	600	500 and 1000 kg hm^{-2}	14.8%−64.4%	-The large number of active functional groups existed onto biochar surfaces improved the sorptivity of phosphate ions. -Biochar application led to improve soil structure and weakened soil erosion by rainwater, leading to minimize P losses in runoff.	Li et al., 2022
Changsha, China	6.27	16.50	Reed	−	1%−8% (w:w)	5.3%−13.3%	-The large surface area and abundant functional groups.	Wang et al., 2022b
Hunan Province, China	5.1	9.17	Wheat straw	500	24 and 48 t ha^{-1}	32.4% and 42.1%	-The strong P sorption capacity of engineered biochar.	Wang et al., 2021
Guizhou, China	6.2	−	Corn straw	400	30−60 t ha^{-1}	12%−28%	-Biochar's surface functionality exhibited abundance of oxonium, pyridine, and proton aromatic structures. -The anion exchange capacity of biochar favored phosphate binding. -The high contents of Fe, Al, Ca, and Mg in the ash content of biochar could bind phosphate groups by precipitation or cation bridges.	Yin et al., 2023
Chinese Loess Plateau	6.2	−	Coconut shells	−	0.1%−1.0% (w:w)	22.90%−43.01%	-Improving water holding capacity of soil and inhibiting transport of phosphate loaded onto soil particles. -The unique structural properties of nano biochar.	Chen and Zhou, 2021

particular), pyrolysis temperature (< 600 °C) and application rate (>10 Mg ha^{-1}) (Glaser and Lehr, 2019). This study also concluded that soil pH value showed a significant role for valuating biochar impact on plant–P availability: 5.1 folds in acidic soils (pH < 6.5), 2.4 folds in neutral soils (pH 6.5–7.5), and insignificantly affected alkaline soils (pH > 7.5). In another meta-analysis investigation (516 data pairs from 86 studies), soil biochar application significantly affected phytoavailability and uptake of P by about 65 and 55%, respectively, in which manure feedstock, pyrolysis temperature of 300 °C, soil pH less than 5.0 and deficient P soils having a fine texture are the most significant criteria in this regard (Tesfaye et al., 2021).

In this review, we collected data from 57 recent studies comprising 148 values of P use efficiency as affected by feedstock type, pyrolysis temperature and application rate (Fig. 6). In general, biochar application caused a considerable increase in PUE relative to the unamended soils (43.36 vs. 20.26%). The feedstock type showed a significant effect on PUE being biochars derived from manures/sludges and crop residuals were comparable (approximately 38%) and those derived from woody wastes recorded 29.10%. The low PUE of woody materials derived biochar was also matched with the meta–analysis study of Glaser and Lehr (2019), which concluded that wood biochar is not the ideal candidate for utilization as a feedstock given its low inherent P content and its minimal efficiency to liberate legacy P from soil. In addition, the effectiveness of biochar application on improving PUE varies greatly according to pyrolysis temperature: 21.7, 60.1, 33.4, 37.8, 18.1 and 9.4% for biochars pyrolyzed at temperatures of < 300, 300–399, 400–499, 500–599, 600–699 and >700 °C, respectively. Besides, the application rate of biochar significantly affected PUE, in which the rate of 11–20 Mg ha^{-1} was the superior application rate (88.1%) and the application rate below 1.0 Mg ha^{-1} exhibited the lowest value of PUE (29.9%).

Several studies recommended utilization of manures and sludges as a feedstock material for enhancing the efficacy of

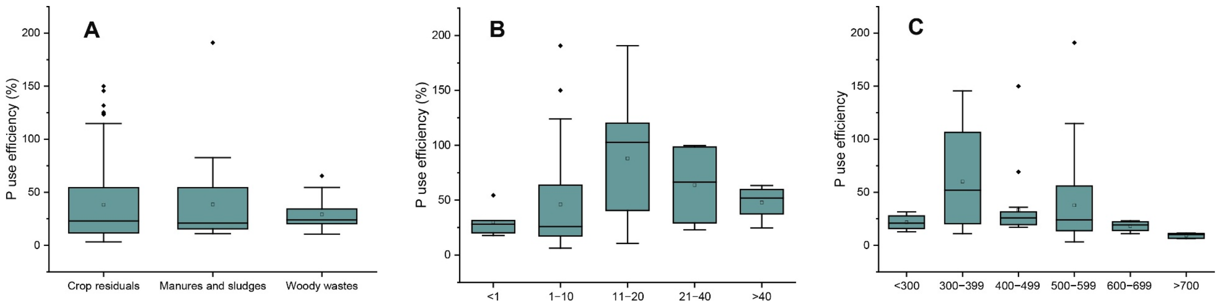

Fig. 6 Effect of biochar application on P use efficiency in soil (%): (A) effect of feedstock type, (B) effect of application rate, and (C) effect of pyrolysis temperature. Data were extracted from 57 recent investigations comprising 148 values. Box charts are presented by mean (dot), median (center line), lower quartile (the lower borders of the box), upper quartile (the upper borders of the box), and whiskers-error bars (the minimum and maximum observations).

biochar to improve PUE. In view of that, the application of chicken litter biochar @ 500 °C to an acidic soil (*Typic Paleudult*, pH= 4.29) increased P concentration in maize leaves by about 68.8 and 7.4% relative to unamended and compost amended treatments, respectively (Ch'ng et al., 2017). Moreover, chicken litter biochar increased PUE relative to the unamended treatments (72.3%), and compost amended treatments (26.1%). Authors attributed this increment of P uptake and its use efficiency to the high content of inherent P in biochar (5.7 times greater than its content in pineapple compost) and its modulating effect on soil pH, which increased up to 5.91 to precipitate soluble and exchangeable Al and Fe ions into insoluble hydroxides.

Pyrolysis temperature showed also a considerable effect on PUE since the inherent P content in biochar became more thermodynamically stable in apatite species at high pyrolysis temperature (> 600 °C) (Bruun et al., 2017). Meanwhile, Oladele et al (2024) demonstrated that pyrolysis temperature had no significant effect on the activity of alkaline phosphatase enzyme, P phytoavailability and uptake by maize as well as P use efficiency. Conversely, Wang et al.'s study demonstrated that rice–residue–derived biochar pyrolyzed at high temperature increased solubility of soil P by about 144% relative to that engineered at low pyrolysis temperature (Wang et al., 2022a).

Plants are able to release certain active compounds (e.g., malic acid, indole-3-acetic acid, nicotinic acid, abscisic acid and 3-hydroxypropionic acid) to deal with P deficiency in soil (Pantigoso et al., 2023). However, biochar's effect on certain root exudate–derived compounds and P transporter genes are still not clear, and the future research should emphasis on this research topic. In acidified paddy soil (pH = 4.8) with low P supply potential (available P = 8.4 mg kg^{-1}), 500 °C rice straw biochar application improved the adaptability of rice roots to uptake P through stimulation of citrate exudation from roots, and enhancing anion–transporter–related OsFRDL4 gene and the OsPT1 phosphate transporter (Zhang et al., 2022d). In a study by Lu et al. (2020), application of biochar increased the abundance of genes involved in organic P mineralization (PoMin) and legacy P solubilization (PiSol), but not other genes responsible for in P transportation (PTrans). On the other hand, soil biochar applications might modulate roles of root exudates on the rhizosphere microbiome. For instance, exudation of O_2 from rice roots was also enhanced by biochar, which modulated Eh/pH in the plaque and rhizospheric soil layer and regulated nutrient cycling and availability (P in particular) (Chew et al., 2020).

9 Harnessing the power of functionalized biochar to improve phosphorus phytoavailability

9.1 Physical activation

Ideally, biochar–based slow–release P fertilizers should be activated prior to its soil application. Physical activation has received a growing interest in this respect (Table 3). An earlier study introduced hot water treatment as a non-sophisticated technique to improve P solubility in the incinerated waste activated sludge (Matsuo, 1996). Similarly, hot steam activation doubled the positive effects of original biochar (wood biochar pyrolyzed at 475 °C) for improving P phytoavailability and uptake by Italian Ryegrass (Borchard et al., 2012). Low–temperature–steam activation; however, was introduced by Qian et al. to enhance P availability of biochar derived from enhanced biological P removal sludge through hydrolyzing insoluble poly–P form to soluble forms of ortho–and pyro–P (Qian et al., 2019). Microwave irradiation has been also presented as an alternative method to the traditional thermal pyrolysis, which relies on exposing molecular dipoles of microwaves to the feedstock materials to generate more uniform distribution of heat rather than the unbalanced heat transference from other external sources (Mari Selvam and Paramasivan, 2022). In the study of Fang et al., the higher residence time of microwave irradiation stimulated the conversion of non–apatite inorganic P into apatite P (Fang et al., 2021).

Table 3 Effect of biochar functionalization techniques on phosphorus phytoavailability in soil.

Country	Soil Olsen-P (mg kg^{-1})	Feedstock	Pyrolysis Temp.	Application rate	Modification techniques		Characteristics of original biochar			Soil phytoavailable P after original biochar application		Characteristics of functionalized biochar			Soil phytoavailable P after functionalized biochar application		Modulation mechanisms	Ref-erence
							pH	S_{SA}	P_T	P_S	P_O	pH	S_{SA}	P_T	P_S	P_O		
China	201	Corn Stalk	500 °C	5 g kg^{-1} 10 g kg^{-1} 20 g kg^{-1} 40 g kg^{-1}	**Chemical**	Fe/Al hydroxide	10.9	149.7	1340	13.18 11.1 8.89 8.2	118.6 147 169.6 208.5	7.85	258.6	250	9.89 7.9 5.34 3.2	147 107 91.9 44.6	M1	[1]
Algeria	22	Wheat straw	400 °C	4% 8%	**Chemical**	Citric acid	8.9	–	–	–	–	7.3	–	–	–	64.3 86.1	M2	[2]
China	10.4	Corn straw	600 °C	5 g kg^{-1} 10 g kg^{-1} 20 g kg^{-1}	**Chemical**	Ca-Mn-Synthesized biochar	10.01	43.42	–	–	1.7 3.2 3.7	9.62 9.65	162.01 158.68	–	–	1.3 3.2 4.3	M3	[3]
China Purple soil	34.8	Rice husk	500°C	0.2%= 14 g kg^{-1}	**Chemical**	Modified with amino functional group BC$_{NH_2}$	10.2	–	1350	–	39.05	–	–	–	–	58.62	M4	[4]
						Modified with epoxy functional group BC$_{CH(O)CH}$	10.2	–	1350	–	39.05	–	–	–	–	60.7		
						Modified with ethoxy BC$_{C_2H_2O}$ functional group	10.2	–	1350	–	39.05	–	–	–	–	57.48		
						Modified with sulfhydryl BC$_{SH}$ functional group	10.2	–	1350	–	39.05	–	–	–	–	54.93		
						Modified with selenium BC-Se	10.2	–	1350	–	39.05	–	–	–	–	37.63		
						Modified with chitosan BC$_{chitosan}$	10.2	–	1350	–	39.05	–	–	–	–	50.30		
China	31.4	Corn stalk	500 °C	4.5 t ha^{-1}	**Chemical**	Acid modified BC-HCL	9.14	4.97	–	–	33	7	15.9	–	–	44.1	M5	[5]
						Magnetically modified BC-(FeCl$_3$·H$_2$O)" MBC"	9.14	4.97	–	–	33	6.71	16.6	–	–	50		
China	3.6	Corn Stalk	500 °C	20 g kg^{-1}	**Chemical**	Phosphoric acid modified ball-milling (PBC)	–	14.71	300	3.1	5	–	271.71	44400	17	18	M6	[6]

(*Continued*)

Country	Soil Olsen-P (mg kg^{-1})	Feedstock	Pyrolysis Temp.	Application rate	Modification techniques		Characteristics of original biochar			Soil phytoavailable P after original biochar application		Characteristics of functionalized biochar			Soil phytoavailable P after functionalized biochar application		Modulation mechanisms	Reference
							pH	S_{SA}	P_T	P_S	P_O	pH	S_{SA}	P_T	P_S	P_O		
China	21	Corn Straw	800 °C	0.5%= 2.5 g kg^{-1} 1%= 5 g kg^{-1} 2%= 10 g kg^{-1} 0.5%= 2.5 g kg^{-1} 1%= 5 g kg^{-1} 2%= 10 g kg^{-1}	**Chemical**	Fe/Mn modified ball-milling (Fe/Mn-BMBC) (Fe/Mn-BMBC) +P	–	–	–	–	9.1 9.95 11	–	–	–	–	3 3.6 6.1 57.6 84.9 113.3	M7	[7]
China Acid red soil	43.71	Wheat Straw	600 °C	–	**Chemical**	$MgCl_2$-BC (MBC) $AlCl_3$-BC (ABC) ($MgCl_2$+ $AlCl_3$)/BC (MABC)	–	227.12	11500	–	53	–	292.21 169.60 268.51	12900 18700 13200	–	49.7 40.1 39.98	M8	[8]
China	1.35	Walnut shell	400 °C	–	**Chemical**	Lithium modified biochar	–	–	–	–	–	–	–	5400	–	1.09	M9	[9]
China	31.4	Corn Stalk	500 °C	4.5 t ha^{-1}	**Physical**	Ball-milling (PBC)	9.14	4.97	–	–	33	8.47	34.47	–	–	34	M10	[10]
China Salin-alkaline	92.4	Maize straw	700 °C	10 g kg^{-1}	**Physical**	Ball-milling (BBC)	10.1	85.4	11000	–	139.8	10.8	212	12000	–	172.6	M11	[11]
China	57.1	Bone	600 °C	7.5 g kg^{-1} 15 g kg^{-1} 30 g kg^{-1}	**Physical**	Ball-milling (MB) Fe/Mn modified ball-milling biochar (FMB)	9.51	52.78	103600	–	57.65 59 66.4	7.98 9.26	313.09 109.33	106600 101100	–	66.65 88.20 115 57.25 63.7 86.85	M12	[12]
China	89.53	Sheep manure	500 °C	–	**Physical**	Nano-biochar	10.96	–	8000	–	112.2	10.72	–	4000	–	137.4	M13	[13]
China	3.6	Corn stalk	500 °C	20 g kg^{-1}	**Physical**	Ball-milling (BC)	–	14.71	300	–	–	–	195.56	2100	–	–	M14	[14]
China	31.4	Corn stalk	500 °C	4.5 t ha^{-1}	**Biological**	Effective microorganisms' "EM" (BBC)	9.14	4.97	–	–	33	8.51	6.29	–	–	35.8	M15	[15]
China	3.6	Corn stalk	500 °C	20 g kg^{-1}	**Biological**	Microbial ball-milling phosphoric acid	–	14.71	300	3.1	5	–	271.71	44400	18.9	23.6	M16	[16]

(*Continued*)

Country	Soil Olsen-P (mg kg^{-1})	Feedstock	Pyrolysis Temp.	Application rate	Modification techniques		Characteristics of original biochar			Soil phytoavailable P after original biochar application		Characteristics of functionalized biochar			Soil phytoavailable P after functionalized biochar application		Modulation mechanisms	Ref-erence
							pH	S_{SA}	P_T	P_S	P_O	pH	S_{SA}	P_T	P_S	P_O		
China	6.1	Rice straw + P	450 °C-550 °C	–	**Biological**	Mycorrhizal fungal + BC +P	–	–	–	–	33 46 79.1	–	–	–	–	35.7 43 73	M17	[17]
China	7.2	Rice straw	450 °C-550 °C	–	**Biological**	Mycorrhizal fungal + BC	–	–	–	–	29.8	–	–	–	–	26.9	M18	[18]
China	14.5	Apple wood	500 °C 700 °C	–	**Biological**	Biochar loaded with R. solani BC1M BC2M	–	–	–	–	16.5	–	1.755 3.625	–	–	18.79 19.83	M19	[19]
China	36.65	*Tamarix chinensis* Lour	300 °C 400 °C 500 °C	–	**Biological**	Biochar loaded with *Bacillus subtills*	7.11 8.5 10.11	0.21 0.71 1.77	–	–	30.06 49.86 60.27	–	–	–	–	45.04 47.21 43.52	M20	[20]

P_S: Soluble-P (mg kg^{-1}); **P_O**: Olsen-P (mg kg^{-1}); **P_T**: Total P (mg kg^{-1}); **S_{SA}**: SSA (m^2 g^{-1}). **M1**: Biochar functionalization using Fe/Al hydroxide improved the hydrophilic nature of the modified biochar and maximized the abundance of phenolic hydroxy groups, which maximized the contribution of chemisorption forces in P binding; Fe/Al hydroxide loading maximized surface area and the positivity of functionalized biochar, leading to increase its affinity to P through electrostatic attraction that reduced P leachability and improved P phytoavailability; Functionalized biochar application regulated P solubility and reduced its leachability through increasing soil pH and the activity of several cations such as Al^{3+}, Fe^{3+}, Mg^{2+} and Ca^{2+}; Biochar application led to an increase in the degree of soil P saturation via reducing P leaching. **M2**: Citric Acid modified wheat straw biochar supported biochar with high surface area, pore structure and produced more oxygen and acidic functional groups; Introduced biochar with low pH value which in turn enhanced phosphorus availability in alkaline calcareous soil; Low molecular weight organic acids (LMWOAs) that produced from citric acid modified biochar triggered phosphorus release in the amended soil through releasing H^+ ions resulted in reduction in soil pH and transforming insoluble phosphorus into soluble form; (LMWOAs) protected phosphorus from precipitation via chelating cations by carboxyl and hydroxyl anions; Citric acid have high dissolution constant (*p*Ka 3.14), furthermore, the acid strength of modified biochar which enhanced phosphorus solubility from secondary minerals. **M3**: Biochar Functionalization with Ca and Mn provided biochar with high surface area and chemical sorption sites, which increased P sorption via electrostatic attraction; Functionalized biochar had high negative zeta potential, which provided more negative charge that was more adequate for P adsorption; Functionalized biochar posed more OH functional groups, which created outer sphere complexes with phosphate ions; The release of organic acids from functionalized biochar favored the release of P from soil. **M4**: Loading of amino functional groups onto biochar enhanced soil fertility and P availability; Modified biochar had a larger surface area with more sorption sites; Biochar application enhanced soil organic matter stability and cation bridging formation; Biochar maximized the exchange capacity of soil and nutrients availability; Phosphorus phytoavailability decreased following Se-modified biochar application due to the competition between selenite and phosphate ions onto active sorption sites. **M5**: Modified biochar exhibited higher surface area and more binding sites; Iron loading onto biochar increased P retention in soil via phosphate ions complexation. **M6**: Modification process provided biochar with higher surface area with abundance of functional groups; Stimulating O availability following biochar addition due to minimizing the effect of free cations (e.g., Ca^{2+}, Mg^{2+}, Fe^{3+} and Al^{3+}) responsible for phosphate precipitation; Phosphoric acid treatment led to enhance the total P content of modified biochar. **M7**: Fe/Mn-ball milled biochar posed a larger surface area with more abundant of oxygen functional group (e.g., OH group), which competed with phosphate ions leading to a reduction in phosphate binding onto modified biochar; Biochar modification modulated the value of pH point of zero charge (pH_{PZC}), which maximized the potential of electrostatic repulsion of phosphate ions; Fe /Mn-O loading onto modified biochars can form complexes with phosphate ions through electrostatic attraction. **M8**: Ion exchange was the main mechanism for P adsorption by biochar; The large surface area and the abundance of functional groups contributed significantly in P sorption. **M9**: Modified biochar exhibited larger surface area with abundance of O-functional groups such as OH groups; Surface electrostatic attraction between OH group of biochar surfaces and phosphate ions through ligand exchange. **M10**: Ball milling process supported pristine biochar with high surface area; Small particles of biochar that obtained from ball-milling process was more mobile than the original ones, which enhanced nutrient transportation; Modified biochar application enhanced P-availability due to the abundance of active functional group, high carbon degradation and high carbon fixation. **M11**: Ball milled biochar posed higher pH value that provided more alkaline functional groups; Ball milled biochar exhibited higher surface area and massive of oxygen functional groups; Biochar modification increased phosphate phytoavailability through limiting P fixation via influencing the strength of metal ions (Fe^{3+}, Al^{3+} and Ca^{2+}). **M12**: Releasing phosphate group from modified biochar due

Nano-scale fabricated biochar *via* physical modification methods gained intensive interest during the last decade due to its low-cots and minimum environmental risk as compared with chemical modification methods. Phosphate release performance of ball-milled biochars derived from different feedstock (*Eupatorium adenophorum,* rice straw and distillers grains) pyrolyzed at different temperatures (300, 450, and 600 °C.) was studied (Zhao et al., 2022b). Results of this investigation demonstrated that the performance of ball-milled distillers grains biochar produced at 300 and 600 °C was better than other biochars in releasing P for optimum growth of mung beans. Zhang et al. further reported that ball milling could effectively improve the performance of biochar-supported red P to maximize P availability and promote activities of soil enzymes (e.g., alkaline phosphatase and catalase) through grinding biochar into submicron particles and originating nanoscale P particles (Zhang et al., 2022c). Red P reactivity endows the modified biochar with high ability to provide a long-term supply of phytoavailable P, modulate soil pH and regulate soil P dynamics (Chen et al., 2018). In another study, ball milling combined with red P loading can successfully originate active functional groups (P = O, P–O and –OH) onto the produced biochar (ball–milled red P–loaded 700 °C maize straw) with high ability to ameliorate coastal saline–alkali soil and improve its P supply potentials to maize plants (Zhang et al., 2022b).

9.2 Chemical activation

With the recent advancement in biochar modification, novel chemical methods have been introduced to functionalize efficient biochars tailored in modulating soil P dynamics (Table 3). On this point, exogenous application of Ca^{2+} ions to sewage sludge during pyrolysis catalyzed the transformation of organic P into inorganic orthophosphate, and regulated the pyrolytic transformation of P fractions (Nan et al., 2023). From chemical point of view, exogenous application of Ca^{2+} ions cracked the P–O–P bond in pyrophosphate to be transformed into orthophosphates, and stimulated the transformation of P chemical fractions (soluble–, exchange–, Fe/Al bound–, and occluded P fractions) into Ca–bound P. What's more, Ca–enriched biochar application (10 wt%) to rice seedlings in a paddy soil caused more release of P and enabled rice seedlings to uptake more P relative to the original form. Conversely, Leite and coauthors concluded that Ca–enrichment produced biochar with lower phytoavailable P given the generation of semi–crystalline and crystalline P species; however, Mg enrichment improved the affinity of P supply by biochar (poultry manure) following the formation of Mg–P minerals (e.g., $MgNH_4PO_4$, $Mg_3(PO_4)_2 \cdot 8H_2O$, $MgHPO_4 \cdot 3H_2O$ and $Mg_3(PO_4)_2 \cdot 8H_2O$), which resulted in greater P supply than Ca–P minerals (Leite et al., 2023).

Metals oxide modified biochars have received research attention to maximize P availability in soil matrix given its huge specific surface area, which offers a shelter for phosphate solubilizing microorganisms. In a pot experiment, the effect of two metal oxides–modified biochars application (FeAl– and MgAl–500 °C maize stalk biochars) on P phytoavailability in calcareous and lateritic soils were evaluated (Peng et al., 2023). Metal oxides biochars stimulated plant biomass yield in both soils through different mechanisms: (i) abiotically in the lateritic acidic soil through increasing P availability, and (ii) biotically through increasing phosphatase activity. Biochar derived from *Sedum plumbizincicola* (metal hyperaccumulator) was further chlorinated by polyvinyl chloride in the study introduced by Li and coworkers (2024). Chlorination process not only cleaned biochar from the high content of heavy metals to one-tenth but also maximized plant available P by about 4.5 times. Chemically modified biochar was also exploited to maximize organic P

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to their large surface area and nano particles of modified biochar; Biochar led to increase soil available P due to the high abundance of hydroxyapatite groups that increased P content in soil. **M13**: Nano particles of biochar led to reduce the release of colloidal P and provided biochar with high zeta potential; The function of ligand exchange from the abundance of oxygen functional groups and surface precipitation by the cation minerals affected soil pH and Eh and reduced the loss of colloidal-P. **M14**: Ball-milling process provided biochar with high surface area and abundance of functional groups; Available P was enhanced with biochar addition due to limiting the binding with free cations such as (Ca^{2+}, Mg^{2+}, Fe^{3+} and Al^{3+}). **M15**: Colonization of effective microorganisms onto biochar improved soil organic matter and available P; Effective microorganisms promoted nutrients utilization by plants. **M16**: The modified biochar had a larger specific surface area; Biochar activation enhanced P bioavailability via reducing the resistant P fractions (Fe/Al and Ca bounded phosphorus); Biochar activation facilitated the production of organic acid and phosphatase enzymes, which enhanced the solubility of insoluble phosphates. **M17**: Modified biochar application led to increase soil pH, DOC content, and soil microbial community; AMF elevated soil phosphates enzymes, which enhanced soil P availability. **M18**: The combined application of AMF with biochar promoted the secretion of phosphatase enzyme and phosphate solubilizing organic acids; Modified biochar application could stimulate mycorrhizal fungal community. **M19**: The modified biochar was efficient source for microbial colonization due to its high nutrient content, which facilitated microbial growth; Modified biochar stimulated soil microbial community by increasing the amount of refractory carbon in soil; The modified biochar application led to increase soil enzymes (alkaline phosphates-cellulase-sucrase and urease) that contributed in increasing P availability. **M20**: Modified biochar provided a shelter for microbe due to its physical properties such as highly surface area, pore volume and high-water sorption capacity that protect microbes from dehydration; Modified biochar application led to increase soil CEC and SOC contents of soil. **References**: [1] Peng et al., 2021; [2] Mihoub et al., 2022; [3] Wang et al., 2022a; [4] Li et al., 2023; [5] Gong et al., 2024; [6] Zhang et al., 2023; [7] Che et al., 2024; [8] Zheng et al., 2020; [9] Zhao et al., 2021; [10] Gong et al., 2024; [11] Zhang et al., 2022; [12] Xiao et al., 2024; [13] Jin et al., 2023; [14] Zhang et al., 2023; [15] Gong et al., 2024; [16] Zhang et al., 2023; [17] Liu et al., 2020; [18] Xiao et al., 2020; [19] Chen et al., 2023, 2023c; [20] Jia et al., 2022.

retention in soil matrix. As such, lanthanum modified 400 °C walnut shell biochar improved sorptivity of phytate P onto colloidal soil components (Zhao et al., 2022a). Chemical modification could be also a promising solution to minimize the high pH value of pristine biochar for more efficient utilization in calcareous soils. For example, citric acid modification reduced the pH value of wheat straw biochar from 8.9 up to 7.3 and the combined application of modified biochar with inorganic P could extend the half-life of available P release from the inorganic fertilizer by about 80% over the unamended soil (Mihoub et al., 2022). In another investigation, acidic P-rich biochar was prepared from a pyrolyzed halophyte (*Salicornia europaea* L. @ 400 °C) with acid treatment using H_3PO_4 and H_4P2O_7 (Wang et al., 2022c). Due to the low pH value of engineered biochars (3.31 and 2.17 for H_3PO_4– and H_4P2O_7–modified biochars, respectively), their application to an alkaline soil motivated the transformation of stable P into labile fractions due to modulations in soil pH value. The combined application of sulfur-enriched biochar (cow bone@ 650 °C) and sulfur-oxidizing bacteria were further applied to a high calcareous P-fixing soil in Egypt to provide a slow-release P fertilizer with a high labile P fraction (Amin and Mihoub, 2021).

9.3 Biological activation

Despite the growing interest for utilization of biochar–based slow–release P fertilizers, the phytoavailability of inherent P is still limited given its existence with a high proportion in organic, crystalline and insoluble forms (Yang et al., 2021). Consequently, soil inoculation with phosphate–solubilizing microorganisms has been proven to be an effective pathway to stimulate phytoavailability of P through mineralization of organic P, and facilitating the dissolution of insoluble P (Rawat et al., 2021). Recently, attention has been drawn toward biochar utilization as a potential inoculant vehicle in stimulating P availability in the rootzone (Table 3). Microorganisms immobilization by biochar embedding methods is caried out using stabilizers (e.g. alginates) to initiate microbe–immobilized biochar beads (Zheng et al., 2021). The unique physicochemical characteristics of biochar offers a favorable niche for original and/or inoculated microorganisms in soil to remain viable and sustain their metabolic activities for a long time (Ajeng et al., 2020). In Liu et al's study, biochar–based slow–release fertilizer exhibited a good biocompatibility for P–solubilizing microorganisms (Rs–198) owing to its free radicals' content (0.084 mg g^{-1}), graphitic nature and low aromaticity (Abedian-Dehaghani et al., 2022). Other pros of biochar, including its non–biodegradability, high diffusivity, non–toxicity and nutritive value support its potentiality to be used as an inoculant carrier in sustainable agriculture (Ajeng et al., 2020).

The first evidence that arbuscular mycorrhizal fungi can utilize biochar as a carbonaceous matrix, growth shelter and nutrition source was introduced by Hammer and his coworkers (Hammer et al., 2014). Authors proved that hyphae of *Rhizophagus irregularis* fungus grew onto/into the carbonaceous lattice of biochar surfaces, utilized biochar's labeled ^{33}P radiotracer, and translocated this P to roots of the host plant (carrot) with six times greater efficiency than other fungal mycelia that did not connect physically with biochar. In a field study carried out in a sandy soil in Egypt, mycorrhiza (*Glomus mosseae* BEG12)–inoculated 430 °C peanut biochar application maximized P uptake by different faba bean cultivars (El-Refaey El-Bially et al., 2023). In a further investigation, Głodowska et al. highlighted the high efficacy of biochar–supported P–solubilizing *Pseudomonas libanensis* inoculum as a seed coating carrier for maize cultivation (Głodowska et al., 2016). In yet another report, pine sawdust biochar (@ 500 °C) supporting phosphate–solubilizing bacteria (*Serratia* sp., *Pseudomonas* sp., and *Kosakonia* sp.) proved a high efficacy as an organic carrier to maintain the viability of P solubilizing bacteria from phosphate rock and improve P uptake by *Allium cepa* L. (Blanco-Vargas et al., 2022). In essence, biochar functionalization *via* physical, chemical and biological techniques might stimulate biological activities in soil, modulate soil physicochemical characteristics and maximize water and nutrient supply potentials of soil (Fig. 7).

10 Conclusion and future prospects

Biochar became the "star" of carbonaceous soil amendments in improving agroecosystem multifunctionality given its renewability nature, cost-effectiveness, and simple processing. However, the beneficial effect of biochar on modulating soil P dynamics in the charosphere has not been critically reviewed to date. Taken together, the effectiveness of biochar in improving P phytoavailability in the charosphere depends upon its inherent P content (direct effect), and its amending effect on soil matrix that would modulate complicated dynamics in soil–biota–plant system (indirect effect). The literature pointed to a stimulating effect on the performance of microorganisms mediating P phytoavailability in the charosphere through multiple mechanisms: (i) its unique physical structure is exploited as a shelter for microbial colonization, (ii) its inherent nutrients content is used as a source of microbial nutrition, (iii) stimulating hyphal growth and spore germination, (iv) enhancing the copy number of the P functional genes, (v) catalyzing the secretion of bioactive compounds (e.g., phosphatase, polysaccharides and organic acids), and (vi) stimulating the induced resistance of P solubilizing microorganisms to survive under hostile environments. Further research, however, is urgently needed to bridge the knowledge gaps surrounding P dynamics in the

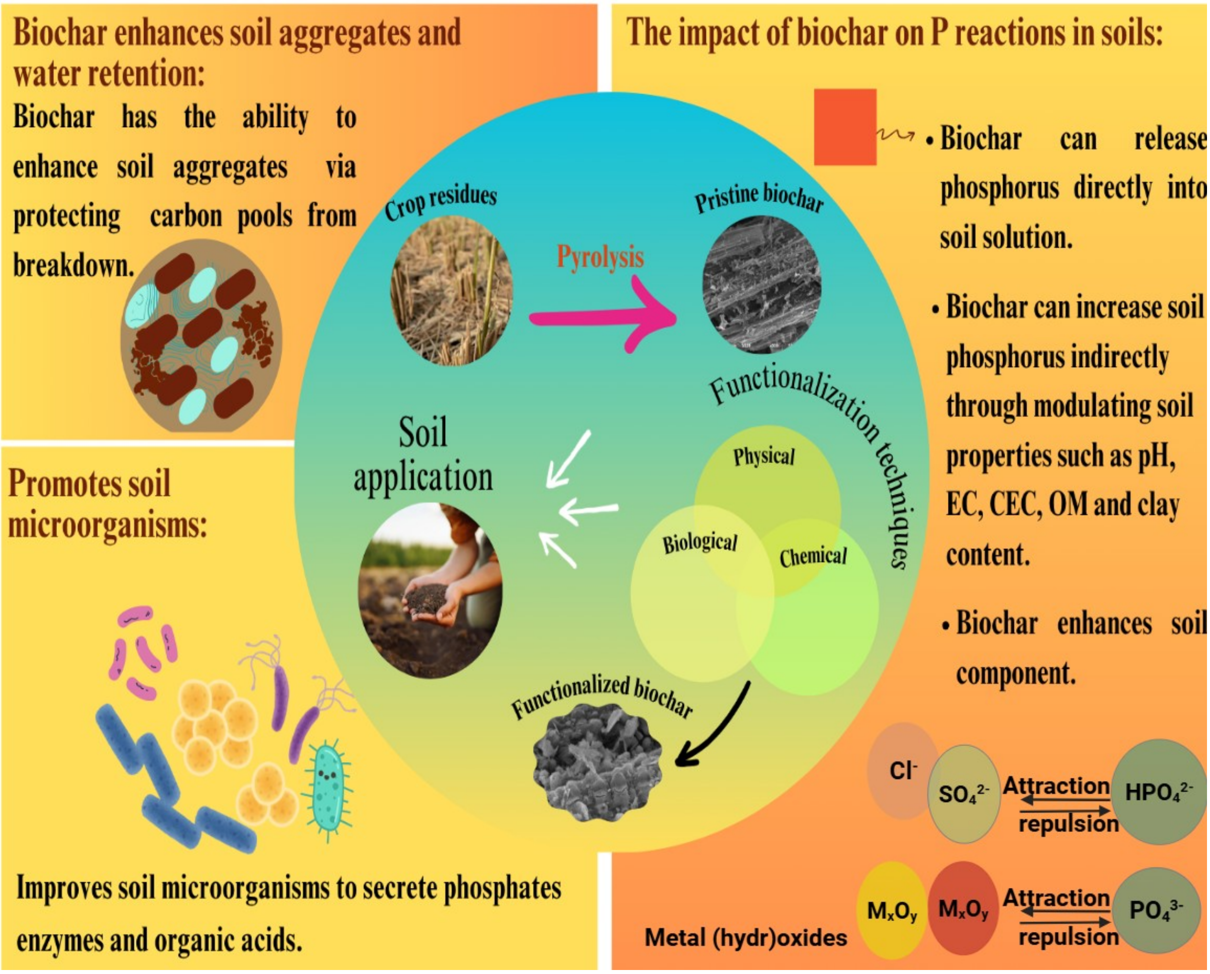

Fig. 7 Role of pristine and functionalized biochars on improving soil physicochemical characteristics and modulating phosphorus dynamics in soil.

charosphere. We propose the following research areas for the foreseeable research:

i. Contextualize lab-scale data according to real field findings to establish a coherent scientific approach for understanding complicated reactions of P dynamics in the charosphere.

ii. Harnessing the power of functionalized biochar to produce fit-for-purpose derivatives tailored in improving P phytoavailability in different soil types.

iii. Developing biochar derivatives as carriers for microorganisms mediating P phytoavailability to remain viable for a long time until soil application.

iv. Studying the kinetic mobility of orthophosphate ions ($H_4PO_4^-$ and HPO_4^{2-}) in the charosphere and monitoring the leachability of P sorbed onto fine biochar particles.

v. Utilization of biochar as a carbon–based coating material to mineral phosphatic fertilizers for controlling P diffusivity in the fertosphere zone (the fertilizer granule region).

vi. Functionalization of modern biochars with high desorbability potentials to reinforce its potential utilization as a short-, mid-, and long-term source for P supply in the rhizosphere.

vii. Studying the effect of biochar on the copy number of the P functional genes involved in legacy P solubilization and organic P mineralization in the charosphere.

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Declaration of interests

The authors declare no potential conflict of interest and that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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