



# Machine learning and computational chemistry to improve biochar fertilizers: a review

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## Abstract

Traditional fertilizers are highly inefficient, with a major loss of nutrients and associated pollution. Alternatively, biochar loaded with phosphorous is a sustainable fertilizer that improves soil structure, stores carbon in soils, and provides plant nutrients in the long run, yet most biochars are not optimal because mechanisms ruling biochar properties are poorly known. This issue can be solved by recent developments in machine learning and computational chemistry. Here we review phosphorus-loaded biochar with emphasis on computational chemistry, machine learning, organic acids, drawbacks of classical fertilizers, biochar production, phosphorus loading, and mechanisms of phosphorous release. Modeling techniques allow for deciphering the influence of individual variables on biochar, employing various supervised learning models tailored to different biochar types. Computational chemistry provides knowledge on factors that control phosphorus binding, e.g., the type of phosphorus compound, soil constituents, mineral surfaces, binding motifs, water, solution pH, and redox potential. Phosphorus release from biochar is controlled by coexisting anions, pH, adsorbent dosage, initial phosphorus concentration, and temperature. Pyrolysis temperatures below 600 °C enhance functional group retention, while temperatures below 450 °C increase plant-available phosphorus. Lower pH values promote phosphorus release, while higher pH values hinder it. Physical modifications, such as increasing surface area and pore volume, can maximize the adsorption capacity of phosphorus-loaded biochar. Furthermore, the type of organic acid affects phosphorus release, with low molecular weight organic acids being advantageous for soil utilization. Lastly, biochar-based fertilizers release nutrients 2–4 times slower than conventional fertilizers.

**Keywords** Climate change · Machine learning and computational chemistry · Phosphorus-loaded biochar · Phosphorus bioavailability · Organic acids · Biochar-based fertilizer

## Introduction

Biochar, a carbon-rich material produced through biomass pyrolysis, has garnered significant interest as a potential agricultural amendment and other environmental applications (Farghali et al. 2023; Osman et al. 2022). Biochar offers promising applications in improving soil quality and nutrient management as a nutrition carrier due to biochar's unique properties, such as high porosity and surface area. Phosphorus, on the other side, is an essential nutrient required for plant growth and various physiological processes; however, phosphorus availability in soil is limited due to phosphorus's

high reactivity and tendency to form insoluble compounds. Traditional fertilizer practices have been used to combat phosphorus deficiency but have several environmental consequences, including water pollution and soil degradation. As a result, there is a growing need to develop sustainable solutions that increase phosphorus availability while minimizing environmental impacts. The availability of phosphorus in biochar is critical for improving soil fertility and promoting plant growth. However, the phosphorus content in biochar can be relatively stable and not readily available for plant uptake. To significantly improve the bioavailability of phosphorus-loaded biochar, scientists have undertaken a pioneering approach, synergistically combining cutting-edge technologies like machine learning and computational

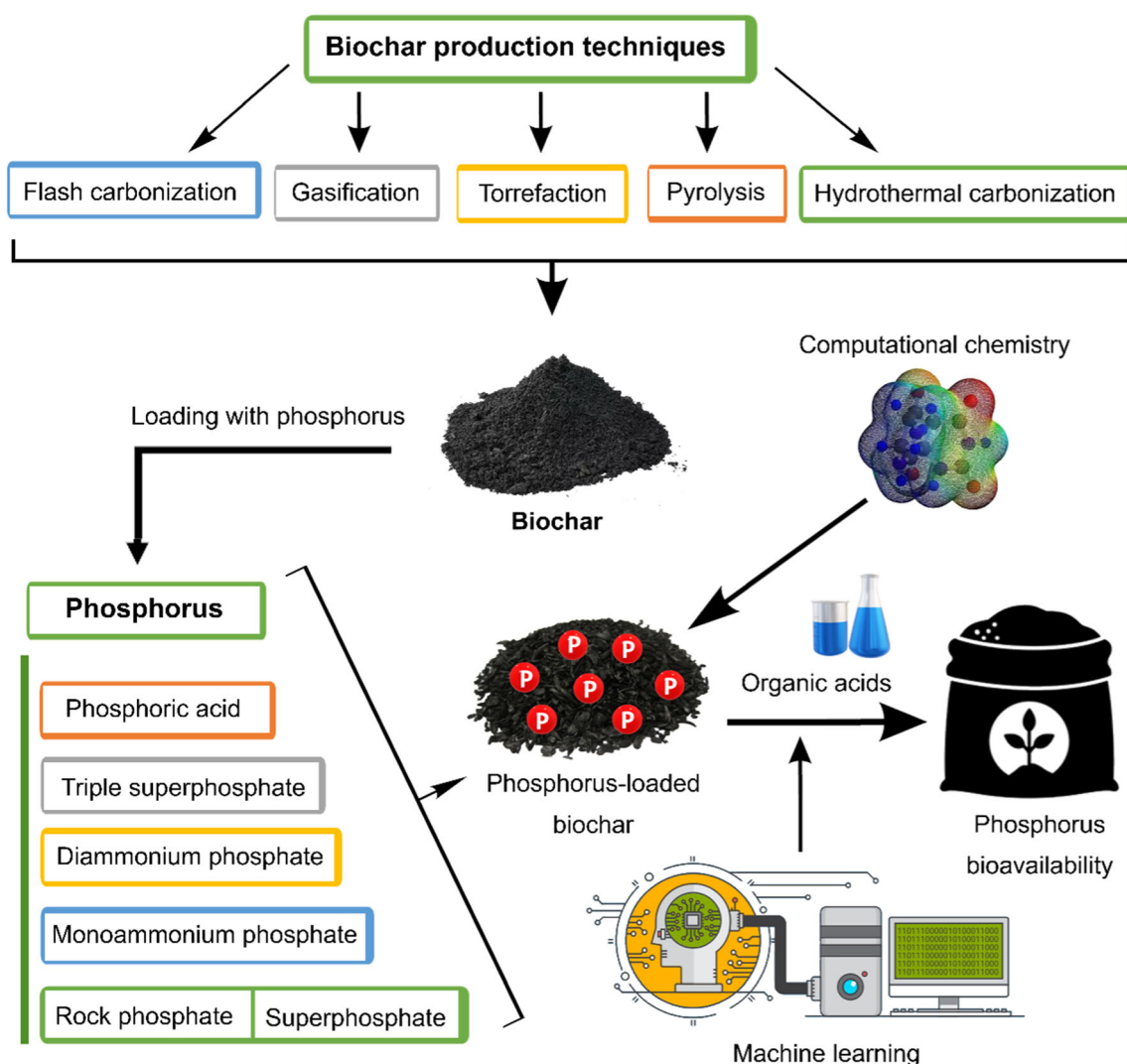
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chemistry with meticulous application and optimization of organic acids (Ahmed et al. 2014; Ahmed et al. 2023; Gros et al. 2017).

Here we review biochar with a focus on production methods, phosphorus loading techniques, and the factors affecting phosphorus release to better understand the underlying mechanisms. The review also highlights the strategies and mechanisms involved in maximizing organic acids for enhancing phosphorus bioavailability from biochar in the context of climate-smart agriculture. Interestingly, machine learning, computational chemistry, and organic acids application and optimization can be applied to optimize phosphorus bioavailability, as shown in Fig. 1. The role of phosphorus in crop growth, the problems with traditional fertilizers, the limitations of phosphorus-loaded biochar, and future research

directions are discussed. The review uniquely focuses on utilizing organic acids to enhance phosphorus release from loaded biochar. Additionally, it explores the potential application of computational chemistry and machine learning algorithms in identifying the most effective organic acids for improving phosphorus bioavailability.

The insights derived from this review will contribute to optimizing phosphorus management strategies in agriculture and promoting the sustainable utilization of biochar to enhance phosphorus availability. Through an in-depth evaluation of current knowledge, the review identifies gaps, limitations, and future research directions, thereby supporting the development of sustainable agricultural practices that maximize phosphorus utilization while minimizing environmental impacts.



**Fig. 1** Biochar-based fertilizer loading with phosphorus and enhancing phosphorus bioavailability using organic acids. This figure illustrates the process of biochar production techniques, loading biochar with phosphorus to make a biochar-based fertilizer, and the subsequent enhancement of phosphorus bioavailability for plants. Various

organic acids are employed as effective agents to facilitate phosphorus release. Integrating machine learning and computational chemistry with organic acids application could optimize phosphorus bioavailability

## Application of computational chemistry in phosphorus-loaded biochar

Despite extensive experimental efforts, a complete understanding of the underlying mechanisms behind specific chemical reactions or physical processes is not always achieved. The intricate interplay of factors influencing phenomena like phosphorus bioavailability further adds complexity. In this context, computational chemistry is a valuable tool that can complement experimental findings and provide a more profound comprehension of these processes. Additionally, it can offer insights into identifying suitable materials for climate-smart agriculture.

This section will consist of two main subsections. The first subsection will provide a concise introduction to computational chemistry, exploring different levels of theory and highlighting the advantages and limitations associated with each level. Then, we will discuss how computational chemistry enables a systematic investigation of potential molecular mechanisms and binding patterns involved in phosphate binding to reactive soil constituents, even under diverse experimental conditions.

### Overview of computational chemistry

Computational chemistry is vital in chemistry and related fields like biochemistry, chemical physics, and material science. Computational chemistry is a discipline that leverages fundamental principles from physics to investigate a wide range of molecular properties and phenomena. Employing advanced computational techniques allows researchers to study molecular structures, thermodynamics, spectroscopic data, reaction rates, and dynamics with high precision and accuracy. It can simulate different phases like gases, liquids, solids, solutions, and interfaces (Ahmed et al. 2023; Cramer 2004; Jensen 2017; Kubicki 2016). Computational chemistry enables the simulation of adsorption/desorption processes, accounting for the impact of surface composition, spatial configuration, solution environment, ionic strength, and solution pH. Furthermore, computational chemistry can calculate and interpret spectroscopic data like infrared, ultraviolet, nuclear magnetic resonance, and X-ray spectroscopy. The accuracy and efficiency of the level of theory significantly impact these calculations and simulations. Despite the growing importance and wide-ranging applications, the use of computational chemistry in environmental chemistry, specifically in studying biogeochemical processes within the soil, has been relatively constrained thus far. This is primarily due to the immense complexity inherent in soil, which is characterized by the heterogeneous nature and multi-component composition, posing unique challenges and requiring interdisciplinary collaborations

(Ahmed et al. 2014; Ahmed et al. 2023; Gros et al. 2017; Kubicki 2016; Kwon and Kubicki 2004). However, the integration of molecular simulation techniques and the development of relevant molecular models hold substantial promise. The comprehensive utilization of computational chemistry has great potential in enhancing our molecular-level understanding of phosphorus-related processes, thus improving soil's phosphorus bioavailability.

Computational chemistry encompasses different levels of theory, each offering distinct accuracy and computational efficiency. At the simplest level, molecular mechanics employ empirical potentials to describe the energy of molecular systems, with three primary resolution levels: all-atom, united-atom, and coarse-grained representations (Cramer 2004; Jensen 2017; Kmiecik et al. 2016).

In the all-atom depiction, individual atoms are considered particles, with the treatment of electrons being implicit. On the other hand, the united-atom representation consolidates groups of atoms, such as a CH<sub>2</sub> group, into a single pseudo-atom. Taking a further step, the coarse-grained representation involves grouping atoms, functional groups, or even whole molecules into beads. These various representations encompass both bonded and non-bonded interactions, encompassing potentials for bonds, angles, dihedral angles, electrostatic forces, and van der Waals interactions.

For a more detailed description, quantum mechanics explicitly treats nuclei and electrons, solving the Schrödinger equation. Quantum mechanics can be broadly categorized into three main approaches: *ab initio*, density functional theory, and semi-empirical methods. Each of these methods provides different levels of accuracy and computational cost in capturing the quantum behavior of molecules (Cramer 2004; Jensen 2017; Kubicki 2016). *Ab initio* methods are computationally expensive and limited to simple model systems. Semi-empirical methods utilize approximations and empirical parameters, making them computationally more efficient and applicable to larger systems.

Density functional theory, the most prominent method, balances efficiency and accuracy by calculating the electron density using Kohn–Sham molecular orbitals. The choice of the so-called exchange–correlation functional and basis set significantly affects the quality of density functional theory results (Jensen 2017; Lee et al. 1988; Perdew et al. 1996). In practice, computational chemistry employs various basis sets, such as Gaussian atom-centered and periodic plane-wave basis sets, to represent electronic wave functions. Hybrid Gaussian and plane-wave methods have been developed to combine the benefits of both approaches (Kuhne et al. 2020; Lippert et al. 1997). Incorporating long-range van der Waals dispersion interactions often requires the inclusion of empirical dispersion corrections (Chai and Head-Gordon 2008; Grimme et al. 2011).

Moreover, the hybrid QM/MM method combines quantum mechanics (QM) calculations for the reactive part of the system with molecular mechanics (MM) estimates for the rest, such as the solvent (Senn and Thiel 2009). This approach efficiently tackles larger and more complex systems. Various QM/MM schemes, including mechanical and electrostatic embedding, have been developed to link quantum mechanics and molecular mechanics calculations, capturing the interplay between different regions. The hybrid QM/MM method offers advantages such as computational efficiency, versatility, accurate modeling of reactions with environmental effects, and valuable insights into chemical reactions, transition states, and excited states. However, implementing it requires specialized software and expertise, and the results from QM/MM can be influenced by force field parameters and the chosen quantum mechanics method. Additionally, interpreting calculations and analysis can be challenging due to the complexity involved. In this context, in the following, we present a summary of the benefits and limitations of commonly utilized levels of theory, as well as potential levels, for conducting phosphorus research.

Density functional theory (DFT) is widely used in phosphorus research due to DFT's favorable balance between accuracy and computational cost. It offers versatility in studying molecules, materials science, and solid-state physics and enables the simulation of chemical reactions, transition states, and excited states. Moreover, density functional theory can predict materials and molecules' electronic and thermodynamic properties. However, density functional theory has limitations that should be considered. It relies on empirical parameters, which can limit the density functional theory accuracy. The choice of functional theory is crucial and can impact the results. Dispersion interaction corrections are often necessary to account for non-covalent interactions. Moreover, there are limitations in the time and length scales of molecular dynamics simulations within the framework of density functional theory.

Semi-empirical methods provide an alternative to density functional theory and offer certain advantages. They are computationally less expensive compared to *ab initio* and density functional theory methods, resulting in higher efficiency. These methods are particularly suitable for studying molecular systems containing hundreds to thousands of atoms. They can access longer time scales in molecular dynamics simulations compared to *ab initio* and density functional theory methods, making them useful for simulating chemical reactions, transition states, and excited states. However, semi-empirical methods have their own limitations. They rely on extensive empirical parameters, which can affect their accuracy. Additionally, parameterization often requires *ab initio* calculations or experimental

data, limiting their transferability to other molecular systems.

When considering molecular mechanics-based methods, the all-atom representation offers several advantages. It is computationally efficient and fast compared to all quantum mechanics methods. It enables the description of large molecular systems containing thousands to millions of atoms and often achieves good accuracy in reproducing experimental observations. This representation is particularly suitable for situations with limited computational resources. However, the all-atom representation relies on empirical parameters, which need to be carefully parameterized through quantum mechanics calculations or experiments. Generally, it has lower accuracy compared to all quantum mechanics methods. Furthermore, the all-atom representation cannot simulate chemical reactions and accurately capture electronic properties.

The coarse-grained representation reduces the complexity of molecular systems by grouping atoms into larger entities, significantly reducing the computational cost. This makes it highly suitable for studying large molecular systems consisting of millions of atoms. The coarse-grained representation also enables access to longer time and length scales in simulations, making it useful for studying slow processes such as adsorption/desorption, diffusion, and self-assembly. However, the coarse-grained representation has limitations. It requires all-atom calculations and/or experiments for parameterization, which can be time-consuming. The potential lack of parameter transferability to other molecular systems is another challenge. Additionally, the coarse-grained representation sacrifices atomistic details, which may limit the ability to study precise molecular structures.

Irrespective of the level of theory in computational chemistry, a wide range of techniques can be employed to achieve stable molecular geometries and optimized structures. Molecular dynamics simulations are utilized to incorporate statistical properties that account for the thermal motion of nuclei at finite temperatures (Marx and Hutter 2009). By solving Newton's equations of motion, molecular dynamics generate trajectories that sample the system's thermal ensemble at a specific temperature, enabling the determination of average geometries and capturing the explicit behavior of the entire system. Implicit solvation models offer a simplification by representing the solvent as a classical dielectric medium that responds to the electron density of the reactive quantum region (Cossi et al. 2003; Klamt and Schuurmann 1993; Marenich et al. 2009). When considering macroscopic systems like surfaces, there are two main approaches: finite cluster models and periodic treatments. Periodic boundary conditions are commonly used for surface-related processes in crystalline or amorphous materials.

In summary, different levels of theory and techniques employed in phosphorus research possess distinct advantages and limitations. The selection of the optimal approach relies on specific research objectives, system size, computational resources, and the desired level of accuracy.

### Computational chemistry in phosphorus research

To the best of our knowledge, no molecular modeling study has yet examined the impact of biochar on phosphorus bioavailability. However, computational chemistry has significantly contributed to investigating phosphorus-related processes and enhancing phosphorus bioavailability in soil. It has been employed as a complementary tool to experimental studies, specifically to understand phosphate binding to soil constituents, particularly mineral surfaces. For instance, Kubicki and colleagues made pioneering strides in understanding the phosphate binding process through the use of density functional theory calculations (Kubicki et al. 2009; Kubicki et al. 2007; Kubicki et al. 2012; Kwon and Kubicki 2004). In an early investigation, they utilized an embedded-molecular-cluster approach to study pH-dependent phosphate binding to goethite ( $\alpha$ -FeOOH). The goethite surface was represented by a small cluster of two edge-sharing iron octahedra, with a few explicit water molecules simulating the solvent environment. By comparing vibrational frequencies with experimental data, the study proposed the formation of a diprotonated bidentate complex at low pH, a deprotonated bidentate or a monoprotonated monodentate complex at intermediate pH, and a deprotonated monodentate complex at high pH.

Further investigations examined the impact of surface charge distributions, phosphate speciation, competitive water, pH, and hydrogen bonds on phosphate binding to the same small cluster (Acelas et al. 2013; Rahnemaie et al. 2007). Furthermore, the phosphate binding to aqueous uranium complexes as well as various mineral surfaces such as boehmite ( $\gamma$ -AlOOH), corundum ( $\alpha$ -Al<sub>2</sub>O<sub>3</sub>), and ferrihydrite has been explored using similar cluster models (Acelas et al. 2013; Khare et al. 2007; Kubicki et al. 2009; Li et al. 2010; Ren et al. 2012). It should be noted that these observations were obtained through cluster calculations, which may not fully capture the behavior of extended or periodic systems.

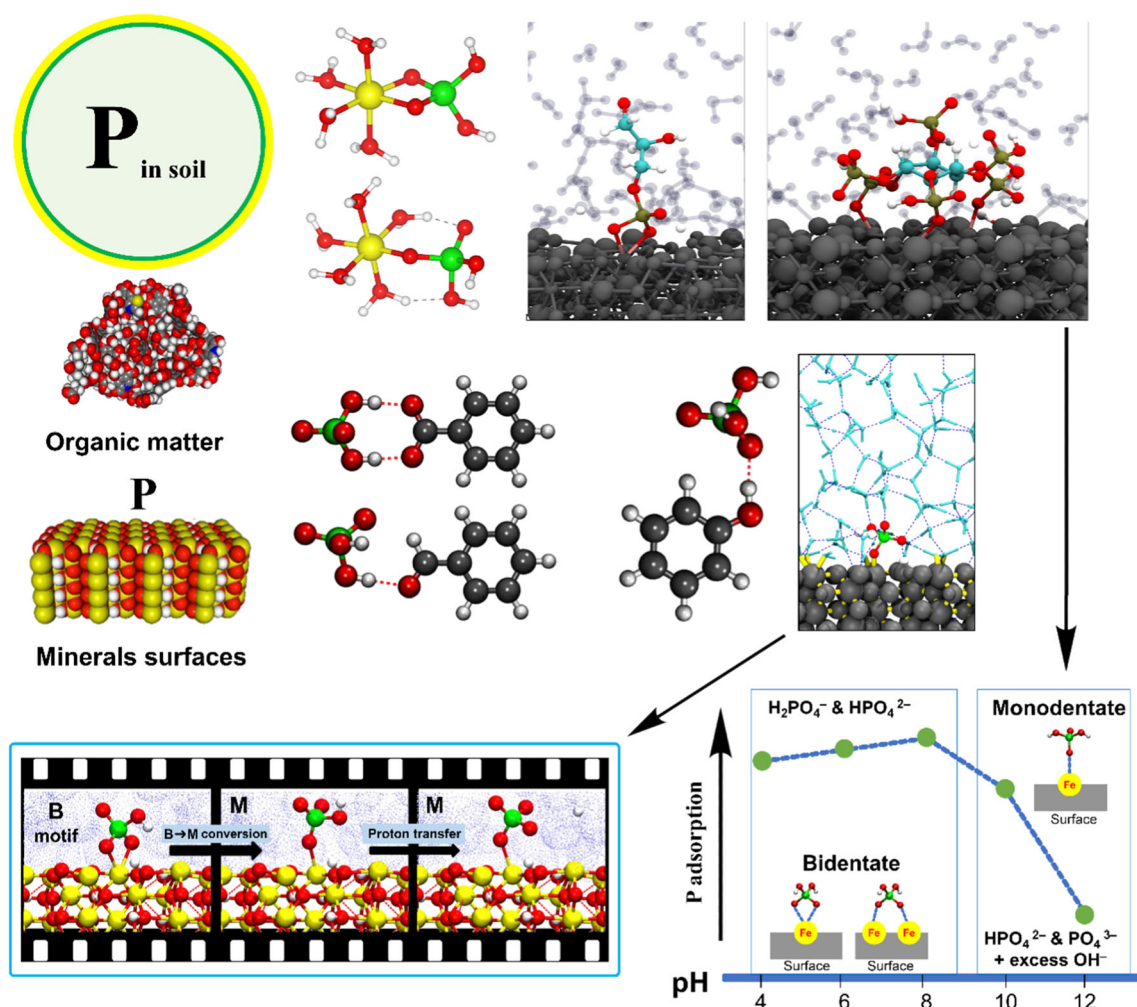
Extending the cluster approach applied in previous research on phosphate-surface binding motifs, Kubicki et al. (2012) conducted periodic density functional theory calculations. Their study encompassed goethite surface planes and employed stationary calculations and molecular dynamics simulations to analyze the HPO<sub>4</sub><sup>2-</sup> species. Additionally, infrared spectroscopy vibrational frequencies were calculated for extracted molecular clusters, aiding in

identifying phosphate binding motifs. The findings indicated the formation of monodentate complexes on the 001, 210, 101, and 100 surface planes, while bidentate complexes were observed on the 010, 101, and 100 surface planes. Similarly, Beelli et al. (2014) utilized periodic calculations to investigate the behavior of phosphate complexes on pure and aluminum (Al)-rich goethite surfaces (110 planes), exploring previously unexplored complexes. Their vibrational frequency calculations, compared with experimental data, indicated the prevalence of protonated bidentate mononuclear complexes at pH 3.1, bidentate binuclear complexes within the pH range of 4.2–7.9, and protonated bidentate binuclear complexes at pH 12.8. Furthermore, Weng et al. (2020) performed molecular dynamics simulations using periodic density functional theory calculations to study the phosphate binding on the 100 goethite surface plane. The results demonstrated that the monodentate complex is the most abundant, followed by the physisorbed configuration.

Furthermore, Ahmed et al. (2020) investigated the interaction between inorganic and organic phosphorus compounds and diverse soil components. These components include mineral surfaces, free metal ions, and soil organic matter, as illustrated in Fig. 2 (Ahmed et al. 2019; Ganta et al. 2019, 2020a, b; Ganta et al. 2021; Shaheen et al. 2022). Their calculations involved larger simulation boxes, incorporating phosphate-mineral-water molecular models with explicit solvation at a water density of 1 g.cm<sup>-3</sup>. The simulations employed molecular dynamics with density functional theory or quantum mechanics/molecular mechanics (QM/MM) methods, using hybrid Gaussian and plane-wave basis sets and accounting for long-range dispersion correction. To elucidate the mechanisms underlying phosphorus binding, their investigations considered multiple factors, including surface morphology, saturation, central metal ion exchange, metal ion valency, soil organic matter (SOM) composition, water, pH, and redox potential. The research yielded important insights into phosphate binding in soils, revealing more robust binding to mineral surfaces and metal ions than organic matter (Ahmed et al. 2019; Shaheen et al. 2022).

Phosphate formed inner-sphere complexes through covalent or coordination bonds with mineral surfaces and metal ions while binding to the organic matter involved dispersion interactions and hydrogen bonds. Hydrogen bonds and dispersion interactions also played significant roles in the binding to metal ions and mineral surfaces. Consequently, phosphate species bound to organic matter may contribute to readily available and mobile phosphorus compared to mineral surfaces. Furthermore, soils rich in pedogenic oxides are expected to have stronger phosphate binding, while soils with lower concentrations exhibit weaker binding. Under reducing conditions, phosphate





**Fig. 2** Interaction between phosphate and various soil constituents. This interaction includes optimized structures of orthophosphate complexes with metal ions (in monodentate and bidentate binding motifs), organic molecules, and the goethite surface in the presence of water. Additionally, the binding of glycerolphosphate and inositolphosphate complexes to the goethite surface in the presence of water is shown. The influence of pH on orthophosphate binding at the

shows weaker binding to soil constituents, especially metal ions and metal oxides, compared to oxidizing conditions. This suggests that reduced soil conditions can increase phosphorus availability. The subsequent paragraphs will delve further into the computational chemistry perspective of the phosphate binding process.

The results obtained from molecular modeling and simulations conducted by Ahmed and colleagues have shed light on the intricate influence of pH on the binding and mobilization of phosphorus in soil. Notably, the pH effect is not uniform across all soil constituents (Ahmed et al. 2020; Shaheen et al. 2022). While phosphate binding to free metal ions increases with higher solution pH, binding to organic matter and mineral surfaces decreases as the pH rises. This implies that the composition of soil constituents

goethite surface and the dynamic behavior and conversion of binding arrangements and proton transfer are depicted. In the figure, “M” and “B” represent monodentate and bidentate binding motifs, respectively. Goethite atoms are depicted in gray, while orthophosphate ( $\text{PO}_4^{3-}$ ) atoms are color-coded with green (P, phosphorus), red (O, oxygen), and white (H, hydrogen)

and solution pH significantly impact phosphorus binding in a specific soil. Moreover, pH is crucial in determining phosphate binding motifs on mineral surfaces. For instance, monodentate binding motifs dominate at 010 and 100 goethite surface planes under extremely low and high pH conditions, while the bidentate binding motif prevails in the intermediate pH range.

Additionally, mineral surfaces’ nature and surface planes notably affect phosphorus binding. For instance, goethite ( $\alpha\text{-FeOOH}$ ) generally exhibits stronger phosphate binding compared to diasporite ( $\alpha\text{-AlOOH}$ ), particularly for specific binding motifs (Ganta et al. 2019; Ganta et al. 2021). All monodentate binding motifs of phosphates (orthophosphate, glycerolphosphate, and inositol-hexaphosphate) show more robust binding to goethite than

diaspore. However, in the case of the 3 monodentate (3M) binding motif of inositol-hexa-phosphate, diaspore demonstrates stronger binding than goethite for both 010 and 100 surface planes (Ganta et al. 2019; Ganta et al. 2021, 2020a; b).

Moreover, both glycerolphosphate and inositol-hexa-phosphate exhibited stronger binding to the less saturated surface plane of diaspore (010) compared to the more saturated plane (100) for all binding motifs (Ganta et al. 2019, 2020b). This can be attributed to the higher surface saturation of the 100-plane, which results in more negative charges and a lower electrostatic potential than the 010-plane. As a result, phosphates, carrying negative charges due to partial deprotonation, are more strongly bound or adsorbed to the 010-plane than the 100-plane. Furthermore, the surface morphology plays a significant role, as different dominant binding motifs are observed depending on the surface plane. For example, orthophosphate exhibits a preference for the bidentate mononuclear ( $2O + 1Fe$ ) binding motif on the 010-goethite surface plane, whereas it favors the bidentate binuclear ( $2O + 2Fe$ ) motif on the 100-surface plane (Ahmed et al. 2019).

Moreover, the distribution and positions of surface central metal ions (such as  $Al^{3+}$  in diaspore or  $Fe^{3+}$  in goethite) on both surface planes enable glycerolphosphate and inositol-hexa-phosphate to form more stable multiple covalent bonds with the 010-diaspore surface plane compared to the 100-plane. Specifically, the 3 monodentate (3M) binding motif prevails for inositol-hexa-phosphate on the 010-diaspore surface plane, while the 2 monodentate (2M) motif dominates on the 100-plane (Ganta et al. 2019, 2020b). Regarding glycerolphosphate, the bidentate binding motif is dominant on both surface planes, with significantly higher occurrence observed on the 010-diaspore surface plane. Furthermore, the stronger binding of inositol-hexa-phosphate compared to glycerolphosphate on both diaspore surface planes, similar to goethite, suggests a higher prevalence of inositol-hexa-phosphate in soils (Missong et al. 2016).

It was also explored that water plays a vital role in regulating the phosphate binding process on mineral surfaces through diverse mechanisms. It forms hydrogen bonds with phosphates and surfaces, leading to dissociation and the generation of  $H^+$  and  $OH^-$  ions. Proton transfer processes occur between phosphates, surfaces, and water, influencing the solution's acidity and potentially inducing soil acidity after phosphorus fertilization. The presence of water molecules introduces strain into phosphate-mineral complexes, especially for phosphates like glycerolphosphate and inositol-hexa-phosphate, which engage in intermolecular hydrogen bonds with water. This strain causes instability in specific binding motifs and depends on the

water-accessible surface area of the phosphate species. Inositol-hexa-phosphate also exhibits intramolecular hydrogen bonds between adjacent phosphate groups, contributing to strain and the dissociation of covalent bonds in specific motifs. Interaction energies reveal that phosphates show an increasing affinity for goethite and diaspore surfaces compared to water, enabling them to displace water molecules on these surfaces. Ultimately, all these investigations emphasize the critical role played by water as well as the molecular structure of both phosphates and the adsorbent surface, as supported by numerous experimental studies (Amadou et al. 2022; Ganta et al. 2021; Gypser et al. 2018; Wang et al. 2015a; Yan et al. 2014). In addition, these investigations have resolved debates regarding the assignment of phosphate-mineral binding motifs and can be applied to characterize experimental infrared spectra in similar cases. Further discussion of these findings can be found in the review article (Ahmed et al. 2023).

In conclusion, molecular modeling is a potent tool for unraveling the complexities of phosphorus binding and bioavailability in soil, complementing experimental investigations. It provides crucial insights into the impact of various factors on the binding process, including phosphorus compound type, soil constituents, mineral surfaces, binding motifs, water, solution pH, and redox potential. Phosphate predominantly binds to mineral surfaces and free metal ions, exhibiting a stronger affinity than organic matter. The binding mechanisms involve inner-sphere complexes, covalent/coordination bonds, hydrogen bonds, and dispersion interactions. Various factors, including the characteristics of mineral surfaces, positions of surface metals, properties of phosphate groups, interactions with water, and solution pH, influence phosphate binding. The pH effect on binding is intricate and varies among soil constituents. To enhance our understanding of phosphorus bioavailability in soil, future research should address outstanding questions and challenges in molecular modelings, such as optimizing organic acids to improve phosphorus bioavailability from biochar in climate-smart agriculture. This will drive the development of sustainable soil management strategies and efficient phosphorus fertilizers. Integrating computational chemistry methods with experimental data enables a comprehensive comprehension of molecular systems, propelling advancements in chemistry and related fields.

## Machine learning for improved phosphorus bioavailability from biochar

Artificial intelligence enables computers to solve complex challenges and perform tasks like humans. Machine learning algorithms convert input data into new solutions

and various algorithms. Machine learning refers to the prediction and judgment of another part of the data after the computer has acquired the appropriate knowledge and rules by learning some of the data. General supervised learning algorithms for machine learning include linear regression models, artificial neural networks, and random forests. For the linear regression model, Nguyen et al. (2022) pointed out that the machine uses least squares or partial least squares to estimate parameters and find estimates of parameters to minimize the sum of square errors. Zhu et al. (2019) noted that artificial neural networks mimic the human brain's operation and consist of three main components: Input, hidden, and output layers, each containing a certain number of neurons. In the course of artificial neural networks, the number of input variables in the input layer is shown by the activation function of the hidden layer and by the weight run of the final progress in the output layer. This setting handles most problems and effectively addresses the issue of insufficient sample size. Zhou et al. (2019a) indicated that random forest is an integrated algorithm, a combination of individual decision trees, where each decision tree relies on values of randomized vectors sampled independently. Random forest is suitable for regression or classification problems, allowing separate decision trees to be randomly sampled from the data set and replaced. Each decision tree in the random forest gives a category prediction, and the most predictive category is the random forest prediction.

Different mechanical learning methods need to be supported by other parameters and data points. Haider Jaffari et al. (2023) introduced the study was analyzed as a sample. Haider Jaffari et al. (2023) selected 3757 data points and 24 input features in machine learning. The input features include 12 adsorption conditions, three biochar synthesis conditions, three biochar characteristics, and six biochar composition features. The researchers used the data for machine learning, and the characterization of the machine learning model allowed one to estimate the capacity of biochar during wastewater and adsorption. Through the characteristic analysis of machine learning, the specific surface area of biochar is an essential factor affecting adsorption ability. When the pyrolysis temperature and time of biochar are 800 °C and 120 min, respectively, the surface area of biochar is concentrated at 427.5 m<sup>2</sup>/g, and the bore volume of biochar is 0.293 cm<sup>3</sup>. Zhu et al. (2019) noted that in addition to physical properties, surface functional groups such as amino, hydroxyl, and carboxyl groups on biochar can significantly affect the adsorption properties of biochar. From the machine learning model, the carbon content of biochar varies between 68 and 88%, representing the degree of biochar's carbonization. In current data models, biochar ash content significantly alters organic matter's physical and chemical

properties and distribution. Hai et al. (2023) found the model the ash content of biochar is between 5.5 and 24%. The data of these models correspond to the actual situation. This model can help environmental engineers accurately predict the potential of biocarbon adsorption performance without a single experiment. Dashti et al. (2023) pointed out that the physical and chemical properties of biochar include specific surface area, pore size distribution, type and quantity of surface functional groups and that these properties depend on the source of raw materials, pyrolysis conditions, and pyrolysis methods. Most experiments on the properties of biochar are conducted at relatively high temperatures by changing the initial metal concentration, adsorbent dosage, and solution acid alkalinity. Based on experimental results, biochar's optimum heating temperature, time, and maximum adsorption capacity are defined. Shaheen et al. (2019) found that experiments need to explain the adsorption mechanism of biochar adsorption and the related contribution of different variables. Bharath et al. (2020) mentioned that it is time-consuming, expensive, and energy-consuming to study the physical properties of biochar and optimize process parameters during plant processing. As a data-driven mathematical method, machine learning provides accurate solutions for predictive models through high-speed computing, self-learning capabilities, and algorithm design.

Each model structure of machine learning has certain advantages and disadvantages. For example, neural network models have simple designs and high predictability with simple models. Nguyen et al. (2021) pointed out that neural models require people to set many parameters for use and that correlating these parameters with biochar models requires careful trade-offs. Deng et al. (2021a; b) proposed using support vector machines to produce more accurate results than neural networks, which can find the best machine learning algorithms based on the most critical factors. However, support vector machines require longer response times, and the models produced by more support vector machines must be more complex and easily understood by environmental researchers and water sector staff. So currently, Zhang et al. (2023a) proposed using artificial intelligence to support machine learning further. When artificial intelligence processes the complex nonlinear correspondence of approximate structures, it can interpret abstract information in the data. Peter et al. (2023) noted that artificial intelligence's self-learning capabilities simplify the algorithmic design to provide accurate forecasting and optimal solutions that reduce labor intensity, time, and usage costs. Biochemical properties in biochar affect the relative performance of biochar during use. Machine learning can create models better to explore the impact of a single variable on biochar, and there are many supervised



learning models in machine learning to cope with different kinds of biochar.

In conclusion, the ongoing loss of phosphorus resources and environmental degradation have increased the need for phosphorus resource recovery and release. This summary stresses the effect of biochar's physicochemical features on phosphorus release. Organic acids with varying molecular weights reveal considerable changes in phosphorus release from biochar when mediated by microbes and roots. Biochar components can be found in abundance in several types of waste biomass. Aside from the influence of the biochar material itself, different application rates have different effects on phosphorus release. Different thermochemical procedures connected to modification approaches can be used to make functional biochar. The properties of biochar make it a good foundation for developing effective phosphorus adsorbents. Using functional biochar to recover phosphorus solves phosphorus loss and environmental contamination. It is possible to create a virtuous phosphorus cycle using biochar. Although applying phosphorus-adsorbed biochar as a slow-release fertilizer is nascent, machine learning will improve phosphorus use efficiency in biochar in the future, generating a virtuous phosphorus cycle.

However, understanding the ways and negative environmental effects of traditional fertilizer can illustrate the importance of using machine learning and computational chemistry with organic acids to improve and optimize the bioavailability of phosphorus. Thus, the following section addressed the negative environmental effects of traditional fertilizer, biochar production, and loading with phosphorus.

## Implications of traditional fertilizer use

Fertilizers are critical resources in agricultural production for plant growth and development (Olad et al. 2018). For a long time, conventional agricultural practices have relied heavily on input-intensive synthetic fertilizers, such as those containing inorganic phosphorus and potassium. Both inorganic and organic fertilizers significantly affect the soil's physical, chemical, and biological properties (Ayaz et al. 2021; Patra et al. 2021). However, due to various factors such as leaching, degradation, insolubility, and decomposition, the availability of these resources is insufficient for plant use, leading to a decrease in crop yields because farmers often mistakenly overuse fertilizers (Fang et al. 2021).

### Inefficient use of fertilizer

Nitrogen is like phosphorus, a vital nutrient required for various essential processes such as growth and

development, photosynthesis, plant hormone production, protein composition alterations, and life cycle completion. Regarding scarcity, nitrogen is the third most limited nutrient after carbon, hydrogen, and oxygen. Excessive and inefficient utilization of nitrogen fertilizer can increase production costs and contribute to air pollution. It is important to note that plants cannot directly access atmospheric nitrogen molecules, which make up approximately 71% of the atmosphere (Shahzad et al. 2019). Enhancing nitrogen usage efficiency in agricultural cropping systems is paramount in promoting sustainable food production and yielding global benefits for the atmosphere. Over the years, agricultural nitrogen fertilizer consumption has increased substantially, from 10 tetragram nitrogen/hectare in 1961 to 77 tetragram nitrogen/hectare in 2016 (Martínez-Dalmau et al. 2021).

Nevertheless, a significant portion of the nitrogen fertilizer does not effectively contribute to crop growth. Instead, it is lost to the environment through volatilization, runoff, or leaching processes. Inefficient utilization of fertilizers can result in various environmental problems, including releasing greenhouse gases, water pollution, soil acidification, and declining biodiversity. Projections indicate that atmospheric nitrogen pollution will rise by 102–156% between 2010 and 2050, with the agricultural sector responsible for 60% of this increase (Elrys et al. 2020).

Improving nitrogen usage efficiency is crucial for minimizing environmental impact and enhancing agricultural productivity. It has recently been proposed to gauge progress toward achieving the sustainable development targets the United Nations General Assembly set. Significant variations are observed globally in nitrogen input rates and the effectiveness of nitrogen recovery during crop harvesting across different nations and regions. According to several research estimates, worldwide nitrogen fluxes reached 163–174 tetragrams in 2009–2010, with an average nitrogen surplus (nitrogen input minus nitrogen absorbed by harvested crops) ranging from 85 to 100 tetragrams. The nitrogen utilization efficiency was calculated to be approximately 0.42–0.45 tetragram (Shahzad et al. 2019). Approximately 53–59% of total nitrogen inputs are derived from synthetic fertilizers, making them the primary source of nitrogen intake. Following this, manure contributes around 16–20%, while bio immobilization and atmospheric deposition account for 16–18% and 6–10%, respectively. Asia, particularly China, India, and Pakistan, is responsible for 67% of the global nitrogen excess and 54% of the surplus imports (Shahzad et al. 2019).

Over the past few decades, developing countries have consistently exhibited low nitrogen use efficiency. In contrast, certain developed countries with high-yield, high-

input systems have significantly improved nitrogen use efficiency. Among these countries, Canada, Europe, and the United States have achieved the highest rates of nitrogen usage efficiency, while Asian nations have recorded comparatively lower rates (Shahzad et al. 2019). This observation highlights the importance and potential for increasing food production in low-income countries without significantly increasing nitrogen input rates. Instead, the focus should be on achieving higher nitrogen usage efficiency. By optimizing agronomic factors that contribute to crop yield within the existing regional nitrogen input levels, it is possible to achieve a gradual improvement in nitrogen usage efficiency. This approach can lead to sustainable agricultural practices that maximize productivity while minimizing nitrogen-related environmental impacts (Móring et al. 2021).

The primary factor contributing to poor nitrogen utilization efficiency is the improper and excessive use of nitrogen fertilizers. The objective should be to minimize fertilizer inputs while maintaining or increasing output. Modern technologies should incorporate agronomic concepts and practices that enhance nitrogen usage efficiency to achieve this. Adopting these strategies makes it possible to optimize nitrogen utilization and achieve sustainable agricultural productivity (Bai et al. 2019a). The amount of fertilizer used depends heavily on the properties of the soil and the agricultural environment. Only 35% of the nitrogen supplied to crops may be used over their life cycle; the remainder escapes to the environment via various processes and activities (Anas et al. 2020). Reducing nitrogen dosage and delaying leaf senescence can significantly enhance nitrogen usage efficiency and mitigate crop production losses. By reducing the amount of nitrogen applied, late-season leaf senescence can be induced, allowing the photosynthetic capability of the crop to be maintained for a longer time. This extended photosynthetic activity positively impacts productivity and output. Consequently, optimizing nutrient utilization and minimizing losses through these practices contribute to improved crop performance and increased yield, enhancing nitrogen usage efficiency (Anas et al. 2020).

In Australia, it has been observed that a reduction of 20% in nitrogen fertilizer application can be achieved without negatively impacting crop production (Anas et al. 2020). This indicates the potential for optimizing nitrogen fertilizer usage while maintaining productivity levels. Similarly, integrated management practices in China can contribute to adopting more efficient nitrogen fertilizer use. By implementing sustainable agricultural techniques and adopting appropriate nutrient management strategies, it is possible to achieve optimal nitrogen application rates that support crop growth while minimizing unnecessary nitrogen usage. These practices aim to balance productivity and

environmental sustainability. Reports from various locations and nations indicate that reducing nitrogen application has the potential to enhance nitrogen utilization efficiency. However, it is essential to consider that several factors influence the outcome, including agronomic characteristics, soil fertility, management practices, and production potential. These factors interact and contribute to the overall efficiency of nitrogen utilization in agricultural systems. Therefore, adopting a holistic approach considering these variables is crucial for optimizing nitrogen management and achieving sustainable agricultural practices. By understanding the interplay of these factors, it is possible to develop targeted strategies that maximize nitrogen utilization efficiency while maintaining or improving crop productivity (Raza et al. 2018).

Nitrogen application rates can be determined by crop productivity and nutritional requirements. For example, in the case of 7-year-old *Coffea arabica* L. trees, maintaining productivity at optimal levels often requires the application of nitrogen at rates of up to 800 kg per hectare per year. However, it is important to note that the maximum yield, considering a relative production of 90%, was achieved with a nitrogen application of 415 kg per hectare. This demonstrates that carefully managing the nitrogen dosage makes it possible to achieve high productivity while optimizing nitrogen usage efficiency in *Coffea arabica* L. cultivation (Neto et al. 2011). Thus, it is crucial to adjust nitrogen application rates based on crop-specific requirements, soil conditions, and management practices to ensure efficient nutrient utilization and maximize crop performance. In this context, the official recommendation for nitrogen fertilizer application is 400 kg per hectare per year. This recommended rate is typically applied twice or four times throughout the growing season. (Termonen et al. 2020). Luo et al. (2018) showed that when plant density is high, 20% of nitrogen can be reduced without causing yield loss, and drip irrigation fertilizer can also be reduced.

Similarly, excessive utilization of phosphorus fertilizer is common in agricultural practices. This is primarily due to the perception that it enhances the yield of both straw and grains, thereby increasing the overall phosphorus content; however, this practice inadvertently decreases zinc content (Zhang et al. 2017a). Buerkert et al. (1998) pointed out that under the application rate of 13 kg/hectare of phosphorus, the total zinc absorption of millet increased while the zinc concentration decreased due to dilution rather than phosphorus-induced zinc deficiency. Therefore, the antagonistic relationship between phosphorus and zinc and the biomass growth improvement resulting in the dilution effect may affect zinc concentration. Ryan et al. (2008) reported similar findings that 20 kg of phosphorus/hectare reduced the zinc concentration of wheat grain by 30–40%. The authors attributed their observations to

reducing arbuscular mycorrhizal root colonization by 50%, which otherwise would have helped absorb nutrients with lower mobility, such as zinc. In a 16-year maize experiment, it was reported that due to phosphorus treatment, the number of spores and root colonization of maize roots decreased (Ortas and Islam 2018).

Furthermore, Zhang et al. (2017b) suggested that phosphorus application may have reduced the root uptake of zinc. Generally, grain zinc content decreases with increasing phosphorus application. The inhibition of zinc by phosphorus application, as well as the inhibition of iron and calcium concentrations to a lesser extent, is related to the increase in inositol hex phosphate content, exacerbating the deterioration of the nutritional quality of agricultural products.

In summary, to mitigate environmental damage and enhance agricultural productivity, it is advisable to reduce the usage of nitrogen and phosphate fertilizers. The negative environmental impacts associated with these fertilizers outweigh their benefits. Excessive application can lead to nutrient losses, water pollution, soil degradation, and disruption of nutrient balances. By adopting responsible and targeted fertilizer management practices, farmers can minimize environmental harm while still maintaining optimal crop yields. This approach involves optimizing nutrient application rates, considering crop requirements, utilizing precision farming techniques, and implementing sustainable soil and nutrient management strategies.

### Environmental impacts of excessive fertilizer use

Mineral phosphorus fertilizer is a conventional fertilizer that plays a crucial role in achieving high crop yields and addressing the global challenge of feeding a growing population. In 2005, the global consumption of phosphorus fertilizer amounted to approximately 14.5 million tons per year. However, projections indicate that this figure will increase to 22–27 million tons annually by 2050. This significant rise in phosphorus fertilizer usage has played a crucial role in facilitating the green revolution and improving food security. Looking ahead, future estimates suggest that by 2050, the demand for phosphorus in croplands will reach 4 million tons per year, while grasslands will require a higher range of 4–12 million tons per year to support agricultural productivity and meet global needs (Mogollón et al. 2018). However, during the last two decades, a substantial body of research has discussed the possibility that phosphorus stocks might run out in 70–300 years and that the peak of phosphorus use would happen around 2030 (Bindraban et al. 2020). The majority of phosphorus added to soils as mineral or organic fertilizers either binds to the soil and forms a residual phosphorus pool or is lost by leaching, runoff, and/or erosion and may

end up in water bodies, which may cause eutrophication (Conijn et al. 2018). Soil organic matter loss may worsen phosphorus leaching because microbial community changes brought on by phosphorus might modify microbial activity and carbon cycling rates (Chowdhury et al. 2017). However, when not leached, excess phosphorus may be retained by adsorption onto metal (ferrum, aluminium) hydroxides, carbonates, and 1:1-layer silicates or by cation bridging with organic compounds.

Fertilization efforts generate a large amount of phosphorus waste. For example, soil erosion and agricultural runoff waste 46% of total mined phosphorus, whereas animals waste 40%. On the other hand, human sewage and processed sludge only release 15% of phosphorus (Vasa and Chacko 2021). Due to point and non-point sources, freshwater phosphorus concentrations have recently grown by 75%. Proper sustainable phosphorus management in agricultural applications is required to minimize such enormous phosphorus losses to surface water bodies. Currently, physico-chemical techniques that employ metal salts to precipitate phosphorus and separate the precipitated sludge from extracting nutrients from wastewater are ineffective (Vasa and Chacko 2021). Furthermore, the safe disposal of this toxic waste is becoming increasingly difficult. Traditional approaches include separate procedures for removing nitrogen and phosphorus nutrients, which increase energy consumption and necessitate bigger land holdings. Furthermore, nutrient recovery and/or reuse have received little attention throughout the process (Sharma et al. 2019).

While conventional fertilizers have advantages in boosting crop yields, it is essential to note that they also come with certain disadvantages. Table 1 provides a summary of the hazards associated with the excessive use of fertilizers. According to the United States Environmental Protection Agency's Pesticide Program Office, the excessive use of conventional fertilizers brings several disadvantages. Firstly, these fertilizers may contain carcinogenic chemicals, posing potential risks to human health (Mirzaei et al. 2020). Secondly, inorganic fertilizers tend to accumulate salts, which hinder water absorption by plants and increase evaporation, resulting in plant wilting or drying (Liu et al. 2022a). Additionally, if rainfall occurs shortly after fertilizer application, the fertilizers can be washed away, contaminating nearby water bodies such as streams and ponds (Vasa and Chacko 2021). This contamination can have adverse effects as the fertilizers seep into the food chain, accumulating and impacting human health.

Furthermore, uncontrolled use of inorganic fertilizers can cause nutritional imbalances, hinder the absorption of other essential elements, contribute to soil acidification, and ultimately decrease crop yields. Many farmers' lack of

**Table 1** Hazards of excessive use of fertilizers

Hazard	Reason	References
Low fertilizer utilization rate	The utilization rate of nitrogen fertilizer is only 30–50% because of the volatilization and loss  The utilization rate of phosphate fertilizer is only 10–25%. Because of the active chemical activity of phosphoric acid, most phosphorus, after application in the soil, combines with zinc, magnesium, calcium, iron, aluminium, and other cations in the soil to form insoluble phosphate fertilizer	Whittaker et al. (2023)
Reduce vegetable and fruits quality	Crop nutrition is not solely dependent on nitrogen, phosphorus, and potassium but also requires other essential elements such as calcium, iron, zinc, selenium, and various trace elements. However, chemical fertilizers typically have a relatively simple composition, lacking the diverse nutrients crops need. Consequently, prolonged reliance on chemical fertilizers can lead to soil nutrient imbalances, making it easier for crops to experience malnutrition. This, in turn, hampers the synthesis and conversion of nutrients within the crops, hindering their overall growth and development	Fang et al. (2021), Iqbal et al. (2020)
Hazardous to human health	A large amount of chemical fertilizer is easy to make the nitrate content in vegetables exceed the standard, and nitrite and amine combined to form N-nitrite compounds is a potent carcinogen	Fang et al. (2021)
Profound income loss to farmers	Most farmers, around 80%, continue to apply fertilizers based on traditional experience without considering the specific characteristics of different fertilizers. This leads to adopting simplistic fertilization methods such as “flushing fertilizer with water” or a “one blast” approach without careful consideration. As a result, one-third of farmers in the country tend to overfertilize their crops, resulting in increased input costs for farmland. While grain production may have increased; as a result, there is a growing concern regarding increased production without a corresponding increase in income. In certain areas, the excessive and prolonged use of chemical fertilizers only raises costs without improving yields, leading to lower-quality agricultural products and slower or even diminished farmer income	Vejan et al. (2021), Yang et al. (2020)
Affect crop quality	The excessive use of single-element fertilizers in large quantities hinders crops’ effective absorption of nutrients. Chemical substances like nitrogen, phosphorus, and potassium tend to accumulate and consolidate in the soil, leading to the buildup of various salts. This accumulation results in soil nutrient imbalances, elevated levels of harmful heavy metals, and excessive harmful bacteria in certain land areas, surpassing acceptable standards. Consequently, soil properties deteriorate, and the conversion and synthesis of vital substances within crops are hindered, leading to a decline in the quality of agricultural products. The overuse of chemical fertilizers also adversely affects the growth characteristics of fruits and vegetables, making them more susceptible to rot and unsuitable for proper storage	Yang et al. (2020)
Threat to food security and agricultural products	Excessive use of chemical fertilizer is easy to make crops lodging, and once lodging occurs, it will inevitably lead to grain production reduction and threaten food security. Excessive use of chemical fertilizer is also prone to diseases and pests. Excessive nitrogen fertilizer will weaken the resistance to pests and diseases of crops and thus increase the number of pesticides for pest control, directly threatening food safety. Once the consumption of contaminated agricultural products, it will pose a severe threat to human health, causing poisoning and other diseases	Vasa and Chacko (2021)

Using chemical fertilizer can lead to several hazards, including low fertilizer utilization rate, reduced crop quality, human health hazards, severe income loss to farmers, crop quality deterioration, and threats to food and agricultural product security

soil evaluation before fertilizing results in long-term reliance on inorganic fertilizers, leading to deficiencies in secondary and micronutrients in both soil and crops. Moreover, relying solely on inorganic fertilizers reduces the organic matter content in the soil, exacerbating soil acidity (Giri et al. 2023). These issues highlight the need for sustainable and balanced fertilizer practices to mitigate

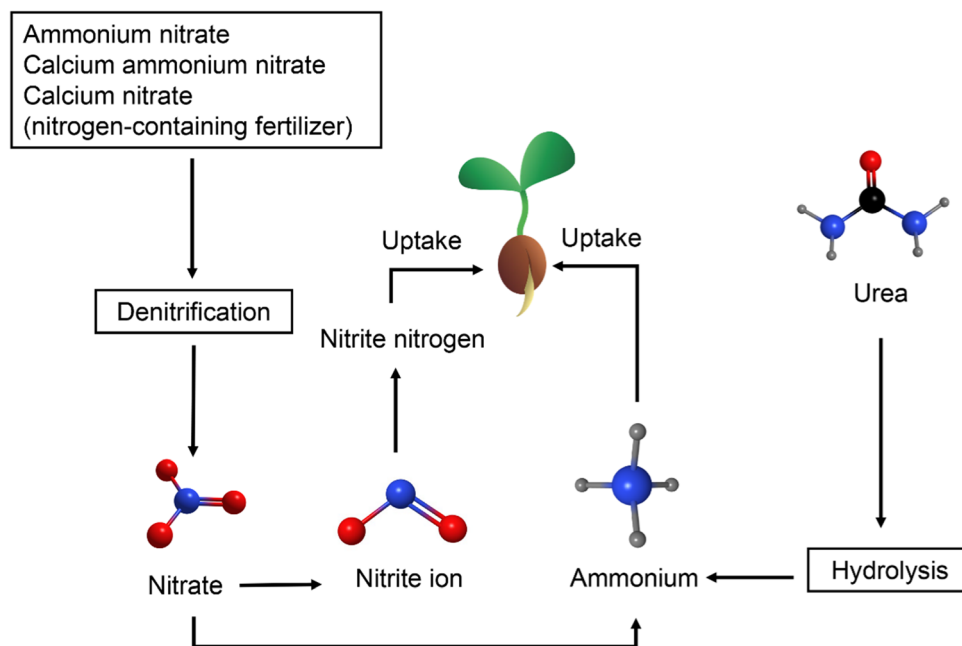
the negative consequences of excessive use of conventional fertilizers.

### Negative effects on soil health and biodiversity

Traditional fertilizers are available as granules or solutions with the same content. They are less expensive than organic fertilizers and have a faster impact since they



**Fig. 3** Mechanism of nitrogen fertilization in the soil. Urea hydrolyzes into the form of ammonium nitrogen, which acidifies the soil. In converting ammonium nitrogen to nitrate nitrogen (called nitrification), a hydrogen ion is released, resulting in soil acidification. This can be avoided by using nitrate nitrogen directly



dissolve rapidly in water. Phosphorus fertilizers, on the other hand, such as mono-ammonium phosphate, diammonium phosphate, and triple superphosphate, include insoluble chemicals that make them difficult to dissolve in water (Basavegowda and Baek 2021). Over-fertilization is the most prevalent hazard linked with these fertilizers. It can cause water contamination (Lv et al. 2020), crop buildup (Jagdeep and Brar 2022), plant growth inhibition (Jagdeep and Brar 2022), leaf burning, and increased susceptibility to pests and diseases (Okey-Onyesolu et al. 2021).

Furthermore, it can deplete soil fertility, promote soil water loss, raise field salinity, and result in the loss of organic matter and critical organisms that contribute to soil quality, depriving plants of necessary nutrients (Dimkpa et al. 2023). Overuse of fertilizers can also lead to soil pollution problems. Most commonly used carbon fibers dissipate into the atmosphere or surface water bodies, causing severe environmental issues (Singh et al. 2017). Excessive phosphorus fixation in soil, for example, produces chemical connections with other elements such as calcium, magnesium, aluminum, iron, and zinc that plants cannot absorb. Similarly, nitrogen is largely inaccessible as it forms ammonia, nitrous oxide emissions, or nitric oxide in runoff (Raliya et al. 2018).

Around 80–90% of phosphorus and 40–70% of nitrogen applied to crops are lost through runoff or transformed into geological formations, resulting in their removal from the agricultural system (Karthik and Maheswari 2021). If this nutrient loss continues, the phosphorus supply can be depleted in a few years. Overuse of inorganic fertilizers such as nitrogen, ammonia, nitrous oxide, nitrogen dioxide,

phosphorus, and potassium has long been a significant challenge in agriculture, as these fertilizers are washed away by runoff, causing eutrophication, and potentially leading to heavy metal contamination in soil, water, and air, posing a severe threat to the environment and human health (Basavegowda and Baek 2021). As shown in Fig. 3, there are many forms of nitrogen fertilizer. The dry-grown water spinach does not like ammonium nitrogen but prefers nitrate nitrogen (Bai et al. 2019b). Urea, which farmers often use, hydrolyzes to form ammonium nitrogen. Excessive application of ammonium nitrogen leads to excess ammonium salt, and vegetables are easy to soften and fall. Switching to a precise application of nitrate nitrogen helps vegetables grow and allows the excess ammonium nitrogen to be used slowly (Bai et al. 2019b). Another big difference between nitrate and ammonium is that ammonium acidifies the soil, whereas direct nitrate use raises soil pH. In converting ammonium nitrogen to nitrate nitrogen (called nitrification), a hydrogen ion is released, resulting in soil acidification. This can be avoided by using nitrate nitrogen directly (Klimczyk et al. 2021).

In recent times, chemical nitrogen fertilizers have become increasingly popular. However, their excessive use has been identified as a significant contributor to soil acidification. This process is often accompanied by decreased phosphate availability, reduced biodiversity, diminished productivity, and aluminum toxicity in the soil (Guo et al. 2019). As a result, an examination of the utilization of animal manure to improve soil nitrogen fixation and assist in reducing soil acidity has been done. According to Wang et al. (2019a), animal manure stimulates non-biological and biological nitrogen fixation, attributable to

increased carbon effectiveness and soil microbial activity at higher soil pH values.

On the other hand, long-term usage of animal dung has been shown to promote soil aggregation. Large aggregates will develop in continually fertilized soils, affecting the stability of soil aggregates (Guo et al. 2018). Because animal feed has a high salt concentration in the feeding system, sodium ions from feces function as dispersants, lowering aggregate soil stability (Guo et al. 2019). This increases the danger of soil salinization, particularly in humid locations like southern China. However, aggregate stability rises significantly in locations with consistent rainfall because soluble potassium and sodium ions are easily leached away under high rainfall and collect less in these areas. These nutrients continue to permeate surrounding water flows and can cause groundwater contamination, a negative consequence that must be recognized (Guo et al. 2019).

Soil organic matter greatly affects soil health, fertility, productivity, and the environment. Regulation of net primary production and soil organic matter cycling by fertilizer application of nutrients is undoubtedly advantageous for soil health in low-fertility habitats (Bruno et al. 2015; Lin et al. 2023a). However, soil health will deteriorate in many positive ways, including improving soil structure, increasing soil carbon storage, and crop plants' capacity to hold water and absorb nitrogen, if soil organic matter levels continue to decline over time as a result of soil mineralization by microorganisms and/or other losses (like leaching and soil erosion) (Sofa et al. 2020). Because microbial carbon and nitrogen cycles are fundamentally linked, and soil capacity and nitrogen mineralization in soils are closely correlated, management practices resulting in soil organic carbon losses significantly impact how much nitrogen can be stored in soils. So, crop yield is effectively harmed when soil organic matter is lost (Whittaker et al. 2023). The mean recovery of a single application of nitrogen-15 fertilizer in aboveground sections of crops at all locations was reported to be 5.7–7.1% in the five following growing seasons (excluding the crop fertilized with nitrogen-15). Therefore, a cropping system's first crop's average nitrogen-15 fertilizer recovery rate was 44% (Whittaker et al. 2023), and in the first five harvests, there was an overall recovery of nitrogen-15 fertilizer of around 50%. The remaining 50% of nitrogen-15 fertilizer would contribute to a sizable soil nitrogen pool, some of which may be lost from the cropping system, assuming that nitrogen-15 in roots had diminished by the sixth growing season (Su et al. 2018). Soil organic carbon will influence crop yields and nitrogen losses to the environment since nitrogen is bonded to capacity in soil organic matter, which is not only the primary source of nitrogen for crops but also

the main sink of nitrogen fertilizer input in current cereal cropping systems (Quan et al. 2020).

There is a growing interest among scholars in minimizing fertilizer usage. Several studies have demonstrated that implementing a moderate reduction in fertilizer application can effectively enhance fertilizer efficiency without compromising crop yields (Guo et al. 2021). This is because the use of fertilizers has exceeded the actual needs of agricultural production, and due to infiltration into aquatic environments and atmospheric emissions, it is even lost from the crop-soil system and cannot be reused by crops, resulting in higher environmental costs. Therefore, there is still much room to reduce fertilizer use. To reduce fertilizer effectively, it is crucial to identify the key factors influencing fertilizer use. From a macro perspective, the use of fertilizers is related to the country's economic development level (Takeshima et al. 2017). It grows fastest in developing countries, while the decline in environmental quality has slowed economic growth. Micro-level related research is comprehensive. More and more researchers are focusing on the key factors affecting farmers' use of fertilizers, mainly including individual characteristics (Fang et al. 2021), market reasons, and government policies (Yang et al. 2020). These studies provide substantial empirical evidence for finding ways to reduce fertilizer consumption.

In summary, fertilizers play a crucial role in modern agricultural production, but their production, especially high-grade phosphate rock and mineral fertilizers, requires significant energy consumption. Excessive use of chemical fertilizers increases production costs and leads to nitrogen emissions and environmental pollution. To address these challenges, researchers are exploring the potential of biofertilizers derived from biological waste as alternative fertilization sources. Additionally, phosphorus recycling is gaining attention as a future trend in sustainable agriculture. These efforts aim to reduce dependence on chemical fertilizers, promote environmental sustainability, and explore innovative solutions for effective and eco-friendly agricultural nutrient management.

## Biochar production and phosphorus loading

### Biochar production methods

Biochar has gained significant popularity and widespread application in various fields, particularly agriculture. The widespread adoption of biochar is primarily attributed to biochar's user-friendly nature, abundant feedstock availability, and production cost-effectiveness (Osman et al. 2023; Osman et al. 2022). This section examines various biochar production techniques and factors influencing the

final product's quality. Biochar can be derived from a range of thermochemical processes. Of these processes, including pyrolysis, gasification, and low-temperature carbonization (such as torrefaction and hydrothermal carbonization), pyrolysis stands out as the most commonly employed technique for producing biochar from diverse feedstocks (Farghali et al. 2022; Osman et al. 2022). Pyrolysis is a thermochemical process that triggers biomass degradation under constant heating at a specified rate in an inert environment by supplying nitrogen or carbon dioxide gas to the reactor (Yadav and Jagadevan 2019).

Biomass combustion occurs in the reactor at a controlled rate when a low oxygen concentration is injected into it, and this has no adverse effects on the pyrolysis procedure. The energy from the combustion products is used to raise the temperature, which lowers the process's overall energy requirement. It is important to note that allothermal and autothermal pyrolysis are the terms used to describe the process in an inert and low-oxygen environment (Ferreira et al. 2020). It has been suggested that a small amount of oxygen can be added to the reactor to make the fast pyrolysis process more energy-efficient. This would enable oxidative fast pyrolysis, which would help to reduce the high energy demand needed to reach pyrolysis temperature and the energy required for effective biomass degradation. Recently, Fawzy et al. (2021) designed a thermodynamic model with the use of the Advanced System for Process Engineering (ASPEN Plus) software and concluded that the slow/intermediate pyrolysis of olive tree pruning residues was self-sustaining, and there is an excess of energy available.

Pyrolysis can be divided into four groups, including slow pyrolysis, intermediate pyrolysis, fast pyrolysis, and flash pyrolysis. Biochar produced via either method can be referred to as pyro-char or biochar. Arauzo et al. (2020) stated that pyrolysis affects feedstock particle size and diffusion mechanism. The categorization of the process is based on the heating rate, operating temperature, retention time, and feedstock size (Patel et al. 2020). According to Zhang et al. (2019a), the slow, fast, and flash pyrolysis temperatures are 300–700 °C, 400–800 °C, and 800–1000 °C, respectively. The heating rates of the processes are 0.1–1 °C, 10–200 °C, and above 1000 °C per second, while the retention times of vapors are more than 600–6000 s, 0.5–5 s, and below 0.5 s. The size of biomass particles for slow pyrolysis (5–50 mm) is larger than for fast (< 3 mm) and flash pyrolysis (< 0.2 mm).

The operating temperature of intermediate pyrolysis lies between slow pyrolysis and fast pyrolysis. Intermediate pyrolysis can be categorized under slow pyrolysis, and both are often the focus of studies for biochar production (Fawzy et al. 2021). Intermediate pyrolysis is conducted at temperatures between 400 and 650 °C at a rate of 1.67–5

°C per second for a residence time of 60–900 s for a biochar yield of 15–25% (De Jesus et al. 2020). Slow pyrolysis has the highest biochar yield, followed by intermediate, fast, and flash pyrolysis. Biochar accounts for 35, 20, and 12% of the final product produced in slow, fast, and flash pyrolysis, respectively (Patel et al. 2020; Zhang et al. 2019b). The trade-off for the shorter reaction time in intermediate pyrolysis compared to slow pyrolysis is the reduced biochar composition due to increased bio-oil production. Intermediate pyrolysis is also advantageous with the higher flexibility for moisture content of the feedstocks than slow pyrolysis (De Jesus et al. 2020).

Due to the different operating conditions, the composition of condensable and incondensable gaseous, liquid, and solid products differs significantly. According to Font (2018), incomplete decomposition is ensured at pyrolysis temperatures below 400–500 °C and a heating rate not exceeding 20–50 °C per min, facilitating biochar production. When the heating rate exceeds 200 °C per min, liquid products will predominate. This is because the formation rate of liquid products from gas decomposition and polymerization dramatically exceeds that of biochar. Since the biochar-producing reaction is limited to a slow rate, more gaseous products are produced at temperatures up to 800–900 °C and heating rates greater than 200 °C per min. The composition was found to vary significantly with the experimental conditions and feedstock composition. Yadav and Jagadevan (2019) explained that a slow heating rate and longer retention time of vapor in the reactor aid in completing the second pyrolysis stage, resulting in a higher biochar yield in slow pyrolysis.

Furthermore, the definition of the operating conditions could differ in a wide range of literature. For example, Adelawon et al. (2022) acquired 38.40, 33.18, and 32.44% biochar in slow, fast, and flash pyrolysis where the final temperature of 600 °C was achieved at a rate of 30, 150, and 100 °C per min for 30, 10, and 3 min, respectively. The higher yield in the fast and flash pyrolysis could be attributed to the long residence time favoring the secondary pyrolysis stage.

Moreover, according to Font (2018), the primary reaction is a reactive process involving raw materials that can decompose or react with oxygen, carbon dioxide, and water. The products of the initial reaction serve as reactants for the subsequent reaction. Multiple primary and secondary reactions can occur concurrently, competitively, or sequentially, resulting in intricate mechanisms during pyrolysis. Yadav and Jagadevan (2019) categorized pyrolysis into two stages, where the first stage involves the removal of water, decarboxylation, and dehydrogenation, while the second stage involves the thermal cracking of large molecules to produce biochar, methane, carbon monoxide, and carbon dioxide. Yaashikaa et al. (2020) and

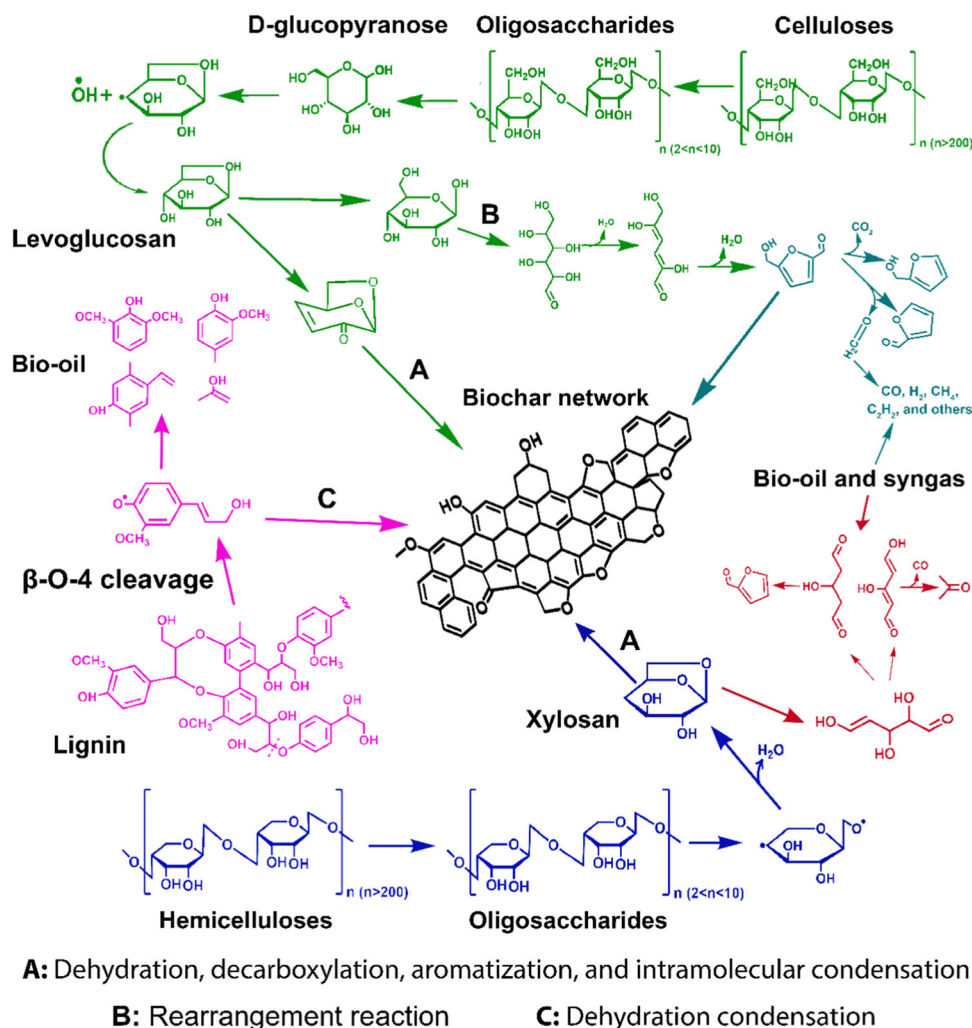
Ghodake et al. (2021) elaborated on the biochar formation mechanism of three essential components of biomass, including hemicellulose, cellulose, and lignin in pyrolysis, as previously proposed in other studies. Figure 4 represents the three mechanisms, as shown below.

Lignin has a relatively straightforward mechanism compared to hemicellulose and cellulose, where biochar is formed from the free radicals released during the breaking of  $\beta$ -O-4 linkage in lignin degradation. Literature showed that protons are emitted from organic species such as phenolic compounds due to the cleavage of O–H and C–H bonds. The free radicals accept the protons to produce various organic compounds, including vanillin, syringol, catechol, and 2-methoxy-4-methyl phenol in bio-oil. During the occurrence of this reaction, chain propagation takes place when free radicals travel in the organic species and ends when the collision and fusion of two free radicals occur to achieve molecular stability, forming a biochar network (Ghodake et al. 2021; Yaashikaa et al. 2020).

The biochar production pathway in the pyrolysis of hemicellulose differs significantly from that of lignin. Pyrolysis of hemicellulose begins with depolymerization, followed by oligosaccharide generation. Glycosidic bonds are the primary linkage between xylans in the hemicellulose structure. Intramolecular rearrangement reactions produce 1,4-anhydro-D-xylopyranose. The compound is then further converted to a complex and dense biochar network. The rearrangement reactions could include water removal, decarboxylation, aromatization, and intramolecular condensation. 1,4-anhydro-D-xylopyranose may degrade to form bio-oil and syngas (Yaashikaa et al. 2020). The pyrolysis mechanism of cellulose also produces oligosaccharides at the initial stage of depolymerization. However, the oligosaccharides are converted to d-glucopyranose when the glycosidic bonds break.

Furthermore, levoglucosan is an intermediate product that undergoes intramolecular rearrangement reactions during cellulose pyrolysis. Biochar production from cellulose involves a series of steps, including desiccation,

**Fig. 4** Pyrolysis products formation mechanism from biomass into biochar and various by-products. The biochar formation mechanism depends on the feeding materials, namely lignin, cellulose, and hemicellulose. Biochar formation from lignin is initiated by the cleavage of  $\beta$ -O-4 linkage, forming free radicals that combine with protons released from O–H and C–H cleavage to complete the reaction. Biochar production from hemicellulose is initiated with depolymerization, followed by oligosaccharide formation, rearrangement, and biochar network formation. Biochar production from cellulose involves oligosaccharide formation, rearrangement, exsiccation, water removal, aromatization, decarboxylation, polymerization, intramolecular condensation, and further intramolecular rearrangement reactions to produce biochar. The degradation of intermediate products generates bio-oil and syngas as by-products





water removal, aromatization, decarboxylation, polymerization, intramolecular condensation, and further intramolecular rearrangement reactions. It should be noted that these intermediate products can also degrade under specific pyrolysis conditions, forming bio-oil and syngas. The initial stage of the process is akin to slow pyrolysis, where the raw materials undergo disintegration and charring (Ghodake et al. 2021). Like fast pyrolysis, volatile compounds are removed concurrently with forming organic compounds in the second stage.

Gasification is carried out at a higher temperature range, reported as 450–1200 °C, 650–900 °C and 800–1000 °C by Zhang et al. (2019a), Yaashikaa et al. (2020), and Ren et al. (2020), respectively. Specifically, the operating temperature range is 450–650 °C, 1000–1200 °C, and more than 1200 °C for fixed beds, fluidized beds, and entrained flow gasifiers (Zhang et al. 2019b). Unlike pyrolysis, syngas comprising carbon monoxide, carbon dioxide, methane, hydrogen, and hydrocarbons are gasification's primary product. This is because partial oxidation of biomass is favored with adequate oxygen supply and relatively higher reaction temperature. Higher temperatures in gasification hinder the formation of methane, hydrocarbons, and carbon dioxide while facilitating the generation of hydrogen gas and carbon monoxide (Yaashikaa et al. 2020). Production of hydrogen gas can be further enhanced by supplying steam to the process to ensure a high ratio of hydrogen gas to carbon monoxide (Ren et al. 2020).

The gasification process proceeds sequentially. Initially, the removal of water content takes place in the drying phase at a temperature of 150 °C. This is followed by releasing volatiles, primarily hydrogen gas, through combustion (Ren et al. 2020). While the desired gasification product is syngas, the reactions also generate liquid tars and biochar. It should be noted that biochar production is relatively limited in gasification, resulting in lower yields compared to pyrolysis. On a dry basis of biomass, the biochar yield typically ranges between 5 and 10% (Yadav and Jagadevan 2019).

Torrefaction is an alternative and widely used method for biochar production, which is recognized for yielding higher outputs than traditional biomass pyrolysis. The biochar yield reaches approximately 70% through biomass torrefaction, enabling efficient biomass conversion into biochar. Furthermore, this process retains around 90% of the energy present in the original biomass material (Chen et al. 2018a). Additionally, the resulting torrefied biochar exhibits properties and energy density similar to coal (Akbari et al. 2020; Choo et al. 2020). Dry torrefaction and pyrolysis share similarities as they both occur in an inert environment to avoid biomass oxidation and enhance the production of solid products. Dry torrefaction, known as mild or low-temperature pyrolysis, operates at lower

temperatures than conventional pyrolysis. The processing temperature typically ranges between 200 and 350 °C at atmospheric pressure. The heating rate during dry torrefaction is usually kept below 50 °C per min to maintain controlled conditions. The process can vary from 30 min to several hours, depending on the specific requirements (Akbari et al. 2020; Choo et al. 2020; Yek et al. 2021).

The process is called oxidative torrefaction when a low concentration of oxygen gas is supplied to the reactor. The limited oxygen supply in a torrefaction reactor serves the same purpose as in autothermal pyrolysis. One advantage of oxidative torrefaction is the thermochemical treatment's shortened duration and higher energy efficiency. However, this feature may not be desired for a solid biofuel application due to the lower energy-mass co-benefit index and higher heating value (Zhang et al. 2019c). As described by Choo et al. (2020), the reduction of the energy demand of the biochar production process is realized with the utilization of heat produced from biomass combustion while reacting with oxygen gas. The drawback is the increase of unwanted gaseous products, including carbon monoxide and carbon dioxide, as well as liquid products, such as acetic acid, phenol, and water.

Hydrothermal processes include hydrothermal carbonization, hydrothermal liquefaction, and hydrothermal gasification. However, only hydrothermal carbonization produces biochar as the primary product. Slow pyrolysis and hydrothermal carbonization are similar processes that can produce higher solid fractions with better efficiency when compared to other thermochemical processes. In hydrothermal carbonization, water is used as a reaction medium, reactant, and solvent at supercritical conditions. The resulting product from hydrothermal carbonization has higher moisture content than the other thermochemical carbonization processes. Biomass sources of low moisture content require higher capital costs of hydrothermal process and torrefaction. Notably, the cost of the dryer accounts for a significant percentage of the overall capital cost in the dry biomass thermochemical process (Akbari et al. 2020), and hence, hydrothermal carbonization is preferred for high moisture-content feedstock and the exclusion of drying in the biomass preparation step (Masoumi et al. 2021).

Biochar produced via hydrothermal carbonization is referred to as hydrochar. Hydrochar production requires an input of subcritical water, and the mechanism consists of hydrolysis, water removal, decarboxylation, aromatization, and condensation, which happens in a high-water content environment (Arauzo et al. 2020; Babinszki et al. 2020; Langone and Basso 2020; Wang et al. 2018). Hydrothermal carbonization is a more environment-friendly and energy-saving thermochemical process for biochar production than pyrolysis (Wang et al. 2020a). The operating temperature

of hydrothermal carbonization lies in the range of 180–250 °C (Langone and Basso 2020; Wang et al. 2018) or 180–260 °C (Arauzo et al. 2020). However, the lower and upper boundaries can be extended to 150 and 350 °C (Chen et al. 2021; Wang et al. 2020a). Pressure implemented in the process lies in the range of 10–50 bar and 2–15 megapascal, as stated by Langone and Basso (2020) and Wang et al. (2020a), respectively.

Moreover, hydrochars exhibit various properties that distinguish them from pyro-char. In a study by Arauzo et al. (2020), the yield of biochar produced through hydrothermal carbonization in a batch reactor was compared to that of pyrolysis in a muffle furnace. The experiments were conducted at 216 °C, with retention times ranging from 2 to 4 h, using sewage sludge with 80% moisture content as the feedstock. The results showed that regardless of the retention time, the weight-based yield of pyro-char was 19% higher than that of hydrochar, which aligns with the findings of Huang et al. (2022a; b). The findings from Arauzo et al. (2020) and Huang et al. (2022a; b) indicate that pyro-char undergoes more significant modifications, as evidenced by pyro-char's higher fixed carbon content compared to hydrochar produced under the same temperature conditions. Additionally, the higher heating value of pyro-char surpasses that of hydrochar due to the formation of 5-hydroxymethylfurfural from cellulose and hemicellulose in the liquid phase of the biomass, along with the presence of an aromatic outer-layer structure (Arauzo et al. 2020).

In addition, a study by Liu et al. (2019) found that pyro-char derived from sawdust and wheat straw exhibited superior porosity compared to hydrochar. This difference in porosity was attributed to the higher processing temperatures employed during pyrolysis. Specifically, at temperatures of 500 and 700 °C, the specific surface area of sawdust and wheat straw-derived pyro-char ranged from 20.73 to 114.20 m<sup>2</sup>/g and 22.38–32.03 m<sup>2</sup>/g, respectively. In contrast, hydrochar exhibited a specific surface area of only 1.44 m<sup>2</sup>/g at 260 °C. Similarly, the total pore volume of sawdust and wheat straw-derived pyro-char was measured at 0.033–0.143 m<sup>3</sup>/g and 0.028–0.034 m<sup>3</sup>/g, respectively. These findings indicate that the pyro-char derived from sawdust and wheat straw possessed significantly higher porosity than hydrochar.

Moreover, Huang et al. (2022a; b) observed that pyro-char generally possesses larger pore diameters than hydrochar. The pore diameter for pyro-char ranged from 8.96 to 20.43 nm, while for hydrochar, it was recorded as 8.36–15.66 nm. However, pyro-char exhibits a smaller specific surface area and pore volume, measuring 1.40–4.97 m<sup>2</sup>/g and 5.37–11.62 × 10<sup>-3</sup> cm<sup>3</sup>/g, respectively. In contrast, hydrochar demonstrates higher values for specific surface area (3.14–7.75 m<sup>2</sup>/g) and pore volume

(3.67–12.55 m<sup>3</sup>/g). Based on the ultimate analysis results, the higher heating value of biochar falls within the range of 26.04–28.66 megajoules per kilogram. Hydrochar exhibits a higher heating value ranging from 26.61 to 29.37 megajoules per kilogram.

On the other hand, wet torrefaction is similar to hydrothermal carbonization, but a difference exists in the moisture level of feedstock and residence time. The former uses biomass with water content as compared to hydrothermal carbonization. Choo et al. (2020) stated that wet torrefaction is conducted at 180–260 °C under inert conditions. The process is considered to have lower energy intensity than dry torrefaction due to the lower operating temperature. Energy saving in wet torrefaction is facilitated via the omission of pre-drying of biomass and the introduction of subcritical water as a solvent, reactant, and reaction medium. The pressure of the process in the range of 15–160 bar was implemented in past studies (Yek et al. 2020). The residence time of wet torrefaction is usually longer than hydrothermal carbonization (Babinszki et al. 2020).

Babinszki et al. (2020) compared the fundamental properties of char produced from wet torrefaction and hydrochar produced from hydrothermal carbonization. Their findings revealed several dissimilarities between the two processes. Wet torrefaction generally exhibits higher volatile matter and ash content than hydrothermal carbonization. Conversely, hydrothermal carbonization yields a higher char content and fixed carbon content. Moreover, hydrothermal carbonization experiences a faster rate of thermal decomposition of biochar compared to wet torrefaction at similar temperatures. Despite these differences, there are instances where the terms “wet torrefaction” and “hydrothermal carbonization” are used interchangeably. To minimize costs and environmental pollution associated with hydrothermal processes such as hydrothermal carbonization and wet torrefaction, the authors suggested wastewater recycling. Similarly, Akbari et al. (2020) noted that using recycled wastewater in the wet torrefaction process leads to an increased mass yield of biochar while having a minimal effect on the higher heating value of the biochar. They further explain that introducing hot wastewater into the process through a recycle stream preheats the raw materials, reducing the overall energy requirement.

When comparing biochar produced from dry and wet torrefaction, it has been observed that wet torrefaction enhances the soil's water-holding capacity and the adsorption capacity of both polar and non-polar compounds, making it suitable for pollution reduction applications (Akbari et al. 2020). According to Chen et al. (2018a), biochar derived from wet torrefaction exhibits lower hydrophilicity than biochar from dry torrefaction.

This difference in hydrophilicity is attributed to the higher abundance of oxygen-loaded functional groups on the surface of wet torrefaction biochar, which enhances the hydrophilic properties of biochar. However, hydrochar and biochar from wet torrefaction retain a hydrophobic core due to their highly dense aromatic structure (Akbari et al. 2020). Furthermore, the thermochemical carbonization processes, including wet torrefaction, preserve the lignin structure, resulting in biochar with binding effects. This allows for producing pellets with higher hydrophobicity, density, abrasion resistance, strength, and compressibility compared to biochar derived from pyrolysis and dry torrefaction. In summary, slow pyrolysis, dry torrefaction, wet torrefaction, and hydrothermal carbonization are four thermochemical processes used to produce solid fuel. Table 2 summarizes the comparison between these biochar production methods, as discussed in the literature.

On the other hand, hydrothermal carbonization and wet torrefaction show promising potential for energy savings

and minimizing environmental impact. This is attributed to their lower energy consumption and the implementation of wastewater recycling practices. The information was a compilation of data from the recent works of literature (Akbari et al. 2020; Chen et al. 2021; Choo et al. 2020; De Jesus et al. 2020; Langone and Basso 2020; Patel et al. 2020; Wang et al. 2020a, b, c; Yadav and Jagadevan 2019; Yek et al. 2021; Yek et al. 2020; Zhang et al. 2019a, b, c, d).

The operating procedures and conditions of the chosen production method significantly influence the composition of biochar in the final product. Feedstock properties and desired biochar quality and quantity are essential considerations when selecting a production method. Apart from the effects of biomass sources on nutrient types and levels, such as nitrogen, phosphorus, and potassium, the operating conditions of thermochemical treatments also contribute to variations in biochar properties (Ippolito et al. 2020). Moreover, climate conditions and soil properties also

**Table 2** Biochar characteristics and production conditions from different thermochemical processes

Properties	Pyro-char and dry torrefied char	Hydrochar and wet torrefied char
Thermochemical carbonization and operating conditions	Slow pyrolysis (300–700 °C, 0.1–1 °C/second, 600–6000 s, 35% biochar yield) Intermediate pyrolysis (400–650 °C, 1.67–5 °C/second, 60–900 s, 15–25% biochar yield) Fast pyrolysis (400–800 °C, 10–200 °C/second, 0.5–5 s, 20% biochar yield) Flash pyrolysis (800–1000 °C, > 1000 °C/second, < 0.5 s, 12% biochar yield) Dry torrefaction (200–350 °C, < 50 °C/min, > 30 min, ~ 70% biochar yield) Gasification (Fixed bed: 450–650 °C, fluidized bed: 1000–1200 °C, entrained flow: > 1200 °C, sufficient oxygen supply, 5–10% biochar yield)	Hydrothermal carbonization (150–350 °C, 10–50 bar, inert/limited oxygen supply, subcritical water supply) Wet torrefaction (180–260 °C), 15–160 bar, inert, subcritical water supply)
Feedstock properties	Dry biomass Particle size often matters	Wet biomass
Higher heating value	Lower	Higher
Fixed carbon content	Lower	Higher
Ash content	Higher	Lower
Moisture content	Lower	Higher
Cation exchange capacity	Lower	Higher
Energy density	Lower	Higher
Hydrophobicity	Lower	Higher
Capital cost	Higher capital cost due to the pre-drying process	Lower with the omittance of dryer and recycling of wastewater

Four thermochemical carbonization processes aim to produce solid products with higher yields: slow pyrolysis, dry torrefaction, hydrothermal carbonization, and wet torrefaction. Hydrothermal carbonization and wet torrefaction are specifically designed to handle biomasses with higher moisture content than slow and dry pyrolysis. These two processes can be distinguished by their char properties and operating conditions. Dry torrefaction offers improved char yield compared to pyrolysis but still requires significant energy intensity compared to hydrothermal carbonization and wet torrefaction

contribute to biochar efficiency when applied in the soil as a fertilizer (Farhangi-Abriz et al. 2021; Osman et al. 2022). When a high dosing rate is used, particularly above 50 tons per hectare, opposite effects could be exerted on plant germination and early growth. However, a large dosage of biochar, typically 10–50 tons per hectare, is required as the nutrient level in biochar is inadequate for agricultural application. Investigating the effect of plant production under field conditions on nutrient use efficiency is as crucial as biochar properties, which are manipulatable with thermochemical carbonization operating conditions and feedstock characteristics. Ndoung et al. (2021) reported on the dependence of the macro- and micronutrients level in biochar-derived fertilizer on biomass sources, minerals and materials of enrichment, and pyrolysis conditions. Previous studies also show that adding biochar-based fertilizer to agricultural soil improves macro- and micronutrient levels. The positive effect on the overall nutrient level in the soil is caused by the concentration of nutrients in biochar during pyrolysis, the shifting of adsorption–desorption balance in soil that decreases nutrient fixation, the external sources of nutrients incorporated in biochar, including minerals, clays, and compost, and the prevention of nutrient leaching to groundwater. Phosphorus fixation in soil requires coexisting cations of aluminium, iron, silica, calcium, and magnesium (Piash et al. 2022).

Generalizing the effects of biochar application in soil should be avoided. Instead, thorough investigations should be conducted under field conditions, taking into account the specific properties of the soil and the biochar. It is crucial to determine the appropriate dosing rate based on actual field conditions (Osman et al. 2022). Works of literature show that the nutrient leaching in soil decreases when biochar is applied to soil, and this is triggered by the immobilization of the nutrients, especially nitrogen and phosphorus, and organic matter on the porous biochar surface (Stephen Joseph et al. 2021). Organic matter is immobilized by filling the pores on the biochar matrix surface, impeding microbial decomposition to produce nutrients. On the other hand, Farhangi-Abriz et al. (2021) studied the use of biochar derived from animal waste, wood waste, and crop residue produced at different pyrolysis temperatures on the crop field of wheat, maize, rice, and soybean when applied at different rates. They emphasized the effect of climate, biochar properties, soil texture, and soil pH on plant production. Specifically, biochar application in rice and soybean fields did not bring a remarkable positive effect, mainly caused by the differences in the required growing conditions. While legumes can carry out nitrogen fixation, using biochar in the legume field was found to have an inhibiting effect on nitrogen fixation.

Feedstocks for biochar production can be categorized into two primary types: woody and non-woody materials

(Jafri et al. 2018). The former category, woody feedstocks, primarily consist of forestry products. Conversely, non-woody feedstocks encompass various agricultural wastes such as crop residues, manures, poultry litter, food waste, and municipal waste. Additionally, pyrolysis can convert algal biomass with high lipid content, commonly used in liquid biofuel production, into nutrient-rich biochar. This biochar can benefit agricultural applications as algal biomass contains significant amounts of potassium, sodium, calcium, and magnesium (Sarwer et al. 2022).

Previous studies have revealed the importance of selecting suitable biomass sources to produce for specific applications. According to Amalina et al. (2022), lignin has a higher degradation temperature than cellulose and hemicellulose, reaching up to 500 °C. In contrast, cellulose and hemicellulose degrade at 375 and 350 °C, respectively. During rapid volatilization above 300 °C, the presence of oxygen-loaded groups significantly contributes to mass loss. This process leads to a greater reduction in the oxygen-to-carbon ratio (O/C) compared to the hydrogen-to-carbon ratio (H/C). Consequently, lignin has the lowest initial volatile content and the least amount of oxygen-containing groups and is more suitable for producing high-biochar yield.

Moreover, Jafri et al. (2018) reported that non-woody biomass lacking lignocellulosic compounds possessed lower calorific value, density, and higher ash and water content. Ash content and nutrient availability in biochar have a positive correlation (Ippolito et al. 2020), and both parameters could be enhanced by the high composition of lignin in biomass, which is not necessarily beneficial to obtain high carbon content in the biochar (Wan et al. 2020). Under similar heat treatment conditions of biomass, biochar properties primarily depend on the feedstocks' lignin content. However, the distinctions between different biochars become less prominent as the treatment temperature exceeds 500 °C (Janu et al. 2021). In the experiment conducted by Pariyar et al. (2020), pine sawdust, rice husk, food waste, poultry litter, and paper sludge were used as the feedstocks to produce biochar at pyrolysis temperatures of 350, 450, 550, and 650 °C at 10–12 °C per min for 40 min. They reported the highest ash content in biochar produced from poultry litter and paper sludge. In contrast, sawdust, rice husk, and food waste-derived biochar possess better carbon fixation values at 650 °C.

In the research by Kalina et al. (2022), hemicellulose- and cellulose-based biomass, which are oat and corn, were found to be more vulnerable to temperature effects than lignin-based woodcuts. Regarding degradation temperature, they stated that the value lies at 220–315 °C and 315–400 °C for hemicellulose and cellulose, respectively. Lignin degradation occurs at a broader range of temperatures between 160 and 900 °C, attributed to the



heterogeneous and complex structure. However, biochar productivity is impeded at higher pyrolysis temperatures despite the positive effect on chemical and microbial degradation resistance. According to Kalina et al. (2022), using lignin-based biomass sources could enhance the composition of carbon and aromatic groups in biochar and the material stability, porosity, acidity, cation-exchange capacity, and specific surface area.

Aromaticity and minerals in biochar are essential factors in determining the lifespan of biochar. Han et al. (2018) revealed in their study that aromatic groups densify biochar structure resulting in better oxidation resistance and hence, more excellent stability of biochar. They also emphasized that, in addition to aromaticity, minerals, mainly silicon, effectively reduce biochar oxidation through the interaction between silicon and amorphous carbon. Determining hydrogen-to-carbon and oxygen-to-carbon ratios via ultimate analysis, oxidation resistance with proximate analysis, thermal degradation techniques, and carbon dioxide emission using incubation and modeling experiments are helpful in the biochar stability evaluation (Fawzy et al. 2021). In the first method, the high stability of biochar is reflected by the low hydrogen-to-carbon and oxygen-to-carbon ratios, which are limited at 0.7 and 0.4, respectively, according to the international biochar initiative and the European biochar certificate (Farghali et al. 2022). In the oxidation resistance assessment, potent oxidizing agents, including hydrogen peroxide, potassium dichromate, and potassium permanganate, are used to remove labile carbon via oxidation, which is later quantified to evaluate the stability of biochar. Modeling is implemented to assess the biochar stability by unitizing the mineralization data in the incubation of biochar under the field conditions with long experiment duration to easily distinguish between labile and recalcitrant carbon.

The thermochemical carbonization operating temperature significantly influences the characteristics of biochar. Thus, scientific research has extensively studied and optimized it to obtain desired biochar properties. Typically, higher operating temperatures result in lower mass yields of biochar, as gasification and liquefaction processes are favored. However, the energy density of biochar is notably increased at higher temperatures. In addition to affecting the composition of the solid product, operating temperature plays a crucial role in heavy metal adsorption. Mainly, temperatures exceeding 700 °C can decrease the cation exchange capacity, which is closely linked to the adsorption and retention of heavy metal and nutrient cations (Fawzy et al. 2021). Higher pyrolysis temperature enriches biochar with heavy metals due to volatilization, but their thermal stability affects the composition of heavy metals (Raj et al. 2021). Copper concentration in the sewage-derived biochar was found to drop when the pyrolysis

temperature was raised from 350 to 450 °C, indicating the thermal instability of the element at the temperature range.

Furthermore, incomplete combustion during thermochemical carbonization results in polycyclic aromatic hydrocarbon (PAH) formation. Lighter and heavier polycyclic aromatic hydrocarbons are produced below and above 500 °C, respectively. However, polycyclic aromatic hydrocarbon concentration is generally lower in slow pyrolysis than at higher heating rates, such as fast pyrolysis and gasification. (Fawzy et al. 2021). Based on the study by Raj et al. (2021), all low-molecular-weight polycyclic aromatic hydrocarbons were removed via pyrolysis. Medium and high-molecular-weight polycyclic aromatic hydrocarbons, except for benz[a]anthracene, chrysene, and benzo[a]pyrene, were eliminated from the pyrolysis of sewage sludge. The thermal decomposition of the compounds or conversion reaction to form oil and gases causes the elimination of the polycyclic aromatic hydrocarbons during pyrolysis. Their study also shows that the total polycyclic aromatic hydrocarbon reduction increases in the following order of pyrolysis temperatures: 400, 450, 500, and 350 °C. According to Chen et al. (2019), the total concentration of polycyclic aromatic hydrocarbons in a sewage sludge-derived biochar decreased with the pyrolysis temperature depleted from 15.49 to 1.48 mg/kg when the temperature increased from 400 to 700 °C. Although the operating temperature of the biochar production technique significantly influences the synthesis of polycyclic aromatic hydrocarbons, feedstock type is also the pivotal factor in the concentration of polycyclic aromatic hydrocarbons in the final product (Fawzy et al. 2021).

Ortiz et al. (2020) studied the production of biochar from almonds and nutshells and reported the correlation between pyrolysis temperature and several properties of biochar, which includes biochar yield, hydrogen-to-carbon ratio (H/C), oxygen-to-carbon ratio (O/C) ratio, higher heating value, electrical conductivity, and pH. The negative effect of pyrolysis temperature and heating rate on the mass yield of biochar was elaborated on previously. Additionally, a reaction temperature below 302 °C favors the slow degradation of biomass instead of the fast decomposition that produces liquid and gaseous products, bringing about higher biochar yield. They also stated that wet biomass could yield greater biochar, although the experimental result did not observe the effect. At pyrolysis temperatures above 500 °C, oxygen-containing groups are readily removed, causing the hydrophilicity of biochar to drop beside the increase in pore size and surface area, which favors the adsorption of inorganic pollutants on biochar (Enaime et al. 2020).

Pariyar et al. (2020) investigated the impacts of pyrolysis temperature on biochar aromaticity and polarity. They reported the significant influence of pyrolysis temperature

on biochar's morphology, physiochemical properties, and mineralogical characteristics. Specifically, the surface area of sawdust- and rice husk-derived biochar was improved from 3.39 m<sup>2</sup>/g and 11.61 m<sup>2</sup>/g to 443.79 m<sup>2</sup>/g and 280.97 m<sup>2</sup>/g, respectively. In addition to the increased alkalinity observed in various biochars at higher temperatures, the cation exchange capacity tends to decrease. This finding is consistent with the research conducted by Das et al. (2021), who also reported the positive impact of pyrolysis temperature on total carbon content and bulk density. The increase in density can be attributed to the reduction in voids and the growth of aromatic structures. At the same time, the condensation process contributes to a higher degree of polymerization, resulting in high carbon content. Similarly, hydrochar yield is negatively affected by increasing hydrothermal carbonization temperature. Nakason et al. (2018) reported that the depletion in the hydrochar yield, hydrogen-to-carbon ratio (H/C), and oxygen-to-carbon ratio (O/C) to 9.3 and 0.2%, respectively, when the temperature was raised from 140 to 200 °C, because of dehydration and decarboxylation of biomass.

In summary, torrefaction and hydrothermal processes offer advantages in terms of cost-effectiveness and environmental friendliness compared to conventional slow pyrolysis processes. However, slow pyrolysis is preferred for producing biochar with higher porosity, which can be attributed to the higher processing temperature. It is important to note that the quality and composition of biochar produced in all thermochemical processes mentioned heavily rely on the operating temperature and characteristics of the biomass used. This is due to the similar mechanisms of degradation and decomposition involved in these processes.

### Phosphorus sources for biochar loading

Investigating phosphorus sources for enriching biochar is crucial for ensuring process effectiveness, cost efficiency, and environmental safety. Therefore, this section explores various phosphorus sources for loading biochar with phosphorus. The choice of feedstock strongly influences the phosphorus content in unloaded biochar. The high nutrient content of waste-based biomass, particularly in materials like municipal sludge and animal wastes, is widely recognized as a promising phosphorus source. Furthermore, utilizing waste-based biomass provides the additional advantage of assisting in waste management. Recent studies have explored the use of solid and liquid waste as sources of phosphorus. However, it is essential to note that the nutrient content of waste-based biomass can vary significantly depending on the specific sources employed.

Municipal or sewage sludges are considered phosphorus-rich biomass with higher phosphorus content than other biomasses. Based on the studies by Frišták et al. (2018) and Singh et al. (2022a; b), the concentration of phosphorus pentoxide in sewage sludge was reported as 34.68 and 24.6–32.0 g/kg, respectively, which also corresponds to the total phosphorus content of 15.14 and 10.74–13.97 g/kg. The phosphorus content differs from the stages of the sludge produced during wastewater treatment. Fermentation wastes also contain a high total phosphorus content; as Kim et al. (2018) reported, the total phosphorus concentration in the fermentation waste used in their study is 7.4 g/kg. Animal manures have a wide range of phosphorus content, which could be due to the differences in their diets and the storage conditions and duration compared to agricultural wastes that have a higher consistency (Green 2022). Zewide et al. (2018) reported that the total phosphorus content in cattle manure during Belg and Meher seasons is 13.74 and 11.9 g/kg, respectively. The difference is caused by the optimum pH, temperature, and moisture content that favor the breeding of microorganisms and manure decomposition. A higher decomposition rate could lead to a lower carbon-to-nitrogen ratio (C/N), which promotes nutrient release when applied in soil and increases soil alkalinity. Referring to the study by Adekiya et al. (2020), the total phosphorus content increases in the order of green manure, rabbit manure, pig manure, cow dung, and poultry manure with 5.2, 5.4, 8.0, 8.2, and 8.4 g/kg, respectively. The phosphorus content in the cow manure used by Afonso et al. (2021) to produce compost with wheat straw, hop leaves, and hop stem ash is 3.3 g/kg.

Compared to animal manures, lignocellulosic biomasses generally have lower total phosphorus content. For instance, the total phosphorus concentration in lignocellulosic biomass, such as corn stover, was reported to be 1.27 g/kg, with phosphorus pentoxide concentration removed during harvest is 2.9 g/kg (Battaglia et al. 2018). Phosphorus concentrations in wheat straw, hop leaves, and hop stem ash were measured at 1.0, 1.2, and 5.7 g/kg, respectively (Afonso et al. 2021). Ash had a higher phosphorus content than cow manure because the combustion process removed volatile matters and reduced the material mass. Similarly, the total phosphorus content in maize stover is 3.43 g/kg, which is lower than the biochar produced from biomass by 5.44 g/kg (Cao et al. 2021). The result indicates the positive effect of pyrolysis at 500 °C for 2 h on the total phosphorus concentration of the lignocellulosic material due to the mass loss via volatilization. Moreover, the digestate of fruits, vegetables, and agricultural wastes has lower phosphorus levels than livestock manure and sewage sludge (Tuszynska et al. 2021).

Phytoremediators, used for restoring polluted water affected by eutrophication, show promise in producing

phosphorus-enriched biochar due to their high nutrient content. This is supported by the findings of Cui et al. (2020a), who reported the total phosphorus content in wetland plants such as *Hydrocotyle verticillata*, *Myriophyllum spicatum*, and *Cyperus indica* as 7.77, 8.91, and 4.40 g/kg, respectively. These values are comparable to the phosphorus content found in livestock manures, which typically range between 3.3 and 13.7 g/kg. Utilizing phytoremediators to produce biochar-based fertilizers enables the reclamation of polluted water sources and the recycling of nutrients. However, the agronomic efficiency of these biochar-based fertilizers requires further validation through additional research conducted under field conditions.

When studying phosphorus bioavailability and plant uptake, the fraction of water-soluble phosphorus becomes a primary consideration. Ortho-phosphorus is the predominant form of phosphorus found in sewage sludge, which sets it apart from animal manures and plant residues that predominantly contain organic phosphorus (Buss et al. 2020). Consequently, sewage sludge is expected to exhibit higher extractability of phosphorus in the water. The presence of different phosphorus species in biomass can indirectly influence the extractable phosphorus availability of biochar. Additionally, thermochemical carbonization, particularly pyrolysis, can influence the solubility of phosphorus through phosphorus mineralization, thus contributing to the overall phosphorus dynamics. Rose et al. (2019) reported the total phosphorus concentrations in biochar derived from various feedstocks and produced at temperatures between 500 and 550 °C. The recorded values for cow manure, wheat chaff, poultry litter, papermill sludge, rice husk, sugarcane trash, sugarcane bagasse, sugarcane mill mud, and green waste were 7.1, 11, 21, 8.1, 1.5, 2.6, 3.1, 32, and 2.4 g/kg, respectively. The water-soluble phosphorus concentrations were measured at 1.0, 2.2, 4.9, 0.5, 0.6, 0.1, 0.1, 0.1, and 0.1 g/kg. In contrast, citric acid-soluble phosphorus concentrations were found to be 5.1, 3.3, 19, 5.4, 0.8, 1.0, 0.4, 13, and 1.0 g/kg, respectively. Formic acid-soluble phosphorus concentrations were recorded as 4.0, 3.6, 22, 5.4, 0.9, 1.2, 0.4, 14, and 1.1 g/kg, respectively. In studies conducted by Kim et al. (2018) and Yang et al. (2021a), the highest total phosphorus contents in biochar derived from phosphorus-rich biomass (fermentation wastes and pig carcasses) through hydrothermal carbonization and pyrolysis were recorded as 84.7 and 83 g/kg, respectively. Following closely are municipal sludge-derived biochar and hydrochar, with total phosphorus concentrations of 57.01 and 30.03 g/kg, as reported by Frišták et al. (2018) and Cui et al. (2020a), respectively. Animal manure, municipal sewage, and fermentation products are considered excellent sources for producing biochar-based phosphorus fertilizers compared to agricultural wastes. However, it should be

noted that organic fertilizers derived from these biomasses and their biochar still exhibit lower phosphorus availability compared to inorganic fertilizers such as triple superphosphate, which typically contains around 200 g/kg of total phosphorus. As a result, additional processes are often required to enhance the phosphorus content in biochar.

In recent studies, di-ammonium phosphate and potassium hydrogen phosphate solutions are commonly employed sources of phosphorus for loading lignocellulosic material-derived biochar. Potassium dihydrogen phosphate solution is a popular chemical used to load biochar with phosphorus via adsorption, which was investigated in the studies by Ahmad et al. (2018), Wu et al. (2019a), Li et al. (2020a), Nardis et al. (2022), Mihoub et al. (2022), and Arwenyo et al. (2022). On the other hand, Wali et al. (2020), Wali et al. (2022), and Suwanree et al. (2022) used di-ammonium phosphate as the enrichment source. Adsorption is a commonly employed technique to load biochar with phosphorus, and it often involves the use of liquid phosphorus sources. This method typically entails impregnating or immersing biochar in solutions that contain phosphates. In the study by Zhang et al. (2022a), a less common phosphorus source, solid red phosphorus, was used. The biochar loading process with red phosphorus relies on the reaction of phosphorus with water and oxygen present in the biomass to generate phosphates, which also release acids that reduce soil alkalinity and improve mineral-phosphate solubility.

When utilizing waste-based biomass to produce biochar-based phosphorus fertilizer, it is essential to consider various factors, including health and environmental considerations. These measures are crucial to ensure the safety and sustainability of the fertilizer production process. Vanotti et al. (2020) stated that evaluating products obtained through nutrient recovery from potentially toxic or contaminating wastes should be based on two critical criteria. Firstly, agronomic efficiency, which assesses the yield achieved per unit of phosphorus input, is crucial as it directly impacts the product's value. Secondly, contaminants in fertilizers must be carefully monitored to minimize environmental impacts. Specific limits for concentrations of polycyclic aromatic hydrocarbons, arsenic, lead, cadmium, and mercury have been established, with thresholds set at 4, 2, 10, 1, and 0.1 mg/kg, respectively (Osman et al. 2022). Due to lower heavy metal content, animal manures are less polluting than municipal and industrial wastes (Vanotti et al. 2020). However, antibiotics and antibiotic-resistance genes enter water and soil via solid and liquid animal wastes and organic fertilizers, negatively affecting micro and macro ecosystems (Tian et al. 2021a). Therefore, all possible pollution sources caused by applying waste-derived biochar-based phosphorus fertilizer shall be identified to avoid long-term effects.

Manure management shall be carefully carried out to minimize or avoid soil and water pollution. Available options for phosphorus recovery from animal manures are through the precipitation of struvite, newberyite, iron phosphate, and calcium phosphate (Vanotti et al. 2020). These products can be converted to or applied as inorganic phosphorus fertilizers for agricultural soil. Inorganic fertilizers could adversely affect soil structure and aggregation, soil properties, pH and nutrient balance, and important soil organisms (Roba 2018). Consequently, nutrient content depletion is occasioned by fixation, gas release, and leaching. Thermochemical carbonization of animal manures and sewage sludge is essential to stabilize or fix the toxic contaminants and remove the pathogens, thus lowering the leaching risk. Biochar-based organic fertilizer has become increasingly popular as the promising substitute for inorganic fertilizers, but studies suggest the simultaneous use of organic and inorganic fertilizers.

Lignocellulosic biomass has a lower risk of environmental pollution and health concerns than animal, industrial, and municipal wastes. Furthermore, biochar derived from lignocellulosic materials can be excellent water and soil remediation adsorbents. Therefore, wastewater can be used as a source of phosphorus to enrich lignocellulosic material-based biochar fertilizers. The phosphorus adsorption efficiency of biochar from wastewater depends on the surface functional groups and the porosity, resulting in tunable fertilizer properties.

Concerning soil remediation, heavy metal adsorption is positively affected by the phosphate release from biochar, leading to the secondary benefit of using biochar-based phosphorus fertilizer to reduce heavy metals in the exchangeable state from the soil. Heavy metal immobilization in soil could positively affect plant health and, consequently, consumer health. The role of biochar in immobilizing heavy metals was reported by Dang et al. (2019), where lead and zinc in the exchangeable form are lower by at least 50% while that of cadmium declined by at least 70%. Irfan et al. (2021) reported that biochar addition to soil could lower the uptake of heavy metals by plants. This is demonstrated by a significant decrease in the concentration of lead, cadmium, and chromium at the roots of maize, with reductions of approximately 79.08, 66.91, and 78.13%, respectively.

Specific functional groups on the biochar surface immobilize heavy metals in the soil. Referring to Palansooriya et al. (2022), biochar properties significantly impact the efficiency of heavy metal immobilization in soil. Increasing the concentration of oxygen-containing groups, including carboxyl, phenolic, and hydroxyl, that have a solid affinity for heavy metals allows better immobilization. Their study also emphasized the importance of high-concentration nitrogen-containing groups in

heavy metal immobilization. Phosphates, on the other hand, help remove cadmium, lead, zinc, and copper in the soil, in addition to the positive effects on microbial community in soil, which is supported by Sha et al. (2023) reported the effects of phosphorus-loaded biochar addition to mine soil. Heavy metals are immobilized by phosphates from phosphorus-loaded biochar via several mechanisms, including precipitation, electrostatic attraction, and complexation, where precipitation is the main pathway.

In conclusion, the utilization of waste-based biomass for biochar fertilizer production may face challenges due to the lower phosphorus availability compared to inorganic fertilizers, as well as the potential for secondary pollution resulting from the initial soil contaminant content in the biomass. Developing efficient organic phosphorus fertilizers that exhibit high phosphorus release capacity while maintaining a slow-release rate for long-term soil phosphorus supply is crucial. Hence, conducting a phosphorus fractionation study is essential to comprehend and optimize phosphorus's release dynamics from biochar. This will ensure the efficient utilization of biochar as a sustainable fertilizer.

## Phosphorus loading techniques and methods

This section explores the different techniques and methods for loading biochar with phosphorus. It is worth noting that previous studies have employed various classification methods, resulting in some variation in categorizing these techniques. The classification of biochar loading techniques can be approached from different perspectives, considering the mechanism of nutrient enrichment. In the study by Ndoung et al. (2021) and Karim et al. (2022), the techniques for loading biochar with nutrients, including phosphorus, were classified based on the production process sequence. They identified three main categories: direct treatment, pre-treatment, and post-treatment. In the direct treatment method, the phosphorus loading performance relies heavily on the initial phosphorus content present in the biomass. This technique uses biomass with high nutrient content to directly produce phosphorus-enriched biochar. The pre-treatment method involves loading biomass with external phosphorus sources before the biochar production process. This approach aims to enhance the phosphorus content in the biomass prior to biochar formation. Using various external phosphorus sources during pre-treatment enrich the biomass with phosphorus.

On the other hand, the post-treatment method focuses on loading nutrients, including phosphorus, onto the already-produced biochar. This technique aims to improve the phosphorus levels in the biochar material by subjecting it to nutrient-loading processes. It is important to note that pre-treatment techniques may also improve the biomass's



physiochemical properties, thereby enhancing the efficiency of nutrient loading. The classification by Ndoung et al. (2021) and Karim et al. (2022) is relatively simpler than other grouping methods. Nonetheless, the classification may not be suitable for all cases since the combination of direct, pre-, and post-nutrient loading techniques have been used. Essentially, nutrient loading techniques are categorized by considering the mechanism of nutrient enrichment in biochar. Table 3 shows different loading techniques reported in the literature that focus on phosphorus loading in biochar of various feedstocks. Loading techniques are divided into thermochemical treatment, adsorption, chemical modification, microbial treatment, and granulation.

Thermochemical carbonization is a method to directly convert nutrient-rich feedstocks into biochar, a carbon-rich material enriched with nutrients. Among the various processes, pyrolysis is the most widely employed. It has been observed that biochar derived from nutrient-rich biomass obtained from municipal waste, fermentation byproducts, and animal waste contains higher levels of total phosphorus than lignocellulosic materials. However, biochar produced from phytoremediators for treating eutrophic water shows similar total phosphorus content to animal manures. According to Zhu et al. (2018), different forms of phosphorus found in soil include iron-containing compounds such as strengite and vivianite, aluminum-containing compounds such as variscite, and calcium-containing compounds such as dicalcium phosphate dihydrate, dicalcium phosphate, B-tricalcium phosphate, hydroxyapatite, fluorapatite, and octacalcium phosphate. The inorganic fraction of phosphorus is the largest in typical agricultural soil, reported as 60–80% of the total phosphorus. The environmental factor, especially the soil pH, also determines the soil's dominant ortho-phosphate form. The adsorption–desorption equilibrium of labile phosphorus, which is solid and bonded with mineral cations, controls the phosphorus level in the soil. In contrast, inositol phosphorus has relatively high stability and cannot be efficiently uptake by plants. Thermochemical carbonization converts the insoluble organic phosphorus content to inorganic phosphorus, mainly through mineralization.

Ndoung et al. (2021) reported the importance of pyrolysis temperature on the final level of nutrients in biochar. This agrees with Zolfi Bavariani et al. (2019), who stated that pyrolysis at higher temperatures improves phosphorus, potassium, iron, zinc, manganese, and copper levels in a pyrolyzed product. High-temperature pyrolysis triggers sublimation of the abovementioned elements, where potassium and phosphorus are reportedly the most volatile, with sublimation temperatures between 700 and 800 °C. By maintaining pyrolysis temperature below the sublimation range, biochar is enriched with various elements, not only

phosphorus, attributed to the significant reduction in the product mass caused by the removal of water and organic compound vaporization. The authors stated that pyrolysis of biomass improves phosphate polymerization, but manipulating pyrolysis temperature could vary the degree of P–O–P structure. They selected 400 °C as the optimum pyrolysis temperature for lower phosphorus loss and a high degree of P–O–P structure.

Generally, the pyrolysis temperature adopted in the previous studies is considered low and is advantageous to conserve target minerals. Frišták et al. (2018) converted municipal-activated sludge and industrial-activated sludge into phosphorus-loaded biochar through conventional slow pyrolysis in the absence of oxygen gas at 430 °C for 2 h. Phosphorus content in the municipal-activated sludge- and industrial-activated sludge-derived biochar was increased from 34.68 g/kg and 9.62 g/kg to 57.01 g/kg and 16.84 g/kg, respectively. Since the former has a higher phosphorus level in biomass and biochar, there is greater potential for municipal wastes to be used as feedstock for biochar-based phosphorus fertilizer production. Moreover, the utilization of biochar derived from phosphorus-loaded municipal sludge has been found to decrease the availability of heavy metals in soil. The reduction percentages were reported as 40–46% for cadmium, 36–42% for chromium, 11–17% for copper, 13–19% for nickel, 26–32% for lead, and 1–3% for zinc, in comparison to the control samples. Similarly, phosphorus-loaded biochar obtained from industrial sludge demonstrated reduction percentages of 51–57% for cadmium, 38–46% for chromium, 18–24% for copper, 22–28% for nickel, 35–44% for lead, and 1–2% for zinc, respectively.

The effect of pyrolysis temperature, particularly between 200–600 °C, on the total phosphorus concentration and the phosphorus extractability of the sewage sludge-derived biochar across various soil acidity conditions was studied by Figueiredo et al. (2021). They revealed that increasing the pyrolysis temperature positively affected the total phosphorus content in the biochar, with the most significant impact observed above 200 °C. At 600 °C, the biochar displayed the highest phosphorus concentration, measuring 37 g/kg, 67% higher than the sewage sludge. However, while higher pyrolysis temperatures increased the total phosphorus content, the short-term availability of phosphorus showed slight improvement. The extractability of phosphorus pentoxide with neutral ammonium citrate increased from 83% at 200 °C to 79% at 300 °C but then decreased to 54 and 40% at 500 and 600 °C, respectively. In contrast, the fraction of phosphorus soluble in citric acid remained relatively constant between 26 and 49% from 200 to 500 °C and then increased to 53% at 600 °C. This suggests that higher pyrolysis temperatures may contribute to converting the soluble phosphorus

**Table 3** Phosphorus-loaded biochar techniques of various feedstocks

Methods	Biomass	Biochar production procedures	Phosphorus source	Direct/pre-loading method	Biochar loading procedures	Key findings	References
Thermo-chemical carbonization	Municipal activated sludge	Pyrolysis at 430 °C for 2 h	Biomass	Direct	Pyrolysis	Total phosphorus: 57.01 g/kg; heavy metal availability in soil reduced by 1–46% as compared to the control	Frišák et al. (2018)
	Industrial activated sludge					Total phosphorus: 16.84 g/kg; heavy metal reduced by 1–57% as compared to the control	
	Wet and dry <i>E. coli</i> fermentation waste	Pyrolysis at 600 °C and 40 °C/min for 2–4 h	Biomass	Direct	Pyrolysis	Total phosphorus: 84.7 g/kg (52% water-extractable; 61% citric acid-extractable)	Kim et al. (2018)
	Sewage sludge	Pyrolysis at 200–600 °C and 2.5 °C/min for 5 h	Biomass	Direct	Pyrolysis	Total phosphorus: 37 g/kg at 600 °C; 65.2% neutral ammonium citrate-extractable on average; 42% citric acid-extractable on average; Higher pyrolysis temperature resulted in increased citric acid-extractable phosphorus content and reduced Mehlich-extractable phosphorus	Figueiredo et al. (2021)
	<i>Hydrocotyle verticillata</i>	Hydrothermal carbonization at 200–260 °C and 3 °C/min for 2 h	Biomass	Direct	Hydrothermal carbonization	Total phosphorus: 22.85 g/kg at 260 °C (0.91% water soluble; 0.13% sodium bicarbonate-extractable; 0.18% sodium hydroxide-extractable; 85.30% hydrochloric acid-extractable; 0.26% residual)	Cui et al. (2020a; b)
	<i>Myriophyllum spicatum</i>					Total phosphorus: 30.03 g/kg at 260 °C (1.57% water soluble; 0.53% sodium bicarbonate-extractable; 6.56% sodium hydroxide-extractable; 83.72% hydrochloric acid-extractable; 0.20% residual)	
	<i>Cyperus indica</i>					Total phosphorus: 13.78 g/kg at 260 °C (8.78% water soluble; 19.09% sodium bicarbonate-extractable; 4.21% sodium hydroxide-extractable; 58.06% hydrochloric acid-extractable; 0.73% residual)	
	Pig carcass	Pyrolysis at 650 °C for 2 h	Biomass	Direct	Pyrolysis	Total phosphorus: 83.0 g/kg; dissolved cadmium reduced by 8–19% (reducing conditions); lead reduced by 55–82% (reducing conditions)	Yang et al. (2021b)
	Pig carcass	Pyrolysis at 650 °C and 15 °C/min for 2 h	Biomass	Direct	Pyrolysis	Water and sodium bicarbonate-extractable phosphorus increased from 0 to 6% and 9%; hydrochloric acid-extractable phosphorus reduced from 46 to 20%; mobile lead reduced by 23%; carbonate-lead reduced by 27.9%; exchangeable lead reduced by 76.7%	Chen et al. (2022)

Table 3 continued

Methods	Biomass	Biochar production procedures	Phosphorus source	Direct/pre-loading method	Biochar loading procedures	Key findings	References
Adsorption	Date palm tree wastes	Pyrolysis at 600 °C and 5 °C/min for 3 h	Potassium dihydrogen phosphate	Post	Biochar is mixed with potassium dihydrogen phosphate solution at 150 revolutions per min for 24 h until an equilibrium state is reached before centrifugation and oven-drying at 65 °C	Total phosphorus: 4.277 g/kg (72.87% available phosphorus); cadmium in soil reduced by 3% at the application rate of loaded biochar of 65.39%; lead, zinc, iron, copper, and manganese in soil reduced by 24.93, 16.21, 14.88, and 7.75%, respectively at the application rate of loaded biochar of 3%	Ahmad et al. (2018)
	Maize stalk	Pyrolysis at 350 °C and 600 °C for 2 h	Potassium dihydrogen phosphate	Post	Biochar is placed in saturated potassium dihydrogen phosphate solution for immersion of 24 h with a solid–liquid ratio of 1:20. Solid is isolated via simple filtration and rinsing with purified water, followed by drying at 40 °C	Total phosphorus: 83 g/kg at 600 °C	Li et al. (2020a)
	Wheat straw	Pyrolysis at 350–400 °C and 10 °C/min for 1 h	Di-ammonium phosphate	Post	Hot method: Hot biochar is added to a mixture of sterilized sand and di-ammonium phosphate at the specified mass ratio, followed by a sprinkling of warm distilled water until dissolved. The product is dried in an oven and stored in a sealed container  Cold method: Biochar is cooled to room temperature before mixing with sterilized sand and diammonium phosphate	The highest extractable phosphorus content in soil was 0.0085 g/kg and 0.01006 g/kg for 75:25 of di-ammonium phosphate: biochar over 15 and 30 days of incubation; extractable phosphorus content in post-harvest soil was 0.00712–0.00953 g/kg at the application rates of recommended phosphorus dosage between 0 and 100%	Wali et al. (2020)
Chemical modification	Wheat straw	Pyrolysis at 350–400 °C and 10 °C/min for 1 h	Diammonium phosphate	Post	Biochar is cooled to room temperature and added to a mixture of sterilized sand and di-ammonium phosphate at the specified mass ratio, followed by distilled water sprinkling until dissolved. The product is air-dried and stored in a sealed plastic bag	Improved plant growth, yield, and physiochemical properties at 1% loaded biochar and 50% phosphorus; slow release behavior confirmed by the increased extractable phosphorus content in the loaded biochar-amended soil	Wali et al. (2022)
	Peanut shell	Pyrolysis at 600 °C for 4 h	Potassium dihydrogen phosphate	Post	Biochar is mixed with magnesium chloride solution at high-speed stirring before drying at 105 °C. Modified biochar is heated to 600 °C at 10 °C/min, then cooled and sieved. Modified biochar is impregnated in a solution of potassium dihydrogen phosphate for phosphorus loading	Total phosphorus: 20.3 g/kg; adsorption capacity in phosphoric acid solution was reduced from 3 to 1.2 g/kg when carbonate and sulfate concentration was increased from 0 to 0.16 g/L by 1.80; adsorption capacity in saline soil was increased to 0.05 g/L, which was larger than the unmodified biochar by 32%	Wu et al. (2019a)

Table 3 continued

Methods	Biomass	Biochar production procedures	Phosphorus source	Direct/pre/post-loading method	Biochar loading procedures	Key findings	References
Sewage sludge		Pyrolysis at 700 °C	Biomass	Pre	Dried biomass is sprayed with potassium acetate solution before pyrolysis	Total phosphorus: 20.309 g/kg, 18,965 g/kg, and 19,555 g/kg for unmodified biochar (0.005% calcium chloride-extractable, 0.05% water-extractable, and 2.91% formic acid-extractable over 2 h), 2% potassium-modified biochar (below 0.001% calcium chloride-extractable, 2.97% water-extractable, 10.84% formic acid-extractable over 2 h), and + 5% potassium-modified biochar (1.74% calcium chloride-extractable, 8.69% water-extractable, 14.93% formic acid-extractable over 2 h); water-extractable phosphorus increased to 0.37%, 6.85, and 15.88% over 6 h; potassium addition increases the extractability and precipitation of calcium, magnesium, aluminium, and iron	Buss et al. (2020)
Ground coffee waste		Pyrolysis at 500 °C and 10 °C/min	Potassium phosphate	Pre	Biomass is mixed in magnesium chloride solution at 300 revolutions per min for 8 h, followed by pyrolysis and mixing with potassium phosphate at 500 revolutions per min for 48 h	Adsorption capacity: 14 g/kg phosphates in 24 h; unmodified biochar did not adsorb phosphates due to the surface negative charges that exert repulsive force to the phosphate ions; 70% and 90% of total phosphates were released in distilled water over 12 h, respectively; bioavailability and release of phosphates increase in the order of Mehlich (pH 2.2), citric acid (pH 2.5), alkaline (pH 9.4), and neutral	Shin et al. (2020)
Wheat straw		Pyrolysis at 400 °C and 20 °C/min for 1.5 h	Potassium dihydrogen phosphate	Post	Biochar is impregnated in citric acid solution at 300 revolutions per min for 2 h, followed by cooling, washing, crushing, and sieving before implementation with the inorganic fertilizer in the soil	Available phosphorus in the 4% and 8% citric acid-modified soil was increased by 0.0235–0.0625 and 0.0414–0.086 g/kg, respectively, as compared to the non-amended soil over 9–54 days of incubation; citric acid modification promoted the binding of citrate, consisting of carboxyl group on the biochar surface and hence, the acidification of soil, which inhibit the conversion of ortho-phosphates to non-bioavailable form	Mihoub et al. (2022)
Sugarcane filter cake		Pyrolysis at 600 °C and 6 °C/min for 3 h	Phosphoric acid	Pre	Dry filter cake powder is mixed with magnesium oxide or calcium oxide, followed by adding phosphoric acid to the biomass and drying before pyrolysis	Total phosphorus: 12.0 g/kg for unmodified biochar (2% water-extractable and 70% formic acid-extractable), 74.1 g/kg for magnesium-modified biochar (1% water-extractable and 40% formic acid-extractable), and 73.4 g/kg for calcium-modified biochar (1% water-extractable and 24% formic acid-extractable) over 30 min; slow-release behavior was confirmed by the gradual release of phosphate from both modified biochar over 240 h	Jetsrisuparb et al. (2022)



Table 3 continued

Methods	Biomass	Biochar production procedures	Phosphorus source	Direct/pre/post-loading method	Biochar loading procedures	Key findings	References
Distiller grain		Pyrolysis at 300–600 °C	Biomass	Pre	Biomass is modified by mixing with phosphogypsum at a specified mass ratio before drying	Adsorption capacity: 102.4 g/kg (Langmuir)	Wang et al. (2020b)
Pig manure		Pyrolysis at 500 °C and 10 °C/min for 2 h	Potassium dihydrogen phosphate	Pre/post	Biomass is modified by impregnating magnesium and aluminum chloride solutions at specified concentrations. Biochar is mixed with potassium dihydrogen phosphate solution at 120 revolutions per min for 24 h before membrane filtration	Adsorption capacity: 231 (Langmuir–Freundlich; 100% soluble in Mechlitch-1 and 2% citric acid)	Nardis et al. (2022)
Fish scales		Pyrolysis at 400–600 °C for 2 h	Biomass	Pre	Pre-carbonization of dried materials at 300 °C for 1 h, mixing with magnesium chloride solution for 5 h at 80 °C until dry, followed by pyrolysis	Copper was reduced by 84.2%; cadmium was reduced by 74.2%; lead reduced by 53.7%	Qi et al. (2022a)
Douglas fir		Pyrolysis at 900–1000 °C for 10–30 s	Potassium dihydrogen phosphate	Post	Biochar is modified by mixing with magnesium sulfate and potassium hydroxide solutions, followed by precipitation with potassium dihydrogen solution at 500 revolutions per min and 24 °C for 6 h before leaving for 1 day	Maximum phosphorus use efficiency at the application rate of 32 kg/kg at 90 kg/ha, which is larger than 17 kg/kg triple superphosphate	Arwenyo et al. (2022)
Chicken manures		Pyrolysis at 300 °C and 10 °C/min for 1 h	Biomass	Post	Biochar is modified by mixing with calcium bentonite powder and distilled water at a specified ratio and 20 °C for 20 min before drying in an oven at 105 °C for 1 day. The modified biochar is pyrolyzed again at the same conditions	25% calcium bentonite content reduced phosphorus release significantly in alkaline quartz	Piash et al. (2022)
Sugarcane leaves		Pyrolysis at 600 °C and 10 °C/min	Di-ammonium phosphate and phosphoric acid	Pre/Post	Biomass/biochar is impregnated in diammonium phosphate and phosphoric acid solutions at the specified ratio for 3 h. Biomass/biochar is also modified with magnesium oxide through mixing before impregnation in the phosphorus sources	Total phosphorus: 156 g/kg (40% water soluble and 71% formic acid-extractable) over 30 min; Post-treatment with di-ammonium phosphate and phosphoric acid did not pose a significant effect on the slow release of phosphorus but increased the extractable concentration; slow-release behavior was confirmed by the gradual release of phosphate from the modified biochar over 240 h	Suwannee et al. (2022)
Poultry litter		Pyrolysis at 700 and 10 °C/min for 1 h	Biomass	Co-pyrolysis	Biomass is mixed with banana peduncle and phosphogypsum at the specified ratios, followed by pyrolysis	Total phosphorus: 44.8, 24.4, 28.4, and 38.3 g/kg for poultry litter biochar and biochar composite modified with phosphogypsum at a ratio of 1:1:1, 1:2:1, and 1:3:1, respectively (24.11, 21.72, 18.66, and 16.09% citric acid-extractable; 24.78, 19.67, 20.42, and 20.69% formic acid extractable); higher portion of poultry litters in the composites increased the bioavailability of phosphorus; a smaller ratio of the last to the first extraction of poultry litter biochar indicated slower rate of phosphorus release; high initial phosphorus release in the composites is advantageous for germination	Vimal et al. (2022)

Table 3 continued

Methods	Biomass	Biochar production procedures	Phosphorus source	Direct/pre/post-loading method	Biochar loading procedures	Key findings	References
	Poultry litter	Pyrolysis at 300–700 °C and 10 °C/min	Biomass	Pre	Biomass is mixed with magnesium hydroxide, impregnated in deionized water at a ratio of 1:10, and stirred for 30 min, followed by drying at 70 °C before pyrolysis	At 300 °C, 16.8 g/kg or 96% citric acid-extractable and 16.7 g/kg or 94% formic acid-extractable; At 600 °C, 19.6 g/kg or 90% formic acid-extractable; modification with magnesium cations increased the phosphorus availability in formic acid and citric acid, but the effect decreased at 700 °C; higher pyrolysis temperature reduced water-extractable phosphorus; higher pyrolysis temperature reduced the phosphorus release of the modified and unmodified biomass and biochar in water, but the effect was lesser for biomass	Leite et al. (2023)
	Fermented distiller grain	Pyrolysis at 300–800 °C and 10 °C/min for 2 h	Biomass	Pre	Biomass is modified by mixing with wet-process phosphoric acid at 105 °C for 1 day, followed by activation with potassium hydroxide solution in the heating evaporation process	Total phosphorus: 158.08 g/kg; the skeleton of the loaded biochar released 92.83% phosphorus, 85.94% potassium, 41.49% iron, 78.42% aluminium, and 65.60% magnesium in the soil after 63 days; chromium was reduced by 83.57%	Zhou et al. (2023)
Microbial treatment	Sewage sludge	Pyrolysis at 600 °C for 2 h	Biomass/soil	Post	Spores of <i>Polystyichum aculeatum</i> ATCC10409, <i>Polystyichum bilaii</i> ATCC 20851, <i>Polystyichum glabrum</i> DAOM230974, and <i>Polystyichum expansum</i> ATCC24692w were obtained from the cultivation of the strains on potato dextrose agar plates for one week at room temperature, followed by further separation processes. Incubation of the fungi is carried out in the biochar-amended soil	Citrate and gluconate accounted for the largest share of the organic acids produced by the fungi; biochar and iron-phosphorus were solubilized by citrate; calcium-phosphorus was solubilized by gluconate; solubilizing effect of biochar-phosphorus mainly depends on the complexation of citrates with calcium, iron, and aluminium cations instead of the acidification effect from proton release	Efthymiou et al. (2018)
	Sewage sludge	Pyrolysis at 400–700 °C	Biomass	Post	Biochar is mixed with the <i>Polystyichum putida</i> media for incubation at 25 °C and 130 revolutions per min for a specified period	Weaker crystal structures in biochar produced at 400 °C are quickly attacked by the organic acids produced by the <i>P. putida</i> , resulting in enhanced release of water, sodium bicarbonate, sodium hydroxide, and hydrochloric acid-extractable phosphorus	Qian et al. (2019)
	Apple and grape tree pruning wastes	Pyrolysis at 350 °C and 9 °C/min for 2 h	Rock phosphate and phosphate-solubilizing bacteria	Post	Biochar is modified by impregnation with phosphoric acid and hydrochloric acid at the specified ratio through mixing for 2 h and drying. Phosphorus loading is conducted by mixing with rock phosphate and boiling water at a specified ratio for 2 h, followed by drying and pyrolysis at 220 °C	A available phosphorus 0.048 g/kg (phosphoric acid-treated) and 0.027 g/kg (hydrochloric acid-treated); phosphorus solubilizing bacteria-enriched biochar had higher total phosphorus content and dry matter yield than triple superphosphate but lower than acid-treated biochar; biochar loaded with phosphorus solubilizing bacteria had the highest alkaline phosphatase activities	Mousavi et al. (2023)
					Rock phosphate and phosphate solubilizing bacteria are used to produce enriched biochar		

Table 3 continued

Methods	Biomass	Biochar production procedures	Phosphorus source	Direct/pre/post-loading method	Biochar loading procedures	Key findings	References
Granulation	Rice straw, distiller grain, and <i>Eupatorium adenophorum</i> without roots	Pyrolysis at 300–600 °C and 2.5 °C/min	Potassium dihydrogen phosphate	Post	Biochar is grounded to 150–800 µm or ball milled at 300 revolutions per min for 12 h. Calcium alginate-biochar composite microspheres are produced by mixing sodium alginate and ball-milled biochar at the specified mass ratio before adding to calcium chloride solution at 10 mL/min	Adsorption capacity: 31.8 g/kg for the calcium alginate-modified rice straws produced via pyrolysis at 300 °C (Langmuir, 25 °C)	Feng et al. (2022)
	Maize straw	Pyrolysis at 700 °C and for 4 h	Red phosphorus	Post	Biochar is mixed with red phosphorus at a set mass ratio before ball milling at 300 revolutions per min for 12 h	Increased phosphorus loading through the conversion of red phosphorus to oxide and acid forms; reduced salt content in soil with increased nitrogen, potassium, and phosphorus content, enzymatic activities in coastal saline-alkaline soil	Zhang et al. (2022b)
	Rice straw, distiller grain, and <i>Eupatorium adenophorum</i>	Pyrolysis at 300–600 °C	Biomass	Post	Biochar is ball-milled for 2–24 h	Distiller grain had the largest release capacity than rice straw and <i>Eupatorium adenophorum</i> ; longer duration of ball milling increases specific surface area, total pore volume, pore size, and phosphorus release capacity;	Zhao et al. (2022)

Direct treatment involves using thermochemical carbonization, particularly pyrolysis, to convert nutrient-rich biomass such as sewage, sludge, fermentation, phytoremediators, and animal wastes into phosphorus-enriched biochar. This method directly transforms biomass into biochar, but there is a concern regarding potential secondary pollution due to the toxicity of certain biomasses

Indirect treatments, such as adsorption and chemical modification, are commonly used for nutrient-deficient biomass to produce phosphorus-loaded biochar. These techniques involve adding external phosphorus sources, often inorganic chemicals, to enhance the phosphorus content in biochar. Microbial treatment and granulation are two effective methods for loading phosphorus into biochar. However, further research is needed to validate their efficiency. Waste-based biomass has gained popularity in recent studies due to waste reduction and management advantages

fraction into an insoluble form, predominantly composed of mineral phosphorus resulting from organic phosphorus decomposition and calcium phosphate crystallization.

The experimental result by Kim et al. (2018) showed an improvement in total phosphorus content in biochar compared to dry *E. coli* fermentation waste. The total phosphorus content was measured at 84.7 mg/g of biochar, whereas it was only 7.4 mg/g for the dry *E. coli* fermentation waste. The substantial increase in phosphorus content observed in biochar is attributed to two main factors: the release of phosphorus in the feedstock and the addition of potassium hydrogen phosphate and dipotassium dihydrogen phosphate while cultivating *E. coli* culture. This combination of factors contributes to adequate phosphorus enrichment in the resulting biochar product. Enriched biochar produced by Kim et al. (2018) was reported to release 42% and 52% of the total available phosphorus after 24 h in water and citric acid, respectively. High water-soluble phosphorus in their final product is owed to the lack of other minerals in bacterial wastes, including magnesium and calcium, that could react with phosphorus to form precipitates which generally happens for manure feedstocks and pyrolysis at temperatures above 500 °C. Besides solubility in water, citric acid-soluble phosphorus contributes to the bioavailability of phosphorus since the acid is an important medium for dissolving phosphorus and is generated by soil microorganisms at plant roots (Kim et al. 2018). The phosphorus release from the biochar exhibited a rapid initial rate, but no significant further increase was observed beyond the fifth day. At the end of the five days, 52% of phosphorus release in water and 61% in citric acid were recorded, indicating the biochar's slow-release characteristics over an extended period.

Yang et al. (2021b) and Chen et al. (2022) used pig carcasses as feedstock to produce biochar-based fertilizers. The loaded biochar used by Yang et al. (2021b) had a total phosphorus concentration of 83 g/kg, and they revealed that phosphorus-loaded biochar caused the reduction of lead and cadmium availability in soil by 55–82% and 8–19%, respectively, implying the potential role of biochar in heavy metal-polluted soil remediation. The effect of lead immobilization is more significant because of the abundant phosphate and ash content in the biochar. Chen et al. (2022) conducted additional research to confirm the beneficial impact of phosphorus-enriched biochar on lead immobilization and the bioavailability and short-term availability of phosphorus in soil. The study found that phosphorus-enriched biochar significantly reduced lead's mobile, carbonate, and exchangeable fractions, with 23, 27.9, and 76.7% decreases, respectively. Furthermore, the water-soluble inorganic phosphorus content decreased by up to 6%, while the sodium bicarbonate-soluble inorganic phosphorus increased by 9%. These findings suggest that

applying biochar effectively enhanced the bioavailability of phosphorus and provided a short-term supply of phosphorus in the soil.

The direct method of phosphorus loading is not limited to pyrolysis, which produces pyro-char of low moisture content. Cui et al. (2020a) implemented hydrothermal carbonization to produce wetland plant-derived hydrochar. Wetland plants, namely *Hydrilla verticillata*, *Myriophyllum spicatum*, and *Ceratopteris indica*, are used for phytoremediation of polluted water from eutrophication. Their study demonstrated the potential of utilizing hydrochar derived from wetland plants to recover and recycle phosphorus from contaminated water sources, including wastewater. Hydrochar's resistance to phosphorus leaching in the soil makes it a promising option for soil fertilization and amendment, effectively addressing the issue of phosphorus pollution. Specifically, the maximum total phosphorus content in *Hydrilla verticillata*, *Myriophyllum spicatum*, and *Ceratopteris indica* was 22.85, 30.03, and 13.78 g/kg of biochar produced at 260 °C, respectively. Hydrochloric acid-extractable phosphorus accounted for the largest share of total phosphorus content in the biochar, which are 85.30, 83.72, and 58.06% for *Hydrilla verticillata*, *Myriophyllum spicatum*, and *Ceratopteris indica*, respectively. The composition of water-soluble phosphorus was recorded as 0.91, 1.57, and 8.78%, while sodium bicarbonate-soluble phosphorus was reported as 0.13, 0.53, and 19.09%, respectively. The low phosphorus leaching rate of the hydrochar is caused by the conversion of water-soluble phosphorus to a more stable form, which is the hydrochloric acid-extractable fraction, during hydrothermal carbonization. *Myriophyllum spicatum*-derived biochar has the highest leaching resistance, indicated by the highest hydrochloric acid-extractable phosphorus of 11.55–25.14 g/kg at 200–260 °C. Residual fraction is depleted in all hydrochar compared to the biomasses because of the higher decomposition rate.

The study by Cui et al. (2020a) demonstrated the reclamation of phosphorus from eutrophic water to produce phosphorus-enriched biochar that can be used in agricultural soil. Using phytoremediators as feedstocks for biochar-based phosphorus fertilizer production helps manage and reduce waste and recycle nutrients for planting food crops. However, waste-based biochar fertilizer's toxic and heavy metal content threatens food safety and soil health. Future studies should consider the phosphorus use efficiency, which mainly depends on the water and organic acid-extractable phosphorus, as well as the toxicity of the biochar due to the potential leaching of heavy metals in long-term applications.

Two common approaches for enriching nutrient-deficient biochar with external phosphorus sources are adsorption and chemical modification. The adsorption



method primarily creates phosphorus-enriched biochar from low-nutrient biomass, particularly lignocellulosic materials. Phosphorus adsorption onto the biochar surface is typically facilitated through electrostatic attraction, precipitation, surface complexation, pore filling, ligand exchange, and anion exchange. These processes enable the efficient binding of phosphorus to biochar, enhancing biochar's nutrient content and potential agricultural applications (Nobaharan et al. 2021). Referring to Ambaye et al. (2021), the adsorption mechanism depends on the biochar properties, the adsorbent dosage, and the substrate conditions, such as the pH and the adsorbate concentration. Preferably, a physical bond is favored over a stronger chemical bond between a phosphorus-containing group and biochar, as it allows for easier cleavage and desorption of phosphorus when applied in the soil. Several mechanisms contribute to the stability of the phosphorus fraction, including ligand exchange, surface complexation, precipitation, electrostatic attraction, and anion exchange. The effectiveness of pore filling relies on the porosity of the biochar, with larger pore sizes promoting easier diffusion.

Anion exchange involves the substitution of phosphate ions for hydroxyl groups from mineral cations on the biochar surface. However, the efficiency of anion exchange is pH-dependent, with limited adsorption under acidic conditions. Mineral cations play a crucial role in phosphorus adsorption through surface complexation, precipitation, electrostatic attraction, and anion exchange, necessitating cation-based modifications of biochar. The efficiency of phosphorus adsorption is influenced by factors such as pyrolysis temperature, adsorbent dosage, phosphorus-containing solution acidity, and coexisting ions. Wu et al. (2019a), Wang et al. (2020b), and Feng et al. (2022) investigated the dependence of phosphorus adsorption efficiency on these factors using different modified biochars, including magnesium oxide-modified peanut shell-derived biochar, phosphogypsum-pre-treated distiller grain-derived biochar, and ball-milled calcium alginate-biochar composite, respectively.

Pyrolysis at high temperatures alters surface morphology and properties, including specific surface area and roughness (Wang et al. 2020b). This could be advantageous for phosphorus diffusion into the pores and adsorption with the increased number of active sites. Higher pyrolysis temperature could promote phosphorus adsorption on biochar via electrostatic attraction and surface precipitation when the biochar is mineral-rich. In comparison, lower pyrolysis temperatures could enhance the phosphorus adsorption of mineral-lacking biochar by retaining the surface functional groups (Feng et al. 2022). Thermochemical carbonization of biomass eliminates organic phosphorus and oxygen-containing surface functional groups through decomposition and volatilization. Thus, at

high pyrolysis temperatures, the increased concentration of mineral cations, which act as the active sites, favors the cation-based adsorption mechanism, namely electrostatic attraction and surface precipitation.

However, literature shows that phosphorus adsorption is facilitated via ligand exchange, which is less dependent on the biochar net surface charge and the environment pH than electrostatic interaction (Feng et al. 2020, 2022). Phosphorus adsorption capacity increased with the solution alkalinity, and the adsorption rate was the most rapid at pH 6–7 due to the abundance of dihydrogen phosphates and hydrogen phosphates, which are the primary forms of phosphorus at pH 2.12–7.21 and 7.21–12.31, respectively (Feng et al. 2022). The said inorganic species are readily adsorbed on the biochar surface through electrostatic interaction at low pH and ligand exchange with the biochar surface hydroxyl groups. Surface precipitation occurs with the crystallization of the phosphates with mineral cations under alkaline conditions.

Similarly, in the study by Wang et al. (2020b), the maximum adsorption capacity was found at pH 6, recorded as 79 g/kg, attributed to the dominating dihydrogen phosphate ions having great affinity to the modified biochar at pH 3–7, which also promotes phosphorus adsorption via ligand exchange. The dominating form, phosphoric acid at pH below 3, has a very low affinity to the biochar, leading to ineffective adsorption, and the adsorption capacity was recorded as 75 g/kg. At pH 8–12, the excess hydroxyl ions could cause hindrance to the coordination of the dominating hydrogen phosphate ions on the modified biochar, owing to the similar charges that cause competition for the active sites. In addition, Shin et al. (2020) reported a decrease in adsorption capacity at equilibrium at increasing pH, particularly 14.64 g/kg, 14.35 g/kg, and 9.43 g/kg at pH 4, 7, and 10, respectively, which further validates the correlation between phosphorus source solution pH and the adsorption capacity. They explained it in terms of the zero-charge point, where the solution pH exceeding that of zero charge point would result in the net negative charge, which impedes the adsorption of phosphates on the biochar surface.

The adsorbent dosage positively correlates with the phosphorus adsorption capacity to an extent. To explain, adding biochar into the phosphorus-containing solution could increase the number of active sites for effective adsorption. However, the phosphorus adsorption capacity reaches a constant value when the driving force, particularly the phosphorus concentration gradient, is reduced. 1.25 g/L and 0.20 g were selected by Wang et al. (2020b) and Feng et al. (2022), respectively, as the optimum dosage of biochar for the maximum phosphorus adsorption efficiency since, beyond the dosages, no remarkable improvement in the phosphate adsorption was recorded.

On the other hand, the adverse impact of the common ion effect was also demonstrated in the study by Wu et al. (2019a) and Feng et al. (2022). For example, Wu et al. (2019a) reported that the inorganic phosphorus adsorption capacity of the unmodified biochar had dropped from 3 to 1.2 g/kg when the sulfate and carbonate ion concentrations were raised from 0 to 0.160 g/L. Conversely, the adsorption capacity of the magnesium oxide-modified biochar experienced less significant depletion at increasing common ion concentration and exceeded that of the unmodified biochar by 80%. Sulfate ions exhibited the most robust inhibition of phosphate adsorption. At the same time, carbonates improve phosphate adsorption, owing to their interaction with the calcium cations used for the biochar modification to produce calcium carbonate, leading to more dispersion of the biochar in the phosphorus-containing solution (Feng et al. 2022). However, they reported that the inhibitory effect of the carbonate ions became evident at the concentration of 0.1 mol per liter. This may imply that without the addition of binding cations as the chemical modification agents, carbonate ions also impede phosphorus adsorption on biochar by competing for the limited adsorption sites, like sulfate ions.

The studies conducted by Ahmad et al. (2018), Li et al. (2020a), Wali et al. (2020), and Wali et al. (2022) focused on the adsorption-based loading of phosphorus onto biochar intending to recover phosphorus from eutrophic water for agricultural purposes. In a previous investigation by Ahmad et al. (2018), they examined the performance of phosphorus-loaded biochar derived from date palm tree wastes in the phytoremediation of contaminated water sources. The total phosphorus content in the loaded biochar was found to be 4.277 g/kg, comparable to that in the unloaded biochar derived from lignocellulosic materials. Additionally, the adsorption capacity of the loaded biochar was reported as 3.104 g/kg. When they applied the biochar on heavy metal-contaminated soil, the concentration of lead, zinc, iron, copper, and manganese in the soil was reduced by 24.93, 16.21, 14.88, and 7.75%, respectively, at the application rate of 30 g loaded biochar per kg soil. In comparison, cadmium was lowered by 3% at 653.9 g of loaded biochar per kg of soil. These are less than the unloaded biochar, recorded as 46.53, 44.51, 32.34, 41.27, and 48.05% for lead, zinc, iron, copper, and manganese, respectively, at the rate of 30 g/kg, and 3% for cadmium at the rate of 585.4 g/kg. Furthermore, the impacts on plants, measured in terms of biomass weight and phosphorus uptake, were found negligible. The practical use of the biochar needs to be further assessed due to the reported low agronomic efficiency of phosphorus and the high application rate needed for significant heavy metal removal.

Qi et al. (2022a) also studied the adsorption efficiency of copper, cadmium, and lead ions, where the biochar's oxygen, nitrogen, and phosphorus-containing group play an essential role in immobilizing the heavy metal cations. The removal efficiency of copper, cadmium, and lead ions in soil was reported as 84.2, 74.2, and 53.7%, respectively, over 60 days of application. However, assessment on the leaching of heavy metal ions over a longer application duration shall be included, especially under field conditions since the soil properties are highly dependent on the climate and the variation of soil nutrient content.

Wali et al. (2020) and Wali et al. (2022) implemented hot and cold methods to enrich wheat straw-derived biochar with phosphorus via adsorption. The former method added hot biochar to a solid mixture of sterilized sand and di-ammonium phosphate at the specified mass ratio. This is followed by sprinkling warm distilled water on the solid mixture until dissolved. Lastly, the loaded biochar was stored in a properly sealed container after air drying or oven drying. In the cold method, biochar was cooled to room temperature before mixing with di-ammonium phosphate and sterilized sand. Both articles reported an increase in phosphorus content in the loaded biochar, indicating the effectiveness of the loading method.

The slow-release behavior of the biochar incorporated with di-ammonium phosphate through post-treatment was confirmed by the higher extractable phosphate concentration in the loaded-biochar amended post-harvest soil (Wali et al. 2020; Wali et al. 2022). The extractable phosphorus in the loaded biochar-incorporated post-harvest soil was reported as 0.00712–0.00953 g/kg at the inorganic phosphorus fertilizer application rate of 0–100%, which is higher than that without the loaded biochar, ranging between 0.00407 and 0.00543 g/kg. Similarly, the extractable phosphorus concentration increase in the 1% loaded-biochar-amended post-harvest soil was 100% higher than inorganic fertilizer-treated post-harvest soil (Wali et al. 2022). The lower extractable phosphorus in the post-harvest soil without the loaded biochar amendment at all inorganic phosphorus fertilizer application rates was caused by the higher phosphorus fixation in highly alkaline calcareous soil. Adding the loaded biochar removed calcium and magnesium cations, reducing the complexation reaction between phosphates and the cations to produce insoluble mineral-phosphorus complexes and higher availability of extractable phosphorus.

The chemical modification involves biomass or biochar surface alterations to enhance phosphorus enrichment through adsorption. Previous studies have utilized various chemical modification agents, such as magnesium cations (Arwenyo et al. 2022; Jetsrisuparb et al. 2022; Leite et al. 2023; Nardis et al. 2022; Qi et al. 2022a; Shin et al. 2020;

Suwanree et al. 2022; Wu et al. 2019a), calcium cations (Jetsrisuparb et al. 2022; Piash et al. 2022), aluminium cations (Nardis et al. 2022), potassium cations (Arwenyo et al. 2022; Buss et al. 2020), citric acid (Mihoub et al. 2022), phosphoric acid (Suwanree et al. 2022; Zhou et al. 2023), phosphogypsum (Vimal et al. 2022; Wang et al. 2020b), to achieve this goal.

The commonly used modifier is metal cations, which can be sourced from the solutions of aluminium chloride, calcium chloride, magnesium chloride, potassium permanganate, manganese chloride, and zinc chloride (Ghassemi-Golezani and Rahimzadeh 2022). In the process, metal cations are introduced to create insoluble metal oxide nanoparticles that deposit onto the biochar surface. These cations serve as binding agents for phosphorus, forming bonds that effectively fix the phosphorus in the labile pool. When the soluble phosphorus levels in the soil decrease, the labile phosphorus can be converted back into a soluble form to restore equilibrium. Thus, adding cations, where magnesium ions are the most studied, effectively expands the labile phosphorus concentration and forms a slow-release biochar-based phosphorus fertilizer, which is helpful for long-term applications. The addition of metal oxides on the biochar surface provides additional active sites for the binding of phosphate anions such as dihydrogen phosphate, hydrogen phosphate, and phosphate, which often is impeded by the net negative charge of the unmodified biochar surface and the negatively charged surface functional groups, including carboxyl, phenolic, and hydroxyl groups (Wu et al. 2019a). Other factors lowering the affinity of biochar toward phosphorus-containing anions are the limited adsorption capacity and the common ion effect, which are dependent on the adsorbent dosage and the presence of anions, particularly sulfate and carbonate (Feng et al. 2022; Wu et al. 2019a).

According to Wu et al. (2019a), the adsorption of inorganic phosphorus in saline soil was measured at 0.05 g/L, which exceeded the adsorption capacity of the unmodified biochar by 0.016 g/L. The primary adsorption mechanism involved the precipitation of magnesium phosphate in the saline soil at a pH of 7.5. In a study by Shin et al. (2020), coffee ground wastes were immersed in a magnesium chloride solution for 8 h as a pre-pyrolysis modification. The resulting modified biochar exhibited a maximum adsorption capacity of 14 g/kg over 24 h, whereas the unmodified biochar adsorbed only a negligible amount of phosphorus. This difference can be attributed to the net negative charge of the unmodified biochar, which generates repulsive forces toward phosphate anions. The Langmuir isotherm analysis recorded an adsorption capacity of 63.5 g/kg.

Jetsrisuparb et al. (2022) used magnesium and calcium oxides to modify the sugarcane filter-derived biochar. The

phosphoric acid solution was used as the source of phosphorus in their study, although it is also considered a chemical modifier in several studies (Suwanree et al. 2022; Zhou et al. 2023). Using magnesium and calcium oxides, the biochar modification improved the total phosphorus from 12.0 g/kg to 74.1 g/kg and 73.4 g/kg. During 30 min, the total phosphorus release in formic acid was measured as 8.4, 18, and 30 g/kg, which accounted for 70, 24, and 40% of the total phosphorus content in the unmodified biochar, calcium-modified biochar, and magnesium-modified biochar, respectively. The concentration of formic acid-extractable phosphorus release was higher than water-extractable phosphorus, resulting in a maximum release of 1 g/kg, corresponding to 1–2% of the total phosphorus content in the biochar. These findings indicate that magnesium ion had a more pronounced effect on the chemical modification and availability of labile phosphorus content compared to calcium ion, as evidenced by the higher content of organic acid-extractable phosphorus in the former.

The negative correlation between calcium cations and phosphorus adsorption was demonstrated by Piash et al. (2022). The calcium cations used in the study were obtained from calcium bentonite and mixed with biochar at 10 and 25% concentrations. When chicken manure-derived biochar was modified with calcium bentonite, the total phosphorus content decreased from 19.5 g/kg to 16.2 g/kg and 15.2 g/kg, respectively. The authors attributed this reduction to the dilution effect caused by the addition of calcium bentonite. They explained that calcium bentonite has lower nitrogen, potassium, phosphorus, calcium, and magnesium levels than biochar. Therefore, mixing biochar with a lower ratio of calcium bentonite would naturally result in lower content of these elements. However, the authors also suggested that using a 25% concentration of calcium bentonite was sufficient to release an adequate amount of available phosphorus into the soil. They further proposed that the modified biochar's potential slow-release behavior could be attributed to the formation of less soluble calcium and magnesium-phosphorus compounds facilitated by adding calcium cations.

Leite et al. (2023) reported that magnesium cations positively impacted the phosphorus release capacity in water, citric acid, and formic acid, except when the magnesium-to-calcium ratio was 0.2. They also found a direct relationship between the pyrolysis temperature and the release capacity and rate of phosphorus in organic acids. For the magnesium-modified biochar produced at 300 °C, the amounts of citric acid and formic acid-soluble phosphorus were 16.8 and 16.7 g/kg, respectively, which accounted for 96 and 94% of the total phosphorus in the biochar. The unmodified biochar had 14.4 and 14.6 g/kg of citric acid and formic acid-soluble phosphorus,

respectively. Pyrolysis at 600 °C increased the formic acid-soluble phosphorus to 15.8 and 19.6 g/kg for unmodified and modified biochar, respectively. However, pyrolysis at 700 °C did not have a significant effect, possibly due to the decomposition of magnesium-phosphorus, leading to lower amounts of organic acid-soluble phosphorus. On the other hand, the water-soluble phosphorus concentration decreased with increasing pyrolysis temperature, primarily because available phosphorus was converted to mineral phosphorus. Interestingly, a higher magnesium-to-calcium ratio, especially 0.16, increased phosphorus availability, likely due to the inhibition of calcium-phosphorus formation.

The studies conducted by Jetsrisuparb et al. (2022) and Leite et al. (2023) showed that magnesium cations are better than calcium cations in terms of the improvement of organic acid-extractable phosphorus, which belongs to the labile pool. The conversion of insoluble mineral-phosphorus to soluble phosphorus, which is extractable in water and readily available for plant uptake, is a reversible process dependent on the pH and the soil's phosphorus level. The high composition of labile phosphorus is important to ensure sufficient available phosphorus replenishment in the soil in the long term. While both magnesium and calcium cations contribute to the expansion of the labile pool, magnesium-phosphorus is more easily broken due to the higher solubility of the cation. The lower solubility of calcium-phosphorus in water is attributed to the larger cationic size and lower charge density, which lead to lower affinity to water molecules and hence, less feasible cleavage by the molecules. This is supported by the less exothermic hydration enthalpy of calcium cations.

Nardis et al. (2022) compared the effects of chemical modification using magnesium and aluminium cation-containing solutions. They found that the maximum adsorption capacity of the magnesium-modified phosphorus-loaded biochar derived from pig manure was 231 g/kg, as determined by the Langmuir–Freundlich isotherm. In contrast, the phosphorus adsorption capacity of the aluminium-modified phosphorus-loaded biochar was lower, measuring 33.33 g/kg. Furthermore, at the maximum concentration of potassium dihydrogen phosphate solution, the adsorption capacity of the aluminium-modified biochar decreased. One potential explanation for this discrepancy is that the added aluminium caused pore blockage, thereby inhibiting phosphorus adsorption on the biochar's surface. On the other hand, magnesium-phosphorus has a smaller binding energy, resulting in easier desorption and a higher release capacity.

Buss et al. (2020) conducted pyrolysis of potassium-doped sewage sludge to produce a modified biochar at 700 °C. The total phosphorus content was measured in different samples, including the biomass, unmodified biochar, 2%

potassium-modified biochar, and 5% potassium-modified biochar, resulting in values of 10.984, 20.309, 18.965, and 19.555 g/kg, respectively. Interestingly, despite the increase in total phosphorus content to 9.325 g/kg, pyrolysis led to a reduction in water and formic acid-extractable phosphorus in the sewage sludge-derived biochar by 0.1194 and 1.164 g/kg, representing reductions of 94.76 and 66.28%, respectively. This reduction in extractable phosphorus can be attributed to converting a proportion of ortho-phosphorus and organic phosphorus into poorly soluble calcium, magnesium, aluminium, and iron phosphates during the pyrolysis process. These phosphate compounds have limited solubility in water, resulting in decreased extractability despite the overall increase in total phosphorus content in the biochar. The biomass pretreatment with potassium cations allows more formation of potassium salts, including potassium dihydrogen phosphate, potassium hydrogen phosphate, and potassium phosphate, which have greater solubility in water than the said phosphate species. They demonstrated the potential of the chemical modifier in enhancing the bioavailability of phosphorus, indicated by the significant increase of water-extractable phosphorus in the biochar modified with 2 and 5% potassium acetate solution, which are 0.5544 and 1.6904 g/kg, respectively, as compared to the unmodified biochar. Similarly, the improvement of formic acid-extractable was recorded as 1.463 and 2.328 g/kg.

Differently, organic acid is used to modify the surface properties of biochar and promote acidification of soil, which could help retain phosphorus in the bioavailable form, particularly ortho-phosphates. Therefore, organic acid-based modification is suitable for soil with high phosphorus fixing capacity, which could be resulted from the soil properties and the abuse of inorganic fertilizers.

The study by Paul et al. (2021) found that citric acid plays a significant role in solubilizing important mineral phosphorus in soil. Among the various organic acids studied, citric acid exhibited the highest phosphorus solubilization capacity. The solubilized phosphorus content for the sewage sludge-derived biochar, produced at different pyrolysis temperatures (220, 320, 420, 520, and 620 °C), was reported as 3.053, 4.174, 3.237, 3.090, and 1.436 g/kg, respectively. Comparatively, the solubilization capacity of other organic acids, such as acetic, quinic, benzoic, oxalic, mucic, malic, succinic, maleic, phthalic, trans-aconitic, and kojic acid, was lower. The concentration of phosphorus solubilized by these other organic acids ranged from 1.187 to 2.225 g/kg, 0.812–1.712 g/kg, 0.532–1.370 g/kg, 0.372–1.216 g/kg, and 0.189–0.683 g/kg for biochar pyrolyzed at 220, 320, 420, 520, and 620 °C, respectively.

Mihoub et al. (2022) employed an impregnation technique using a citric acid solution to create acidic biochar from wheat straw. This process resulted in the introduction



of carboxyl groups on the surface of the biochar matrix, leading to acidification of the soil. The presence of carboxyl and hydroxyl groups from citric acid chelated with mineral cations hinders the conversion of ortho-phosphorus into a form inaccessible to plants through mineral precipitation. The acidification of the soil, caused by the release of protons, triggered the transformation of insoluble phosphorus into soluble forms such as hydrogen phosphates and dihydrogen phosphates. The research findings revealed that adding citric acid at 4 and 8% by weight to the soil increased available phosphorus. Over 9–54 days of incubation, the available phosphorus in the soil amended with citric acid at these rates increased by 0.0235–0.0625 g/kg and 0.0414–0.086 g/kg, respectively, compared to the non-amended soil.

Phosphoric acid is a phosphorus source and a chemical modifier to produce phosphorus-loaded biochar-based fertilizer. Suwanree et al. (2022) impregnated biomass and biochar in di-ammonium phosphate and phosphoric acid solutions. Some samples also were immersed in a solution containing magnesium ions. The total phosphorus content was increased from 7 g/kg of the raw biochar to 81, 34, 77, 82, and 156 g/kg for di-ammonium phosphate-pre-treated, phosphoric acid-pre-treated, magnesium-modified-di-ammonium phosphate-pre-treated, magnesium-modified-phosphoric acid-pre-treated, and magnesium-modified-phosphoric acid-pre-treated-diammonium phosphate-post-treated biochar, respectively. Pre-treatment with di-ammonium phosphates was the most effective in improving the phosphorus content in biochar. In contrast, post-treatment with diammonium phosphates significantly increased the readily water-soluble and labile organic acid-extractable phosphorus fraction. Precipitation occurs with the crystals formed from the interaction between metal cations and phosphates. The phosphorus release rate depends on the dissolution of magnesium pyrophosphate crystals, which were detected only in the samples modified with the cations (Suwanree et al. 2022).

On the other hand, Zhou et al. (2023) used wet-process phosphoric acid to modify distiller grain-derived biochar. Potassium hydroxide was added to introduce potassium cations to promote water-soluble polyphosphate formation, which works based on the same concept as the discussed mineral cations. They also reported the excellent performance of the biochar in chromium removal and the constant phosphorus release to the soil. At initial pH 3 and potassium chromium solution concentration of 50 mg/L, the maximum removal rate of 60.77 and 83.57% using loaded biochar produced via pyrolysis at 400 °C and the remaining biochar after nutrient release, respectively, after 3 days. 400 °C is selected as the optimum temperature for the biochar carbon stability, minimum loss of phosphorus, and adequate polyphosphate formation.

Wang et al. (2020b) and Vimal et al. (2022) used industrial phosphoric acid manufacturing by-products, namely phosphogypsum, as the chemical modification agent of the biochar derived from distiller grain and poultry litter, respectively. The maximum adsorption capacity was reported as 102.4 g/kg, obtained from Langmuir isotherm (Wang et al. 2020b). Additionally, Vimal et al. (2022) provided data on the total phosphorus content in different materials. The poultry litter, banana peduncle, phosphogypsum, poultry litter-biochar, and composites with varying ratios of the banana peduncle, poultry litter, and phosphogypsum had total phosphorus contents of 24.6, 6.3, 9.0, 44.8, 24.4, 28.4, and 38.3 g/kg, respectively. Incorporating unmodified biochar into the composites resulted in higher total phosphorus content. However, the proportion of calcium and magnesium-bound phosphorus was highest in the composite with a ratio of 1:3:1, measuring 25.0 g/kg, compared to the composites with ratios of 1:1:1 and 1:2:1, which had values of 21.3 and 23.8 g/kg, respectively.

On the other hand, the citric and formic acid-extractable fractions were highest in the composite, with a ratio of 1:3:1, measuring 5.6 and 7.2 g/kg, respectively. However, both the mineral-phosphorus fraction and the citric and formic acid-extractable fraction of the composite were lower than those of the unmodified biochar, indicating reduced bioavailability of phosphorus in the composite. These findings suggest that unmodified biochar may be a more effective phosphorus fertilizer. This is due to higher levels of organic acid-extractable phosphorus and the availability of mineral-bound phosphorus for potential slow-release behavior. The effectiveness of using phosphogypsum in the chemical modification method for phosphorus loading requires further validation.

In phosphorus loading via microbial treatment, phosphorus solubilizing bacteria play an essential role in raising the bioavailability of phosphorus through the dissolution of stable biochar-phosphorus. This is revealed in several studies, which include Efthymiou et al. (2018), Qian et al. (2019), and Mousavi et al. (2023). Importantly, biochar could have stimulatory effects on the phosphorus-solubilizing microorganisms in the soil, depicted by the negligible changes in microbial activity without biochar (Efthymiou et al. 2018). Moreno-Bayona et al. (2019) explained that biochar could enhance the population of phosphorus-solubilizing bacteria and promote biofilm production. Additionally, the roughness and hydrophilicity of biochar, which increase with higher pyrolysis temperatures, can impede the retention of phosphatase enzymes. This, in turn, leads to greater nutrient mobility in the soil. Theoretically, phosphorus bound to minerals with larger ionic radii and lower charge density is less accessible to plants due to weaker attraction forces. During pyrolysis, a significant portion of phosphorus becomes locked in

insoluble forms when it binds to minerals. The stability of mineral-bound phosphorus in the soil can be influenced by changes in soil acidity, highlighting the importance of phosphorus-solubilizing microorganisms. Organic acids such as gluconic acid, citric acid, glycolic acid, malic acid, oxalic acid, formic acid, acetic acid, and lactic acid, which are produced by phosphorus solubilizing microorganisms during their growth in the rhizosphere have a greater contribution in enhancing the release and bioavailability of phosphorus in the insoluble compounds, when compared to inorganic acids including sulfuric acid, nitric acid, and carbonic acid, synthesized by nitrifying and sulfur-oxidizing bacteria due to more substantial solubilizing effect (Prabhu et al. 2019). The incorporation of phosphorus-solubilizing microorganisms through incubation with the biochar-amended soil could enhance the water-solubility of the mineral phosphorus, which is present on the biochar matrix and soil colloids, and thereby improve the availability of plant-accessible phosphorus.

Efthymiou et al. (2018) experimented with studying the effectiveness of four *Penicillium* strains (*Penicillium aculeatum*, *Penicillium bilaii*, *Penicillium glabrum*, and *Penicillium expansum*) in solubilizing different forms of phosphorus. The experiment involved incubating these strains in a liquid culture containing sewage sludge-derived biochar, calcium-phosphorus, iron-phosphorus, and aluminium phosphorus. The sewage sludge-derived biochar had minimal amounts of water-extractable (0%) and sodium bicarbonate-extractable phosphorus (1.8%), while the hydrochloric acid extraction method revealed a significant presence of calcium-phosphorus (68.5%). Calcium-phosphorus is commonly produced during the thermochemical carbonization of biomass. All four strains selected secreted citric and gluconic acid as the dominating organic acids, which solubilize the mineral-phosphorus of biochar. The former played an important role in the dissolution of biochar-phosphorus and iron-phosphorus, while the latter was found to contribute to the calcium-phosphorus dissolution. The solubilized fractions of biochar-phosphorus by *Penicillium expansum*, *Penicillium glabrum*, *Penicillium aculeatum*, and *Penicillium billaii* was 14.8, 43.8, 48.7, and 54.3%, respectively, which were considerably higher compared to the culture without the fungi (recorded as only 1.9%). Regarding calcium-phosphorus, the solubilization percentages were reported as 3.9, 44.9, 53.1, 90.6, and 92.5% for no fungi, *Penicillium aculeatum*, *Penicillium expansum*, *Penicillium billaii*, and *Penicillium glabrum*, respectively. Specifically, *Penicillium aculeatum* was observed to increase the phosphorus content in wheat shoots by 6% in biochar-amended soil, while no significant changes were noticed in the unamended soil. This suggests that the effectiveness of phosphorus-solubilizing microorganisms might depend on the

phosphorus source. The enhancement of phosphorus bioavailability can be attributed to the contribution of organic acids. Organic ligands inhibit the conversion of phosphorus to insoluble mineral phosphorus by forming complexes with calcium, iron, and aluminium cations. Additionally, the organic acids' acidification effect promotes the dissolution of calcium-phosphorus. Overall, these findings emphasize the positive role of organic acids in enhancing phosphorus availability.

*Pseudomonas putida*, a soil bacterium, can solubilize phosphorus compounds typically bound to biochar and have low solubility (Qian et al. 2019). Notably, the same authors emphasized the positive effect of high pyrolysis temperature in the degree of metaphosphate polymerization, stability of metaphosphates, and the formation of carbon–oxygen–phosphorus (C–O–P) bond, resulting in impeded phosphorus release to the soil. The researchers suggested that a low pyrolysis temperature, specifically around 400 °C, should be utilized to produce phosphorus fertilizer with slow-release properties. In their experiment, biochar produced at 700 °C exhibited minimal water and sodium bicarbonate-extractable phosphorus. Additionally, a significant portion of phosphorus was found in the residual fraction, accounting for 45.9% of the total, indicating the conversion of phosphorus into a stable form. During the experiment, butyric acid and acetic acid were detected. These organic acids were crucial in solubilizing phosphorus bound to iron and aluminium, releasing hydrochloric acid and sodium hydroxide-extractable phosphorus. Furthermore, the organic acids formed complexes with calcium and magnesium ions attached to oxygen-containing functional groups. This interaction resulted in the release of sodium bicarbonate-extractable phosphorus.

Based on the study by Mousavi et al. (2023), the concentration of phosphorus-Olsen or available phosphorus of the phosphorus solubilizing bacteria-enriched and red phosphorus-and-phosphorus solubilizing bacteria-enriched biochar lay between triple superphosphate and the biochar, which are treated by hydrochloric acid and phosphoric acid as well as enriched with red phosphorus. The concentration of the available phosphorus in soil treated with the phosphoric and hydrochloric acid-modified biochar was recorded as 0.0587 and 0.041 g/kg for the soil with 2 decisiemens per meter and 0.0674 and 0.0386 g/kg for the soil with 15 decisiemens per meter. The phosphorus-solubilizing bacteria-enriched biochar induced the highest alkaline phosphatase activities, while the red phosphorus-enriched biochar had the highest acid phosphatase activity in both soils. Alkaline phosphatase can only be produced by phosphorus-solubilizing microorganisms, and the optimum pH is 11. The optimum pH for acid phosphatase activity is neutral conditions. No further assessment or

validation on the desorption kinetics of phosphorus was taken.

Mechanical process, particularly granulation, is also effective in producing biochar-based phosphorus fertilizer. Pellets, granules, and powder forms of potassium-enriched biochar possess an increasing release rate of potassium in the mentioned order (Fachini et al. 2022). The release rate is positively affected by surface area, the volume of pores and micropores, and particle density. However, pure fertilizer of potassium chloride had a larger release rate of potassium than all three forms of biochar-based fertilizers, indicating the latter's superiority in achieving the long-term release of minerals. They also identified pellets and the granular form of the loaded biochar as a slow-release fertilizer.

Ball milling is a common method employed to reduce biochar particle size. Ball milling is a low-cost, effective, and simple operation to load biochar with phosphorus (Feng et al. 2022; Zhang et al. 2022a; Zhao et al. 2022). For example, Feng et al. (2022) focused on producing calcium alginate-biochar composite as an adsorbent for water remediation, particularly for removing phosphorus and ammonium. By using the Langmuir isotherms, the highest achievable adsorption capacity of phosphorus at 25 °C was reported as 31.8 g/kg for the calcium alginate-modified biochar derived from rice straws via pyrolysis at 300 °C, followed by that of distiller grain and *Eupatorium adenophorum* produced at 600 °C, recorded as 24.1 and 24.0 g/kg, respectively. Their research shows that ball-milled biochar is prone to release phosphates, leading to lower performance as an adsorbent when compared to the composite.

Zhang et al. (2020a) and Zhao et al. (2022) focused on studying ball-milling's effects on phosphorus release capacity and kinetics. The maize straw-derived biochar produced from pyrolysis at 700 °C was ball-milled with red phosphorus for phosphorus enrichment by Zhang et al. (2022a). The authors reported that pristine and ball-milled biochar had the highest phosphorus released to the coastal saline-alkali soil, but both are below 0.3 g/kg. However, the authors claimed that the red phosphorus enriched-and-ball-milled biochar possesses slow-release behavior based on the slightly lower phosphorus released than the pristine biochar; phosphorus release kinetics analysis shall be conducted over a longer period in the soil to provide further validations. Another notable finding is the reduction of soil salinity, indicated by the depletion of sodium, calcium, magnesium, sulfate, and chloride ions in the biochar-amended soil electrical conductivity compared to the control. The reduction is the biggest in the red phosphorus-enriched-and-ball-milled biochar-treated soil. Consequently, the acid and alkaline phosphatase activity in all biochar-treated soil was improved, except for the alkaline

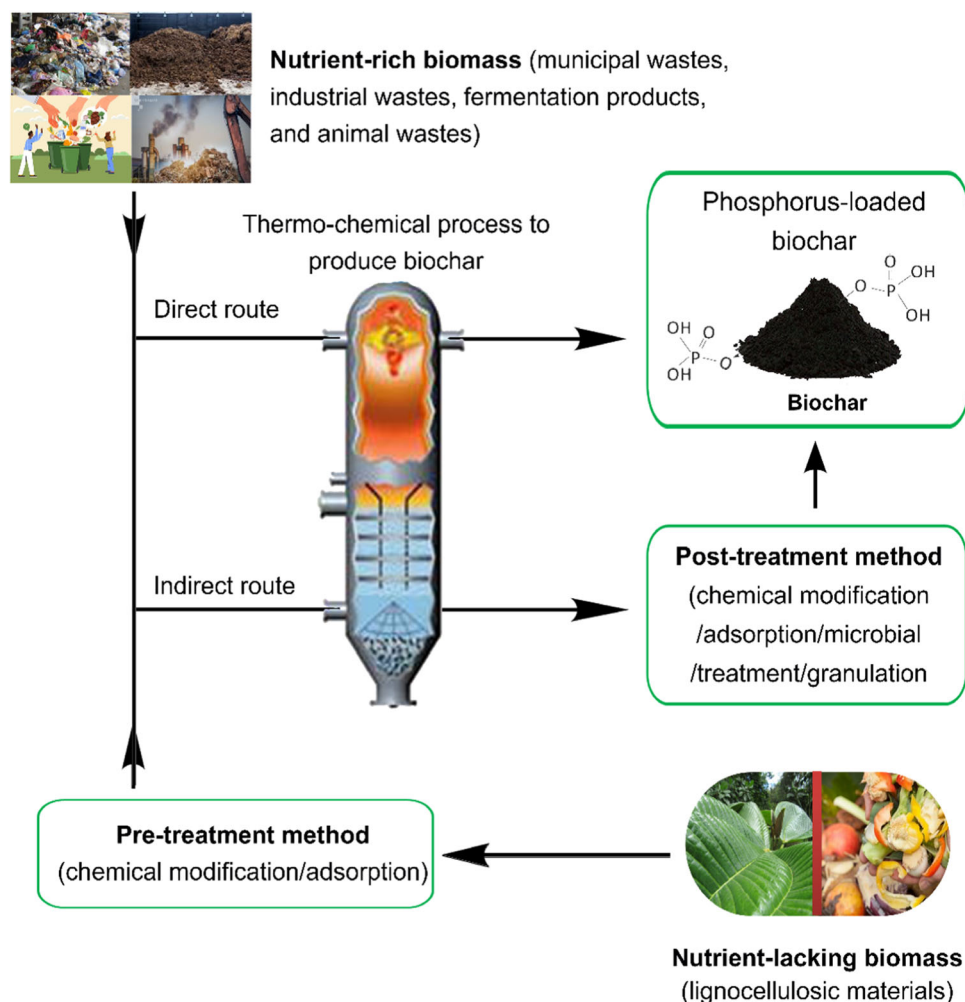
phosphatase activity in the pristine biochar-treated soil, which could be owed to the treated-soil acidity (Zhang et al. 2022a).

Additionally, high temperatures of pyrolysis could cause the collapse of pore structures, favoring metal mineral enrichment and thereby inhibiting the desorption and dissolution of phosphates (Zhao et al. 2022). Besides the pyrolysis temperature, ball milling duration is another controlling factor of pore structure, which also impacts the phosphorus release capacity and kinetics. Rice straw, *Eupatorium adenophorum*, and distiller grains were enriched with phosphorus through ball milling without external phosphorus sources (Zhao et al. 2022). Phosphorus release capacity and slow-release rate were successfully improved by ball milling. The authors obtained the highest phosphorus release at 12-h ball milling, indicating that biomass size reduction, which elevates the specific surface area and total pore volume, could effectively enhance phosphorus desorption. However, the risk of pore blockage by ash rises simultaneously with the milling time.

A solution pH of 6–7 is the optimum value for maximizing phosphorus adsorption capacity, as previously discussed, while Zhao et al. (2022) reported that the release capacity of phosphorus from the ball-milled biochar was the highest at pH 3 and the release capacity continued to decrease when the value rose from 3 to 10. To explain, under acidic conditions, the desorption of phosphates is favored because of the promoted release of mineral cations. They also reported the importance of identifying the optimum dosage of the phosphorus-loaded-biochar in soil, where excess dosage could lead to toxicity, affecting plant germination and growth. Notably, in their experiment, the mung bean germination was impeded by weight at the application rate of 5%. At 10%, no germination of mung beans occurred.

Size reduction could be advantageous in the heavy metal immobilization in contaminated soil as well, as demonstrated by Fahmi et al. (2018), who reported that fine empty fruit bunch-derived biochar with a particle size not exceeding 50 micro-meters had the lowest synthetic rain-water extractability of cadmium in the biochar treated-contaminated, recorded as 10.786 µg, in comparison to the coarse biochar of 2 milli-meters particle size with 12.680 µg cadmium extracted after 8 weeks of incubation. This can be attributed to the larger specific area and more exposed inner porous structure. The biochar application rate is as important as the particle size to achieve remarkable cadmium removal efficiency. The trend of lead extractability in the amended soil was less visible at different application rates, but in general, fine particle size enhances the immobilization of the element.

The selection and arrangement of loading techniques, depicted in Fig. 5, are influenced by the significant



**Fig. 5** Phosphorus loading strategies for biochar. Phosphorus sources can be broadly classified into two groups: nutrient-rich biomass and nutrient-lacking biomass. The high nutrient content of nutrient-rich biomass allows for direct processing through pyrolysis, producing phosphorus-enriched biochar. However, additional post-treatment processes can enhance the biochar's phosphorus availability and properties. In contrast, nutrient-lacking biomass requires an external source of phosphorus to produce phosphorus-loaded biochar. The phosphorus source can be added before thermochemical conversion or

post-treatment. Moreover, pre-treatment and post-treatment can be combined to synthesize phosphorus-loaded biochar from nutrient-lacking biomass. All these methods are well-established and effective techniques for loading phosphorus, but their success depends on the type of biomass feedstock and the loading process conditions. Consistency in the properties and efficiency of biochar-based phosphorus fertilizers is essential for widespread agricultural application

influence of biochar properties on the efficiency of the phosphorus loading process. Adsorption is the primary mechanism for phosphorus loading onto biochar and can be effectively performed using different phosphorus sources. Additionally, combining other treatment methods that modify and enhance biochar properties can further improve the adsorption process as desired. It is worth noting that several studies have demonstrated the potential for biochar-based phosphorus fertilizer synthesis to simultaneously address environmental concerns such as soil and water remediation and waste reduction and management. However, it is crucial to consider factors such as compatibility with existing facilities, the adsorption effluent quality, and

the phosphorus release behavior. These aspects should not be overlooked during the design and implementation of biochar-based phosphorus loading systems.

### Characterization of loaded biochar

Phosphorus-enriched biochar offers the benefits of slow-release fertilizer and potential applications in soil remediation. Various aspects of the biochar must be evaluated using different characterization methods to determine biochar's suitability for specific uses. This section discusses the key methods employed in characterizing biomass, biochar, and phosphorus-loaded biochar, then



compares the results. The fundamental physiochemical properties examined include pH, electrical conductivity, zeta potential, and cation exchange capacity. Additionally, thorough structural and surface characterization is crucial for studying surface functional groups, morphology, elemental composition, intra-structure, the content of

inorganic and organic compounds, adsorption mechanisms, and loading efficiency. Table 4 summarizes the diverse characterizations conducted on biochar loaded with phosphorus.

Furthermore, analysis is conducted to assess the impact of the loaded biochar on plant growth through incubation

**Table 4** Characterization of phosphorus-loaded biochar

Types of characterization	Measured parameters	Importance
Physiochemical properties	pH	Govern microbial decomposition and mineralization of organic contaminants, dissolution and precipitation of heavy metals and organic compounds, enzymatic activities, ammonia volatilization of ammonia, nitrogen cycle, and organic amendments content in the soil The effect of biochar on phosphorus release is boosted at soil pH between 6.5 and 7.5
	Electrical conductivity	Indicate salt content in the soil High salt content resists plant water uptake and triggers soil corrosion and degradation Low salt content causes nutrient deficiency in the soil Measured in decisiemens (dS)/m
	Cation exchange capacity	Support bigger holding capacity of water and nutrient Affect holding capacity of heavy metals during soil remediation pH-sensitive Measured in centimoles (cmol)/kg by ammonium acetate solution method
	Zeta potential	Affect cation adsorption performance pH > zero charge point promotes cation adsorption Affect adsorption efficiency of heavy metals during soil remediation
Surface properties	Surface morphology	Determine microstructure, impurities, pore structure, and fractures Determine the effect of thermochemical carbonization and phosphorus loading Measured by SEM, SEM–EDX, and TEM
	Specific surface area, pore diameter, and pore volume	Affect adsorption efficiency, holding capacity of nutrients, water, cations, and fluid penetration Measured in m <sup>2</sup> /g, Å, and cm <sup>3</sup> /g respectively by nitrogen adsorption technique
	Surface elements and composition	Validate chemical modification efficiency Determine phosphorus distribution on the biochar matrix surface Measured by SEM–EDX, XPS, or AAS
Structural properties	Functional groups and ordering degree	Affect physiochemical properties and adsorption and desorption on the biochar matrix surface Validate phosphorus loading efficiency Measured by FTIR, Raman spectrometry, and NMR spectrometry
	Crystallinity	Measure crystallinity phases Validate cation modification efficiency Measured by XRD spectroscopy

Characterizing biochar loaded with phosphorus involves examining the material's physiochemical, surface, and structural properties. Each of these properties plays a crucial role in various aspects, such as the adsorption and desorption of phosphorus, which directly impact the loading method and fertilizer efficiency. Elemental composition and structural properties are essential to ensure the effectiveness of phosphorus loading through surface morphology investigations. The cation exchange capacity and zeta potential are key indicators for assessing the efficiency of removing heavy metals from the soil by applying phosphorus-loaded biochar

AAS atomic absorption spectroscopy, FTIR Fourier transform infrared spectroscopy, NMR nuclear magnetic resonance spectroscopy, SEM scanning electron microscope, SEM–EDX scanning electron microscopy-energy dispersive X-ray analysis, TEM transmission electron microscopy, XPS x-ray photoelectron spectroscopy, XRD x-ray diffraction analysis

or pot experiments. To investigate the phosphorus release ability of the loaded biochar, it is essential to characterize the soil as well. In cases where the presence of inorganic contaminants is of concern, the analysis is extended to determine the effect of loaded biochar on contaminant availability and mobility in the soil.

The ability of biochar to improve the alkalinity of soil through the release of hydroxyl ions was reported in past studies. Phosphorus release is affected significantly in applying biochar on slightly acidic soil with a pH between 6.5 and 7.5 (Buss et al. 2018). Zhang et al. (2019b) stated that soil with initially high pH would experience less effect of phosphorus enrichment with the addition of unloaded biochar. Moreover, they revealed that phosphorus release is mainly attributed to chemical fertilizer instead of the biochar applied in soil, implying the function of biochar to retain and carry nutrients rather than the source of phosphorus when implemented with chemical fertilizer. Soil pH regulation plays a vital role in maintaining various activities such as the decomposition and mineralization of organic contaminants by microorganisms, dissolution and precipitation of heavy metals and organic compounds, microbial and enzymatic activities, volatilization of ammonia, nitrogen cycle, and availability for organic amendments, in addition to the nutrient level, which is impacted by the release of mineral cations, including calcium, potassium, sodium, magnesium, aluminium, and protons (Neina 2019).

The electrical conductivity of soil is an indicator of salt availability in the medium, and biochar is reported to negatively affect the parameter (Nawaz et al. 2018). High soil salinity could affect salt-sensitive plant growth and health due to increased resistance of water uptake as well as trigger soil corrosion and degradation, but low electrical conductivity could lead to nutrient deficiency. As a result, the effect of biochar on the soil's electrical conductivity shall be known to avoid drastic changes in soil salinity during application. Zhang et al. (2022a) stated that the reduction of electrical conductivity after applying phosphorus-loaded biochar occurs through the precipitation reaction between minerals and oxygen-containing groups, including phosphates attached to biochar, leading to lower alkalinity and salinity. In the measurement of a biochar's electrical conductivity, usually in the unit of decisiemens per meter, a solution of biochar is made by mixing the sample with deionized water at a ratio between 0.1 and 0.05 g/mL, followed by electrical conductivity measurement (Ahmad et al. 2018; Wali et al. 2020).

The cation exchange capacity of biochar is another basic property that is commonly measured in the unit of centimoles per kilogram. When added to the soil, biochar with high cation exchange capacity helps nutrient storage and water retention. In the measurement of cation exchange

capacity via the ammonium acetate solution method, pH adjustment by washing biochar with distilled water and hydrochloric acid shall be conducted to achieve neutrality and electrical conductivity below 0.2 mS/cm, which is done before the biochar immersion in the ammonium acetate solution to avoid measurement errors, which can be caused by dissolved cations associated with salts and ashes, as well as the effect of pH on cation exchange capacity (Munera-Echeverri et al. 2018). The first extraction is conducted using 1 molar (M) ammonium acetate solution and shaking at 200 revolutions per min for 1 day before centrifugal separation. The subsequent three extractions follow this before analysis with inductively coupled plasma optical emission spectroscopy employed to measure cations in the extract, representing the amount of exchangeable portion.

To study the surface interaction with cations, zeta potential is measured as a physical factor influencing the cation adsorption performance on biochar by using a zetasizer. In measuring zeta potential, pH is manipulated as the parameter plays a significant part in the variation of zeta potential. After determining pH at zero charge point, the value is compared with the zeta potential at different pH. At the zero-charge point of an equilibrium system, no potential difference and particle movement exist. When the system pH is below that of the zero-charge point, positive charges dominate, resulting in a net positive charge of the biochar surface, favoring the adsorption of phosphates. In contrast, cation adsorption is preferred at a pH exceeding the zero-charge point.

The degree of the pH effect on the adsorption capacity depends on the dominating mechanisms, where the effect is the most significant for electrostatic attraction. Shin et al. (2020) demonstrated a positive correlation between soil acidity, ranging below pH 4, and phosphorus adsorption capacity, as discussed previously. On the other hand, as reported by Feng et al. (2022), the pH at zero charge point was recorded as 2.94, 2.20, 2.14, and below 2.0 for the distiller grains, rice straw, and *Eupatorium adenophorum*-derived biochar as well as the calcium alginate-biochar composite, respectively. Thus, by theory, soil acidity, particularly below pH 3, shall promote phosphorus adsorption on the biochar. The adsorption capacity, however, increased with pH until the maximum point at pH 6–7 (Feng et al. 2022), suggesting that the dominating mechanisms are ligand exchange and precipitation, which are not dependent on the soil pH. The difference between the results implies the importance of investigating the mechanism of phosphorus adsorption to understand the effect of pH.

The experiment showed that zero-charge-point pH could be reduced chemically in addition to variations in the fundamental properties of biochar (Feng et al. 2022).

However, recent studies have not shown the significance of the correlation between the different chemical modification agents and the zero-charge-point pH of biochar. In the study of heavy metal-contaminated soil remediation, biochar-based fertilizer possessing lower zero-charge-point pH can promote cation adsorption and hence, heavy metals removal from soil. Since heavy metals are adsorbed on a biochar surface via surface sorption, electrostatic attraction, cation exchange, surface complexation, and precipitation (Ambaye et al. 2021), surface morphology and properties are as important as the soil properties in the study of heavy metal removal by using phosphorus-loaded biochar.

Surface properties, such as morphology, surface elements, surface area, pore diameter, pore volume, pore structure, and structural properties, including functional groups, play a crucial role in biochar application. These properties significantly impact adsorption and desorption, as well as the stability and longevity of biochar. The surface properties of biochar are greatly influenced by the pyrolysis temperature and biomass type, which are also manipulated variables in relevant studies.

Fourier transform infrared spectrometry is a reliable and straightforward analytical tool for determining surface functional groups of biochar. The technique was implemented in most of the studies to characterize biochar. Fourier transforms infrared spectrum analysis is conducted in the wavelength range between 400 and 4000 per cm. P=O, R–O–P, and P–O stretching would cause absorption bands at 1240–1300, 920–1088, and 725–845 per cm, respectively (Kim et al. 2018). A phosphate ion complex would cause absorption bands at 750–800 and 1000–1100 per cm (Nardis et al. 2022). These absorption bands indicate the presence of phosphorus in biochar after phosphorus loading. Changes in their intensity can also be used to study the phosphorus release of the biochar-based fertilizer in the soil. Raman analysis can be used in addition to Fourier transforms infrared spectrometry to study the functional group of biochar. This was implemented by Wang et al. (2020a), who focused on producing hydrochar from maize straw, on addressing the inability of Fourier transform infrared spectrometry to study the ordering degree of hydrochar.

Phosphorus-nuclear magnetic resonance is another analytical method to validate the presence of phosphorus in biochar. Qian et al. (2019), Cui et al. (2020a), and Zhou et al. (2023) validated the presence of phosphorus on the biochar matrix surface. To prepare the analyte, phosphorus extraction was started by adding biochar into sodium hydroxide-ethylenediaminetetraacetic acid solution at a specified mass-volume ratio, followed by incubation at 25 °C for 16 h under constant shaking. The extract was obtained through a solid–liquid separation with a

centrifuge and filter before phosphorus-nuclear magnetic resonance analysis. The phosphates extraction efficiency and biochar properties, which vary with the feedstock choice and the biochar-producing temperature, obviously impact the result of nuclear magnetic resonance analysis (Cui et al. 2020a). In the studies by Qian et al. (2019) and Cui et al. (2020a), a comparison between the composition of different phosphate species, including orthophosphates, monoester phosphate, and pyrophosphates, was conducted based on their peak heights in the spectrum.

Nuclear magnetic resonance analysis cannot be used solely to measure and compare the composition of different phosphate species owing to the non-extractable portion of biochar. Hence, other analytical tools are to be implemented for accurate measurement. Qian et al. (2019) applied X-ray diffraction and X-ray photoelectron spectroscopy to address the flaw of nuclear magnetic resonance analysis. X-ray diffraction spectroscopy reveals the crystalline phases of biochar, and the absence of peaks could imply the low crystallinity of phosphorus compounds (Qian et al. 2019). On the other hand, peaks could be formed due to the presence of various species of magnesium and calcium-phosphate crystals, which can be used to validate the effect of cation modification on biochar enrichment with phosphorus, which was demonstrated by Qian et al. (2019), Wu et al. (2019a), Arwenyo et al. (2022), Feng et al. (2022), Nardis et al. (2022), Piash et al. (2022), Qi et al. (2022a), Suwanree et al. (2022), and Zhou et al. (2023).

The surface morphology of biochar is distinctive for each feedstock and can be modified through pre-treatment and thermochemical carbonization of biomass. The surface imaging technique is a dependable method for studying biochar morphology, which has been utilized in numerous previous studies. Scanning electron microscopy is a useful tool for determining the microstructure, impurities, pore structure, and fractures of biochar. This technique can be used to analyze the effects of thermochemical carbonization and phosphorus loading on the surface properties of biochar. It is commonly utilized for characterizing the matrix surfaces of biochar. Comparing images obtained through this technique allows for studying the impact of pyrolysis and various loading techniques on the surface of biochar.

Furthermore, the utilization of scanning electron microscopy-energy dispersive X-ray analysis allows for the identification of the surface mentioned above characteristics and the elemental composition of the biochar matrix, specifically at a shallow depth of merely 10 nm. The analysis also provides information on the elemental composition, which is particularly useful for studying the effect of chemical modification. In the study by Wu et al. (2019a), an increase in surface magnesium composition of 6.81% by weight was observed through scanning electron

microscopy-energy dispersive X-ray analysis. Nardis et al. (2022) used scanning electron microscopy-energy dispersive X-ray analysis to indicate the even phosphorus distribution on the loaded biochar matrix surface. Another option to study surface morphology is transmission electron microscopy which was implemented by Wu et al. (2019a) and Zhou et al. (2023). On the other hand, the elemental composition can be examined using X-ray photoelectron spectroscopy, which effectively examines the effect of cation modification on biochar. In the study by Qi et al. (2022a), the concentration of cations was determined by using atomic absorption spectrophotometry that follows proper acid digestion procedures,

Porosity directly impacts the adsorption ability of biochar, where a larger value could provide a better outcome. However, the parameter is also closely related to the material storage capacity of targeted species, such as nutrients, water, and contaminants during the application in soil. Specific surface area, adsorption average pore diameter, and total pore volume are determined in  $\text{m}^2/\text{g}$ ,  $\text{\AA}$ , and  $\text{cm}^3/\text{g}$ , respectively. The abovementioned parameters determine the porosity effectiveness of a solid porous material where an effective porous structure should have interconnection and allow easy penetration of fluids into the material (Pourhakkak et al. 2021).

Regarding the production of biochar-based fertilizer, the evaluation of pore distribution is employed to assess the nutrient adsorption capability of biochar. The formation of micropores is favored by lower processing temperatures and longer thermal treatment durations, and it is closely linked to the specific surface area of the biochar. The Brunauer–Emmett–Teller (BET) method can determine the specific surface area. In the studies by Arwenyo et al. (2022) and Suwanree et al. (2022), the specific surface area of biochar, pore diameter, and pore volume were measured with the nitrogen gas adsorption technique. To begin the analysis, the samples are first degassed at a temperature ranging from 180 to 200 °C for 6 h or overnight. Approximately 0.1–0.3 g of the sample are analyzed at a low temperature of approximately -196 °C, corresponding to the nitrogen gas boiling point. This measurement is carried out using a surface area and porosity analyzer. Moreover, the total pore volume and pore diameter are determined through desorption data using the Barrett–Joyner–Halenda (BJH) method. Additionally, the volume of micropores is investigated using the t-method.

Porosity and pore distribution contribute greatly to phosphate and heavy metal adsorption by biochar via pore filling. Gong et al. (2019) stated that the penetration of nutrient compounds, particularly hydrated cations, is impeded when the pore size is less than 0.6 nm. As the pyrolysis temperature rose from 300 to 800 °C, a noticeable shift and concentration of the pore distribution

towards sizes below 2 nm were observed. This shift correlated with an increased hindrance in the adsorption of nutrients on the surface of the biochar matrix. Conversely, it was reported that biochar possessing a pore size ranging from 0.6 to 2 nm exhibited outstanding adsorption capacity for phosphorus, nitrogen, and potassium. On the other hand, for the efficient adsorption of heavy metals, a pore diameter exceeding 5 nm was necessary (Pathy et al. 2023). The desorption of nutrients and soil pollutants depends on the type of bonding between the adsorbates and biochar and is readily facilitated with a higher composition of physical bonding. For slow-release phosphorus biochar-based fertilizer, the weak interaction force between the nutrient adsorbates and biochar is desired for easy cleavage by organic acids, as shown in the study by Qian et al. (2019).

A comparison between phosphorus content before and after enrichment must be conducted to ensure effective phosphorus loading in biochar. Hence, an accurate measurement of phosphorus content in biochar is needed. Moreover, phosphorus content in amended soil is to be compared with that of unamended soil to evaluate the effectiveness of biochar-based phosphorus fertilizer.

Before quantitative phosphorus content analysis, phosphorus extraction from biochar samples is carried out. Analyte preparation differs from quantitative methods. The efficiency of phosphorus-containing extract and digestate preparation methods is crucial to ensure accurate phosphorus content measurement. In the experiment by Kim et al. (2018), analytes for inductively coupled plasma optical emission spectroscopy to determine the total phosphorus content in the loaded biochar were prepared through microwave-assisted acid digestion. Ahmad et al. (2018) implemented ultraviolet–visible spectrophotometry for total available phosphorus measurement using the molybdate-ascorbic acid method. Differently, Chen et al. (2022) and Feng et al. (2022) used the ammonium molybdate spectrophotometric method to study available phosphate concentrations in loaded biochar.

Different extractants can be used for phosphorus fractionation, where the most popular solvents include resin, sodium bicarbonate, organic acids, sodium hydroxide, and hydrochloric acid. Sodium bicarbonate-extractable phosphorus is more plant-accessible (Zhu et al. 2018) and can indicate short-term phosphorus availability. Measurement of labile phosphorus was conducted by Frišták et al. (2018) through the extraction with calcium-acetate-lactate. To determine available phosphorus content in soil samples, the molybdate-ascorbic acid method was practiced by Ahmad et al. (2018) to prepare a colored solution for ultraviolet–visible spectrophotometry using sulphuric acid, ascorbic acid, antimony potassium tartrate, and ammonium molybdate. Besides, sodium bicarbonate was used to extract

available phosphorus in the soil, as in the experiment by Chen et al. (2022). Piash et al. (2022) used a mehlich-3 solution to extract phosphorus and other nutrients such as potassium, calcium, magnesium, aluminium, and iron. Then, the digestate of the extract was prepared with nitric acid and hydrogen peroxide for inductively coupled plasma mass spectrometry analysis.

Several studies have employed sequential extraction or fractionation techniques to investigate the various forms of phosphorus in samples, such as biomass, biochar, loaded biochar, unamended soil, and amended soil. These methods involve using different extractants, including deionized or distilled water, sodium bicarbonate, sodium hydroxide, and hydrochloric acid solution, to extract phosphorus from the samples step-by-step. The extracted phosphorus fractions are then subjected to proper digestion before quantitative analysis is performed to measure the total phosphorus content. Notably, sequential fractionation has been utilized in recent studies conducted by Qian et al. (2019), Cui et al. (2020a), and Chen et al. (2022). Based on the experiment result by Qian et al. (2019), the increase in pyrolysis temperature from 400 to 700 °C transformed a more significant fraction of phosphorus into residual phosphorus, which is more stable than the other phosphorus species. *Pseudomonas putida* did not significantly affect the phosphorus solubility in hydrochloric acid and sodium hydroxide for the biochar synthesised via pyrolysis at 700 °C. However, for the biochar produced by pyrolysis at 400 °C, *Pseudomonas putida* improved the phosphorus extractability in water, sodium bicarbonate, sodium hydroxide, and hydrochloric acid by 83.5, 43.0, 56.7, and 54.1%, respectively, as compared to that without *Pseudomonas putida*, recorded as 63.1, 8.6, 29.1, and 33.6%, respectively. The water-soluble fraction of phosphorus in the biomasses, namely *Hydrilla verticillata*, *Myriophyllum spicatum*, and *Cannabis indica*, was reported as 5.64, 6.52, and 3.12 g/kg, respectively, which are higher than the hydrochar produced at 200–260 °C with 0.21–2.74, 0.47–2.71, 1.21–2.15 g phosphorus /kg biochar (Cui et al. 2020a). The reduction of water-soluble phosphorus was caused by the crystallization of calcium-phosphorus in hydrothermal carbonization, which is similar to the effect of pyrolysis. The higher composition of acid-soluble phosphorus is an important indicator of slow-release behavior, but no further studies were conducted by the authors, particularly to examine the phosphorus extractability in different organic acids.

As discussed, Chen et al. (2022) reported that the pig carcass-derived biochar had improved the soluble and sodium bicarbonate-extractable inorganic phosphorus content by 6 and 9%, respectively, in comparison to the untreated soil, which also exceeded the chemical fertilizer-treated soil by 6 and 4%. This indicates that soil

amendment with biochar successfully boosts the immediately soluble fraction and short-term supply of phosphorus in soil. However, the hydrochloric acid-extractable phosphorus fraction in the biochar-amended soil was lower than the untreated and the chemical fertilizer-treated soil by 20, 46, and 49%, respectively. The biochar could enhance the short-term bioavailability of phosphorus, which could be helpful for plant germination, but in the long term, the extractable phosphorus is lowered. Thus, the demand for phosphorus fertilizer in the biochar-amended soil could be higher. The release behavior of phosphorus in the biochar-amended soil shall be studied, particularly in different organic acids over a more prolonged incubation, to assess the efficiency of the biochar as a slow-release phosphorus fertilizer.

As explained, organic acids, particularly citric acid, are the primary extractant of inorganic phosphorus, which is bounded by mineral cations and cannot be uptake by plants easily. Not all studies in Table 3 included the efficiency of the produced biochar as a slow-release phosphorus fertilizer. The choice of the extractant for the analysis of phosphorus release in soil plays a vital role in assessing the slow-release behavior of loaded biochar. In the experiment conducted by Shin et al. (2020), it was observed that an acidic environment positively impacted the bioavailability of phosphorus. This was indicated by higher phosphate release capacities, specifically 43.2 and 28.8% in mehlich at pH 2.2 and 2% citric acid at pH 2.5, respectively, as well as 8.74% at pH 7 and 9.4 after 12 h. Notably, chelators such as 2-keto-gluconic, fulvic, and humic acid, known to bind with aluminum, iron, and calcium, played a role in solubilizing inorganic phosphates bound to minerals. To assess the slow-release behavior of biochar-based phosphorus fertilizer, it is crucial for formic acid-extractable phosphorus to be higher than water-soluble phosphorus (Suwanree et al. 2022). This principle could also be applied to other organic acids produced by phosphorus-solubilizing microorganisms.

Kim et al. (2018) measured the release of phosphorus into water over 24 h. To perform quantitative analysis, they utilized inductively coupled plasma optical emission spectroscopy. The experimental procedure involved placing biochar in deionized water, maintaining a specific mass-volume ratio, and subjecting it to continuous shaking for one day. Subsequently, a simple filtration process was employed to separate the solid biochar from the liquid. During the experiment, the deionized water was replaced with a 2% citric acid solution on the fifth day to examine the behavior of phosphorus release in citric acid-soluble form. The results showed that the amount of phosphorus released in the water and citric acid solution increased over time. Specifically, 42 and 52% of the total available phosphorus had been released into the water and citric acid



solution at the fourth hour, respectively. By the fifth day, these percentages had risen to 52 and 61% for the water and citric acid solution, respectively. The study observed that although the initial phosphorus release rate was rapid, no significant increase was observed after five days. This suggests that the biochar produced can function as a slow-release biochar-based phosphorus fertilizer.

Jetsrisuparb et al. (2022) and Suwanree et al. (2022) demonstrated that magnesium cations could act as an effective chemical modifier in increasing phosphorus availability and ensuring the slow-release behavior of loaded biochar. Jetsrisuparb et al. (2022) conducted a 240-h experiment to examine the release pattern of the unmodified, calcium-modified, and magnesium-modified biochar in distilled water and 2% formic acid. Over 240 h, phosphorus was gradually released for the calcium and magnesium-modified biochar. The magnesium-modified biochar was selected as a better slow-release phosphorus fertilizer, where 1, 4, and 10 g of phosphorus per kilogram biochar was released after 1, 24, and 240 h, respectively. In comparison, the calcium-modified biochar released only 0.9 and 1.2 g of phosphorus per kilogram biochar after 24 and 144 h, which is inadequate and also implies that magnesium cations are a better choice in the chemical modification of phosphorus, owing to the higher solubility in water.

The study by Suwanree et al. (2022) revealed the effect of the sequence of the phosphorus loading process as a determining factor of the slow release behavior of phosphorus in loaded biochar. Phosphorus solubility in an organic acid is affected by the strength of bonding and the crystal stability on the biochar matrix, which could be altered with the treatment procedures. Suwanree et al. (2022) reported that the post-treatment with di-ammonium phosphate after magnesium cations and phosphoric acid modification increases both formic acid and water-soluble phosphorus within 30 min, implying the greater contribution of magnesium cations and phosphoric acid in forming the slow-release behavior of the biochar. However, after the post-treatment with diammonium phosphate, the concentration of the formic acid and the water-extractable phosphorus was the greatest, which are 71 and 40% of the total phosphorus concentration, respectively. The phosphorus release over 240 h was also more aggressive, where more than 80% of the total phosphorus was released. Conversely, the magnesium modified-biochar pre-treated with di-ammonium phosphate and phosphoric acid released only 23 and 18% of the total phosphorus available, respectively. The latter had a lower release amount of phosphorus, recorded as 1.8 g/kg in the first 15 min when compared to 5.6 g/kg by the former, but the release patterns of both biochar are similar, where the release became relatively gradual after 6 h.

Sulfur and calcium-rich phosphogypsum, and potassium-rich banana peduncle were used as chemical modifiers by Vimal et al. (2022). The reduced portion of poultry litter could cause the reduction of citric acid and formic acid-extractable phosphorus in the composites due to mixing with the chemical modifiers. Nevertheless, the phosphogypsum-modified poultry litter-derived biochar had a faster phosphorus release rate than the unmodified biochar, as indicated by the larger ratio of phosphorus released in the last extraction to the first extraction. After 0.25 h, the amount of phosphorus released was 1.06 and 0.24 g/kg for the unmodified and modified biochar with the banana peduncle-poultry litter-phosphogypsum ratio of 1:1:1, respectively. As the ratio was varied to 1:2:1 and 1:3:1, water-soluble phosphorus was higher, leading to more rapid phosphorus release in distilled water, indicated by 1.82 and 1.05 g/kg of phosphorus released at 0.5 h. This resulted in a higher amount of phosphorus released at the initial stage and lower availability of extractable phosphorus when approaching equilibrium. The rapid phosphorus release at the initial stage is advantageous for plant germination.

The choice of extractant can vary the assessment results of the phosphorus bioavailability of a loaded biochar because of the correlation between the biochar properties and the phosphorus solubility. Figueiredo et al. (2021) demonstrated the effect of pyrolysis temperature on the release capacity of phosphorus in 2% citric acid and Mehlich. The former experienced increased phosphorus release capacity at higher pyrolysis temperatures, which is the opposite of the latter. To explain, as temperature increases, organic and soluble phosphorus are converted to stable complexes with aluminium and calcium, such as crandalite and wavelite, as well as residual form. The said stable complexes are more soluble in acidic than neutral solutions. However, Figueiredo et al. (2021) also reported a higher value of neutral ammonium citrate-extractable phosphates, which is 65.2% on average, compared to that of citric acid-extractable, recorded as 42%. This result opposed the finding in past studies, which stated that citric acid-extractable phosphates are usually more than that neutral ammonium citrate. The lower citric acid-extractable phosphorus could be attributed to two possibilities related to the biochar properties, which are the abundance of organic matter and monocalcium phosphates with significant hydrophobicity, resulting in poor solubility in the citric acid solution, as well as the high composition of aluminium phosphate, which dissolve readily in the neutral ammonium citrate solution but not in the citric acid solution. Mehlich shall be used to assess the bioavailability of phosphorus in sewage sludge-derived biochar since the material consists of abundant clay, sand, and inorganic phosphates (Figueiredo et al. 2021).

Leite et al. (2023) also conducted a 240-h incubation experiment with the dried and modified poultry manure, the unmodified and magnesium-modified biochar produced at 300 and 500 °C. The phosphorus release from the dried and modified poultry manures continuously increased over 240 h. In contrast, the modified and unmodified biochar produced at 300 and 500 °C achieved stable phosphorus release in a shorter time. The phosphorus release capacity of the magnesium-modified biochar produced at 300 and 500 °C as well as the unmodified biochar made at 500 °C was significantly smaller than the unmodified biochar produced at 300 °C, recorded as 3, 1, 4.6, and 67% of the respective total phosphorus content. This implies the function of the added magnesium cations in phosphorus fixation. This is not limited to biochar, but the reduction was also noticed for the poultry manures, recorded as 1.91 g/kg from 5.36 g/kg over 72 h. With the reduced phosphorus release capacity of the modified biochar, the duration of the phosphorus release is extended, allowing the long-term phosphorus supply from the biochar and the decreased need for inorganic fertilizer use in the soil. Nonetheless, the study did not include the modified biochar agronomic efficiency assessment, considering the significant reduction in the phosphorus release capacity reported. Hence, validation of the modified biochar effect on plant production and the post-harvest soil is needed.

In the study by Li et al. (2020a), an anion exchange membrane was used to determine the phosphorus level in the soil. The membrane possessed quaternary ammonium as a functional group and was immersed in sodium chloride solution for 1 day before cutting into smaller sizes. One piece of the membrane was buried in the soil, followed by adding water until 80% of maximum capacity. Washing with distilled water followed the immersion of the membrane in soil for 2 days to remove soil on the membrane. Extraction of phosphates adsorbed on the membrane from the soil is carried by impregnation and agitation in sodium chloride solution for 1 h before filtration. Murphy Riley method is implemented to measure phosphate concentration adsorbed by the membrane.

Heavy metal immobilization using phosphorus-enriched biochar has gained much attention in recent studies. To study the performance of phosphorus-loaded biochar in heavy metal removal from the soil, diethylenetriamine penta-acetic acid was used by Ahmad et al. (2018), Chen et al. (2022), and Qi et al. (2022a) to extract various available heavy metals in soil to prepare analyte for inductively coupled plasma optical emission spectroscopy. Besides, atomic adsorption spectrometry coupled with flame automatization was employed by Qi et al. (2022a) to quantify copper (II) ions, cadmium (II) ions, and lead (II) ions in the adsorbent. Three analytical methods were implemented by Frišták et al. (2018) to analyze heavy

metal content in the soil, namely atomic adsorption spectrometry coupled with flame automatization, malachite green microplate method for ultraviolet–visible spectroscopy, and inductively coupled plasma mass spectrometry.

In the experiment by Chen et al. (2022), the Tessier sequential extraction method that uses solutions of magnesium chloride, sodium acetate, and hydroxylamine hydrochloride as extraction media was implemented to extract exchangeable lead, lead-carbonate, and lead-iron-manganese oxides in soil samples respectively. After proper filtration to remove the solid, the extract was sent for inductively coupled plasma optical emission spectroscopy analysis. As discussed, using the pig carcass-derived biochar in soil successfully reduced the concentration of exchangeable lead and lead-carbonate by 76.7 and 27.9%, respectively, due to the immobilization of lead on the biochar matrix surface. Conversely, chemical fertilizer caused an increase of exchangeable lead in soil by 8.1%.

The behavior of heavy metals in biochar-amended soil under different conditions of interest is studied to examine the performance limits of the biochar. The positive correlation between the redox potential and the mobility of chromium in cement-amended soil was reported by Zhang and Lin (2020), where oxidizing conditions would favor the oxidation of immobile chromium (III) ions to mobile chromium (VI) ions, leading to higher leaching rate. Since the redox potential's apparent influence on the mobility of heavy metals in soil, there is a need to study the effect on redox potential caused by the addition of phosphorus-loaded biochar in agricultural soil. Yang et al. (2021b) carried out a redox experiment that aims to provide information about the behavior of heavy metals in flooded soil, particularly in paddy soil. A synthetic laboratory environment simulating paddy soil during flooding, which causes oxic and anoxic cycles, was created by using an automated biogeochemical microcosm. Phosphorus-loaded biochar effectively immobilized heavy metals, notably lead, under different redox conditions.

In summary, to comprehensively understand biochar properties, it is essential to investigate critical factors such as pH, cation exchange capacity, electrical conductivity, and surface properties. These characteristics directly impact the efficiency of phosphorus loading and release rates. Furthermore, it is crucial to assess the effectiveness of biochar-based phosphorus fertilizers for soil remediation and fertilization. This requires efficient extraction or digestion methods and reliable qualitative and quantitative analytical tools. Examining phosphorus release kinetics in various extractants, particularly organic acids, should be included in relevant studies. Organic acids play a significant role as solvents for insoluble mineral phosphorus

found in the labile pool, which is abundant due to phosphorus fixation at high soil pH. Incorporating the study of organic acids will provide valuable insights into biochar's behavior and potential as a phosphorus fertilizer.

## Mechanisms of phosphorus release from biochar

### Impact of biochar properties on phosphorus release

Biochar exhibits a high abundance of active sites that facilitate phosphorus adsorption due to the porous structure and surface groups contained (Wang et al. 2020c). According to studies, the phosphorus adsorption capability of biochar is affected by the concentration of soluble components in biochar (Dugdug et al. 2018). Biochar is extensively employed in current research on phosphorus adsorption and release, with the understanding that these processes are closely associated with biochar's physical and chemical characteristics (Dai et al. 2020a; b). The features of biochar are dictated mainly by the raw materials used and the pyrolysis conditions (Kavitha et al. 2018). Studies have shown that biochar's pH ranges from 5.8 to 10.9, and the cation exchange capacity is between 0.03 and 0.67 mol/kg. Biochar's surface area and mass ratio have been measured to be between 20–169 m<sup>2</sup>/g and 21–401 m<sup>2</sup>/g, respectively (Kaudal et al. 2016). Phosphorus release from biochar can be influenced by various factors, including the type of functional groups present, the cation exchange capacity, and the pH value of the biochar (Weber and Quicker 2018).

The temperature of pyrolysis has a considerable impact on the physicochemical properties of biochar (Uševičiūtė and Baltėnaitė-Gedienė 2020). Figure 6 shows that biochar produced at temperatures less than 600 °C can preserve functional groups in the raw material (Yang et al. 2022a). Lowering the pyrolysis temperature leads to more negatively charged acidic groups in the biochar (Banik et al. 2018). The hydrophilicity and hydrophobicity of biochar will be affected by the two primary processes that occur during pyrolysis. On the one hand, reducing functional groups will alter the material's attraction to water.

On the other hand, it affects the amount of water absorbed. Biochar production at temperatures below 450 °C significantly increased plant-available phosphorus data in improved soil (Glaser and Lehr 2019). Furthermore, as the pyrolysis temperature rises, the effect of biochar on phosphorus availability reduces dramatically.

Some researchers have shown that increasing temperature can cause the disappearance of organic phosphorus, but high temperature also facilitates the synthesis of

inorganic phosphorus (Shi et al. 2019; Yang et al. 2022b). Phosphorus begins to volatilize above 700 °C, so the phosphorus content in raw materials can be recovered in low temperatures and mesophiles but cannot be recovered in high-temperature biochar (Glaser and Lehr 2019). Biochar produced at temperatures below 600 °C can positively impact the effectiveness of phosphorus plants (Tang et al. 2020). Low-temperature biochar at 450 °C and mesophile at 450–600 °C significantly improved the phosphorus availability of biochar in soil, and there were significant differences between them (Masebinu et al. 2019; Quintana-Najera et al. 2021).

The type and quantity of functional groups affect biochar's alkalinity and ability to neutralize soil acids (Lu et al. 2022; Sun et al. 2018a). An increase directly influences the pH value of biochar in alkalinity. In agricultural applications, such as soil enhancement, the pH of biochar plays a crucial role. Notably, this is one of the differences between coke produced through pyrolysis and coke made through hydrothermal carbonization. During pyrolysis, the functional groups separated from the biochar are primarily acidic, such as carboxyl, hydroxyl, or formyl. Moreover, the relative content of ash in biochar also tends to increase during the pyrolysis process, and ash is known to have alkaline properties (Cheng et al. 2020; Weber and Quicker 2018). Therefore, the increased pH value directly results from increased carbonization degree. Applying biochar to acidic soil has the most substantial positive impact on phosphorus availability. This effect is significantly higher than that of neutral ground. In alkaline soil, no significant effects were found (Glaser and Lehr 2019).

A material's cation exchange capacity is the number of exchangeable cations it can support. It is widely used to characterize soil fertility and results from negative surface charges attracting cations. Biochar can increase cation exchange capacity, alter soil pH, and influence plant phosphorus uptake (Mohamed et al. 2017; Phares et al. 2020). The interaction of phosphorus and calcium ions regulates phosphorus solubility in alkaline soil. On the other hand, plant availability of phosphorus in acidic soil is principally controlled by aluminum ions, divalent iron ions, and trivalent iron ions (Sun et al. 2021). When applied to acidic soil, biochar raises the pH and reduces phosphorus adsorption on iron and aluminum oxides (Hong and Lu 2018). In addition, biochar itself can be a source of calcium and magnesium. Excessive calcium and magnesium levels in biochar can cause the creation of calcium phosphate and magnesium phosphate, decreasing plant phosphorus absorption (Nardis et al. 2020; Yang et al. 2021c).

In conclusion, the properties of biochar are influenced by the specific pyrolysis conditions. The physical and chemical characteristics of biochar, including the type of functional groups present, cation exchange capacity, and

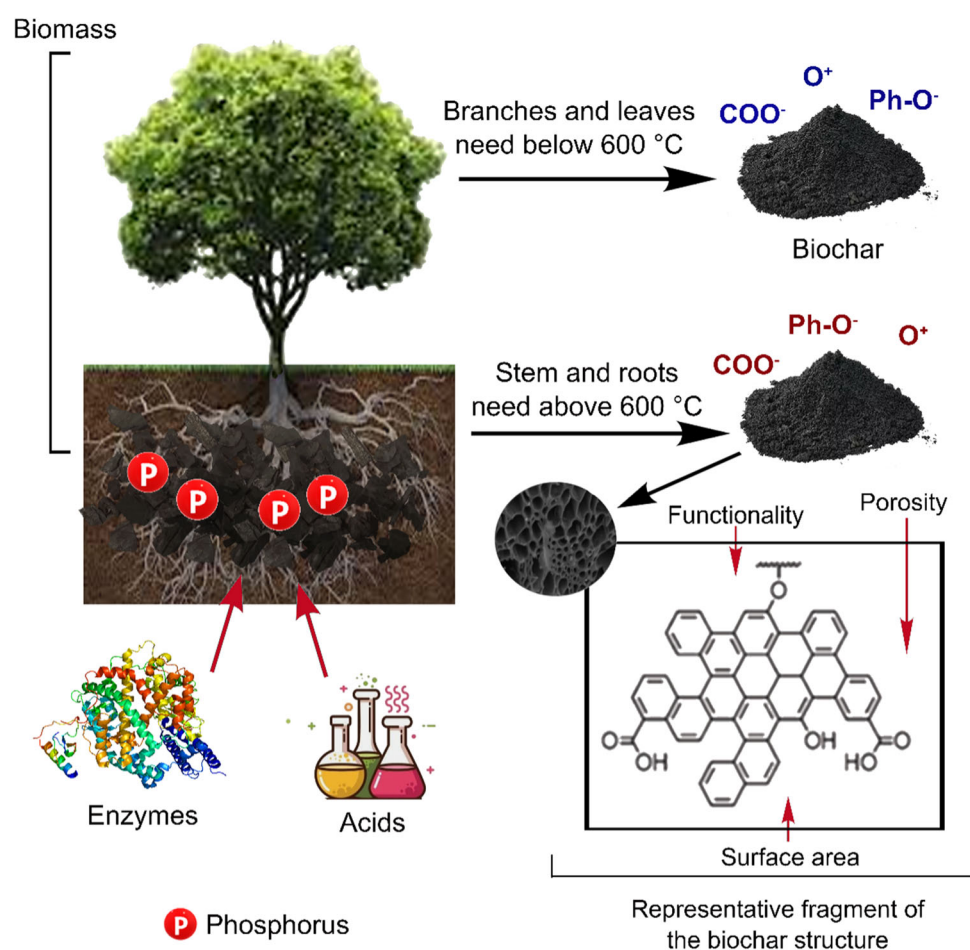
pH, all play a role in phosphorus release. The pyrolysis temperature significantly impacts the release of phosphorus from biomass. This is likely due to the preservation or alteration of different functional groups within the biochar at different temperatures. Moreover, high pyrolysis temperatures can modify the form of phosphorus in the biochar. At the same time, the presence of active groups and cation exchange capacity also affect phosphorus release by influencing the pH conditions.

### Microbial and root-mediated processes in phosphorus release

Biochar harbors a diverse microbial community comprising bacteria and fungi. These microorganisms can

reproduce and migrate within the surface and pores of biochar (Shi et al. 2023a, b). As shown in Fig. 6, some microorganisms can produce phosphorus solubilizing enzymes, which can decompose organic phosphorus or release phosphorus adsorbed on biochar (Gao and DeLuca 2018). These microorganisms promote the dissociation and release of phosphorus through the action of acidic substances and enzymes in their metabolites. Plant roots can emit root exudates and dissolve organic matter in the rhizosphere soil when they grow through or come into contact with biochar, impacting the release of phosphorus in biochar (Li et al. 2022).

Additionally, the organic acids and enzymes in root exudates can increase phosphorus's solubility and dissociation, facilitating plants' mineral absorption (Li et al.



**Fig. 6** Effect of pyrolysis temperature on biochar's physical and chemical properties. Biochar tends to possess a higher concentration of negatively charged acidic groups at lower pyrolysis temperatures. These groups include carboxylate and phenolate, which contribute to a negative surface charge, while oxonium groups can produce a positive surface charge. In contrast, pyrolysis at temperatures exceeding 600 °C decreases functional groups while increasing the porosity of the biochar. Microbial activity and root-mediated processes play significant roles in phosphorus release from biochar. The surface and pores of biochar create a conducive environment for

microorganisms. Certain microorganisms can produce enzymes that solubilize phosphorus, and the acidic metabolites they release can facilitate the dissociation and subsequent release of phosphorus. When plant roots come into contact with biochar, they release secretions containing organic acids and enzymes that stimulate phosphorus release. Plant roots' absorption and metabolic processes can also contribute to phosphorus release.  $\text{COO}^-$  refers to carboxylate,  $\text{Ph-O}^-$  refers to phenolate groups, and  $\text{O}^+$  refers to oxonium groups



2022). Simultaneously plant roots' absorption and metabolic activities can signal phosphorus release through phosphorus absorption and metabolism. Microorganisms take advantage of biochar's surface and pore structure, utilizing it as a suitable habitat to thrive and contribute to phosphorus release through their metabolic activities processes (Jiang et al. 2023). The interaction between plant roots, chemical compounds in the rhizosphere soil, and biochar plays a crucial role in improving the processes of phosphorus dissolution and release (Zhu et al. 2018). These interactions significantly impact the cycling and utilization of phosphorus in the soil-biochar-plant system.

Microorganisms are an indispensable component of phosphorus cycling in soil and play an essential role in regulating phosphorus availability to plants (Dai et al. 2020a; b). Soil microorganisms play a crucial role in the phosphorus cycle, with phosphorus present in these microorganisms being a significant component of the total soil phosphorus content, often equivalent to or surpassing the phosphorus found in plant biomass. Only a small fraction of the total phosphorus in the soil is directly absorbed by plants or microorganisms. Plants primarily use phosphorus in the soil solution as orthophosphate through specialized high-affinity transport proteins in the root epidermis. This process is regulated by coordinated gene expression in response to phosphorus deficiency and is influenced by interactions with mycorrhizal fungi. (Tian et al. 2021b). Phosphorus in the soil is mainly found as inorganic components that are either adsorbed on the surface of soil minerals or stored in a limited amount of accessible sediment. Phosphorus, conversely, exists in organic form, either absorbed and integrated into biomass or connected with soil organic matter (Azam et al. 2019).

Plant roots significantly impact nutrient cycling, productivity, environmental changes, and the composition of soil microbial communities (Garcia and Kao-Kniffin 2018). The absorption of nutrients by plant roots can lead to changes in rhizosphere pH (Custos et al. 2020). Ammonium ion absorption causes net acidification of the rhizosphere. In contrast, nitrate ion absorption causes net alkalization of the rhizosphere, which is caused by the extrusion of hydrogen ions or hydroxide ions from the roots to maintain charge balance (Chen et al. 2018b; Imler et al. 2019). Plant roots also directly impact nutrient availability by producing chemicals that change element solubility or the rates of specific biological processes. Notably, citric acid significantly affects phosphorus release (Sindhu et al. 2022). Plants and microorganisms use organic phosphorus by hydrolyzing substrates with phosphatases, which can come from plants or microbes (Jarosch et al. 2019). The rise in phosphatase activity is in response to phosphorus deficiency. This process in plants involves the release of extracellular phosphatase from the roots, which is thought

to catch and recover lost organic phosphorus from the source or to allow for better access to soil organic phosphorus (Richardson et al. 2022).

Extracellular polysaccharides from root microorganisms have been reported to have a key role in soil aggregation around roots, which may alter the transport of water, nutrients, and harmful materials by sources as well as the habitat of root bacteria (Costa et al. 2018; Naseem et al. 2018). Moreover, microbial and root extracellular polysaccharides also involve chemical processes. For example, this process can protect root tips from aluminum toxicity and obtain nutrients such as phosphate (Prieto et al. 2017). Plants undergo considerable root morphology and physiological changes in response to phosphorus deprivation, making it difficult to assess the relative impact of phosphorus-mediated microbial and plant-mediated processes. However, microorganisms are still an indispensable component of soil phosphorus cycling, and the local enhancement of rhizosphere microbial activity is vital for plant phosphorus nutrition.

In conclusion, enhancing the availability of microbial-mediated phosphorus in soil is a feasible goal. This can be achieved by improving the capability of existing microbial populations to mobilize phosphorus or by utilizing specific microbial inoculants. However, progress in this area has been limited, and unlocking the full potential of these approaches requires a more comprehensive understanding of microbial interactions involving bacteria, archaea, and eukaryotes in the soil ecosystem. Ecological considerations are crucial when considering single microorganisms as inoculants or assessing the dynamics of different soil microbial communities. Factors such as their interactions in the rhizosphere or within the roots, their ability to mobilize phosphorus from various soil compartments, and the impact of soil and farm management practices on these processes should all be considered. To fully exploit the potential of microbial-mediated phosphorus mobilization, future research efforts should focus on expanding our knowledge of microbial interactions and their roles in soil ecosystems, encompassing the domains of bacteria, archaea, and eukaryotes.

### Factors affecting phosphorus release from loaded biochar

Several factors influence biochar's phosphorus release, including coexisting anions, pH value, adsorbent dosage, initial phosphorus concentration, and temperature. The interaction between phosphorus and the dual carbon surface of biochar occurs through an ion bridge mechanism. Consequently, cations and anions in the solution can impact phosphorus migration (Song et al. 2020; Zhang et al. 2022b). Typically, environmental circumstances can



be altered to produce the optimal phosphorus release parameters, such as modifying the concentration of other nutrients or anions in the soil to change the amount or rate of phosphorus release (Joseph et al. 2018; Wang and Lambers 2020). Table 5 presents some factors influencing phosphorus release from biochar, which aids in better discussing the factors influencing phosphorus release from biochar.

pH is among the most critical elements influencing phosphorus release from loaded biochar. The pH of the solution affects the kinds of phosphorus and the surface properties of the adsorbent, consequently influencing the major release and adsorption mechanisms (Hou et al. 2020). The phosphorus's solubility and biochar's surface charge state will alter under different pH settings,

influencing phosphorus release. Generally speaking, lower pH values typically promote phosphorus release, while higher pH values may reduce phosphorus release. The pH of the solution dramatically impacts the surface charge, functional groups, and loaded metals of biochar (Penn and Camberato 2019). There are many different functional groups in biochar, and the surface groups, like carboxylates and hydroxyl groups, change depending on the pH of the solution. At low pH, these groups are protonated and positively charged, whereas surface groups deprotonate as the pH of the solution increases (Longo et al. 2019). Through electrostatic repulsion, the positively charged surface of biochar promotes anionic phosphorus species adsorption. Biochar characteristics determine adsorption behavior, and the adsorption mechanism includes

**Table 5** Factors that influence phosphorus release from biochar

Biochar raw materials	Influence factor	Research results	References
Rice husk	pH value, calcium content	When the pH value is 7.6 to 8.6, and there is excess calcium, the release of phosphorus in biochar decreases. To increase phosphorus transport, biochar requires a concentration of calcium below 1% and a pH value below 7.5. On the contrary, higher calcium concentrations cause some chemical limitations in releasing phosphorus from biochar	Buss et al. (2018)
Poultry manure	pH value	The soil's pH significantly affects poultry manure's biochar and phosphorus released. The release of phosphorus in biochar is acid-driven, and increasing the medium's acidity can substantially promote phosphorus release	Wang et al. (2015b)
Wheat straw, hardwood, willow	pH value, initial phosphorus concentration	The willow water solution's pH is higher than hardwood and wheat straw biochar, indicating the presence of suitable phosphorus and other ions. This observation may explain why willow biochar exhibits superior phosphorus adsorption capacity. The patterns of phosphorus adsorption vary depending on the initial phosphorus concentration and the type of biochar. Willow biochar demonstrates significantly higher phosphorus adsorption compared to other biochar types. However, at low initial phosphorus concentrations, the adsorption mechanism of willow biochar aligns with the two different biochar forms	Dugdug et al. (2018)
Rice husk	Coexisting anions, nutrient elements	Coexisting ions greatly influence orthophosphate and total phosphorus release in biochar, whereas cations and anions in the solution can influence phosphorus migration. The environmental conditions can be changed to provide the best phosphorus release settings	Qian et al. (2013)
Dehydrated sludge biochar	pH value	Because of deprotonation, the electrostatic repulsion between phosphate anion and adsorbent increases as solution pH rises, reducing adsorption effectiveness. Furthermore, at higher solution pH values, numerous hydroxide ions will be released, competing with phosphate for the active site on the surface of lanthanum-modified biochar, further lowering adsorption capacity	Li et al. (2020b)
Sheep manure, oyster shells	pH value, coexisting anions	As oyster shells' content increases, biochar materials' adsorption capacity gradually increases at various phosphate concentrations. The adsorption capacity of biochar increases as the pH of the solution increases	Feng et al. (2021a)
Gangue	pH value, adsorbent dosage	When the adsorbent dosage is low, the phosphorus removal rate increases with increasing adsorbent dose, but the phosphate adsorption capacity steadily declines. The pH value has little effect on the phosphate adsorption capability of biochar	Wang et al. (2021a)

pH is a crucial factor that significantly affects the release of phosphorus from loaded biochar. The pH of the solution plays a pivotal role in determining the types of phosphorus species present and influencing the surface properties of the adsorbent. Consequently, the pH conditions directly impact the major release and adsorption mechanisms. Adjusting environmental variables makes it possible to achieve optimal parameters for phosphorus release

interactions such as physical adsorption, surface precipitation, complexation, electrostatic attraction, and ion exchange.

The amount of adsorbent utilized has a substantial impact on phosphorus adsorption. When designing the phosphorus concentration, adding additional adsorbents results in a high phosphorus adsorption capacity; however, this rise is limited for excessive adsorbents (Du et al. 2022). When coal gangue biochar composite material is employed as an adsorbent, the phosphorus removal rate increases as the adsorbent dosage increases (Wang et al. 2021a). The initial phosphorus content heavily influences the phosphorus release process. A higher initial phosphorus concentration may lead to more phosphorus adsorption onto biochar, thereby releasing more phosphorus in the subsequent release process (Cui et al. 2022; Joseph et al. 2018).

The phosphorus concentration in wastewater can vary depending on phosphorus's source and season. Measuring the initial phosphorus concentration is essential to evaluate the effectiveness of biochar-based adsorbents. Furthermore, the composition of phosphorus species can change due to the potential influence of phosphorus concentration on pH. The biochar adsorption alters the number of hydrogen ions in water, leading to the protonation or deprotonation of hydroxyl groups on the biochar surface (Luo et al. 2022). This, in turn, affects the electrostatic attraction of phosphorus to the biochar surface. The maximum adsorption capacity is related to the initial phosphorus concentration, and different types of biochar may exhibit variations in phosphorus adsorption due to differences in phosphorus concentration. It is not sufficient to assess the effectiveness of charcoal adsorbents solely based on their adsorption capacity. Researchers have proposed using a distribution coefficient to evaluate phosphorus adsorption efficiency. A higher distribution coefficient value indicates less residual phosphorus in the solution (Cui et al. 2020b; Huang et al. 2020).

High temperatures will promote the diffusion process from a thermodynamic standpoint. The increased mobility of adsorbent particles with phosphorus molecules enhances the likelihood of a collision, boosting adsorption. According to studies, high temperatures accelerate the release of phosphorus from wastewater sediment (Gibbons and Bridgeman 2020). The release of phosphorus in biochar is constrained by the same variables that govern phosphorus availability in soil. When biochar is applied to the ground, the composition and pH value of the soil solution are simultaneously affected by both soil and biochar (Ghodsad et al. 2021). Changes in soil moisture may also influence phosphorus release from biochar. Higher soil moisture may increase phosphorus release, as water can

promote the dissolution and migration of phosphorus (Lai et al. 2022).

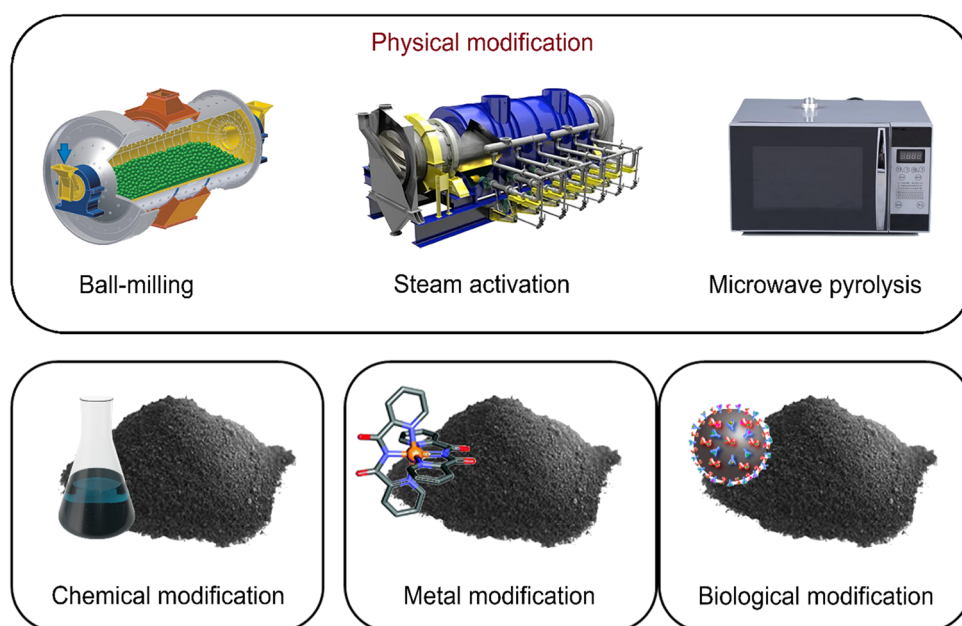
To summarize, several factors, including coexisting anions, pH value, adsorbent dosage, initial phosphorus concentration, and temperature, play crucial roles in releasing phosphorus from biochar. Optimizing these environmental conditions is often necessary to achieve the best parameters for phosphorus release. Among these factors, pH value is significant, as lower pH levels tend to enhance the release of phosphorus from biochar. Additionally, when extracting phosphorus from biochar, the initial phosphorus content and the environment's temperature should be considered significant factors. It is important to note that multiple components can simultaneously influence phosphorus release from biochar.

### Biochar modification and phosphorus reactions

Functionalization modification of biochar has been a hot study issue to improve the effectiveness of phosphorus adsorption and release by biochar. Environmental management, soil remediation, and energy storage are all enhanced by modified functional biochar. Modifying biochar is separated into three stages: pre-treatment, thermochemistry, and post-treatment (Luo et al. 2022). Improvements are primarily focused on the post-processing stage, as indicated in Fig. 7, and typically employed modification methods include physical modification, chemical modification, and biological modification. Different modification phases improve biochar adsorption and release efficacy by increasing surface area, total pore volume, and surface functional groups (Wang et al. 2019b; Zhao et al. 2021). Post-treatment refers to modifying biochar through various physical, chemical, and biological processes. Table 6 lists the relevant studies on different modification methods. Pretreatment regulates the raw materials used to produce biochar to obtain specific properties. Washing, drying, crushing, and enrichment are all typical pretreatment methods (Boakye et al. 2019). Different pretreatment methods are usually used to achieve other effects. Washing and crushing can minimize impurities and moisture in the biochar raw material, while crushing controls the particle size of the raw material. The use of specific solutions is to enrich the target elements in the biochar raw material (Xiao et al. 2022).

The most prevalent physical alteration procedures are steam activation and ball milling. A modification aims to increase the surface area of biochar, add more micropores, and improve the adsorption capacity. Steam activation can boost biochar adsorption capability by increasing biochar's surface area and interior micropores (He et al. 2021). Tar is generated during the carbonization process of biochar, which can block the gaps within the biochar and reduce the

**Fig. 7** Biochar modifications methods. The most common processes for modifying biochar post-treatment involve physical, chemical, metal, and biological modifications. These methods aim to enrich the surface functional groups, increase pore volume, and improve biochar adsorption and release performance. Among these modification methods, physical modification is the most widely employed approach. Physical modification techniques, such as ball milling, steam activation, and microwave pyrolysis, are frequently used to alter the properties of biochar



**Table 6** Different modification methods of biochar

Biochar raw materials	Modification method	Specific methods	References
Waste palm shell	Physical modification	Microwave pyrolysis, steam activation	Lam et al. (2020)
Sugarcane bagasse, bamboo, hickory chips	Physical modification	Ball milling	Lyu et al. (2018)
Eucalyptus bark	Chemical modification	Modification using zinc chloride solution	Yusuff et al. (2022)
Sewage sludge	Chemical modification	Modification using ferrous nitrate solution	Feizi and Hossaini (2022)
Corn cob	Chemical modification	Soak corn cob biochar in the nitric acid solution for 8 h	Vu et al. (2017)
Dewatered sludge	Metal modification	Lanthanum coated biochar	Li et al. (2020b)
Corn cob	Metal modification	Aluminum modified biochar	Deng et al. (2021a; b)
<i>Miscanthus</i> spp.	Biological modification	Fungal decomposition, bacterial digestion	Xu et al. (2022)

The unmodified biochar exhibits limited adsorption capacity for phosphorus. Various modification methods are employed to maximize biochar's adsorption capacity and potential applications. Among these methods, physical modification stands out as it requires less energy and is considered more environmentally friendly than other approaches. However, biochar modified with metal nanoparticles may exhibit higher phosphorus absorption and release efficiency

capacity for adsorb substances (Panwar and Pawar 2020). Water vapor and carbon dioxide are the most common gases in steam activation methods due to their advantages of cleanliness and easier control during operation.

Ball milling is another effective method for post-processing biochar. Because solvents are not used during the processing, nano biochar materials synthesized through ball milling have low costs and green and environmentally friendly characteristics (Kumar et al. 2020). Ball milling, as a simple post-processing procedure, can efficiently reduce the size of biochar particles while increasing the

specific surface area of biochar particles. High-temperature biochar ball milling with a relatively low surface area can improve the inner and outer surface areas. Low-temperature biochar ball milling, however, can only increase the material's external surface area (Lyu et al. 2018). Furthermore, ball milling could deliver oxygen-containing functional groups into the surface of biochar (Lyu et al. 2018).

Microwave pyrolysis is a new technology that has emerged recently (Hadiya et al. 2022). Microwave pyrolysis heating is faster and uses less energy than traditional

pyrolysis processes, making it more environmentally friendly. Microwave pyrolysis is more controlled than conventional pyrolysis, with excellent energy efficiency and cost-effectiveness. Microwave pyrolysis can solve traditional pyrolysis methods' drawbacks, such as slow decomposition and the necessity to crush raw materials into smaller bits. Microwave modification is more successful than classical pyrolysis because it is faster, more effective, and allows for homogeneous interior temperature distribution (Sakhiya et al. 2020). As a result, microwave modification can yield biochar with more functional groups and a larger surface area than typical pyrolysis biochar (Wang et al. 2020d). Microwave pyrolysis can occur at temperatures near 200 °C, whereas conventional pyrolysis requires higher temperatures and longer residence times to obtain comparable results (Robinson et al. 2022). As a result, microwave pyrolysis biochar is more stable than conventional pyrolysis biochar.

Chemical modification is also an excellent way to change the surface area, surface groups, and adsorption selectivity of biochar (Li et al. 2021). Chemical alteration of biochar alters the surface chemical characteristics, enhancing biochar's adsorption capacity following conversion (Usman et al. 2016). Impregnating biochar with acidic or alkaline solutions is a straightforward and efficient modification method. Generally, biochar modified with an alkaline solution demonstrates a greater advantage in phosphorus adsorption. This is due to biochar's positively charged surface, larger surface area, presence of significant oxygen-containing groups, and improved ability to adsorb negatively charged phosphorus through electrostatic attraction and ligand exchange (Eduah et al. 2020).

Metal modification is also a standard post-treatment method, and biochar doped with metal nanoparticles typically exhibits higher phosphorus removal rates than unmodified biochar. Iron-modified biochar materials significantly affect phosphorus adsorption (Huang et al. 2022a; b). There are two standard methods for modifying loaded metal elements. One is to mix metals or metal oxides with the original material and pyrolysis them to form biochar, and the other is to soak biochar with metal ions or metal oxides to obtain some additional performance. Metal-modified biochar typically has a greater specific surface area and pore volume than original biochar, with the increased surface area mainly owing to the development of nanoscale metal particles on the biochar's surface (Akhil et al. 2021). In addition, the thermal decomposition of metal hydroxides at high temperatures will produce many micropores. The increased specific surface area and pore volume resulting from modifications contribute to the availability of additional adsorption sites, thereby facilitating the removal of phosphorus (Zhu et al. 2020).

Transmembrane transport, complexation, ion exchange, precipitation, and physical adsorption are some biological mechanisms that can modify biochar. Many functional sites on the surface of microorganisms can promote biochar adsorption by selling functional groups (Wang et al. 2021a). The most efficient methods for utilizing biomass waste resources are anaerobic digestion and bacterial transformation technologies. Because the digestion process can change the oxidation–reduction potential and pH value of raw material biomass, the digested biochar has a higher pH value, surface area, cation exchange capacity, anion exchange capacity, hydrophobicity, and more negative surface charges than the original biochar (Feng and Lin 2017). Anaerobic digestion improves the adsorption ability of biochar formed from digested beet tailings, bagasse, and dairy waste residue to heavy metals and phosphates compared to undigested biochar. Modification by microbial or biological therapy has the benefits of low cost and environmental friendliness, but it also has the disadvantages of unknown transformation processes and results (Ni et al. 2019; Yao et al. 2011).

In summary, primitive biochar exhibits a low adsorption capacity, necessitating various modification techniques to enhance biochar's adsorption capability and application potential. Physical methods are particularly suitable for practical biochar modification, especially during post-treatment, as they are often more environmentally friendly, cost-effective, and suitable for large-scale operations. Chemical modification offers the advantage of surface customization based on specific biochar uses, but using chemical solvents during the modification process can increase production costs and lead to pollution concerns. Biological methods, while applicable on a large scale, usually require significant modification time.

### Effect of organic acids on phosphorus release from loaded biochar

Many earlier studies have shown that organic acids play an essential role in phosphorus solubility in soil (Adeleke et al. 2017; Panchal et al. 2021). Acidic conditions typically boost the solubility of phosphorus-containing minerals. Soil organic acids are classified into two types, high molecular weight organic acids and low molecular weight organic acids. High molecular weight organic acids are distinguished by their high molecular weight and low water solubility. Organic acids with typical molecular weights are abundant in soil solutions and are mainly produced from plant root secretions. Organic acids of low molecular weight are found in abundance in nature. Evidence suggests that low molecular weight organic acids and their anions can play an essential role in soil and mineral nutrient attribution via a variety of mechanisms, including

anion and cation exchange, complexation events, and mineral dissolution reactions (Lazo et al. 2017; Yang et al. 2019). Organic acids, despite their low molecular weight, are widely found in soil. However, the mechanism of nutrient release mediated by low molecular weight organic acids in biochar remains unknown (Zhang et al. 2020b). Table 7 depicts the impacts of various organic acids on the release of phosphorus from multiple forms of biochar, which may aid in investigating the influence of low molecular weight organic acids on the release of phosphorus from biochar.

Research on biochar-based phosphorus adsorption materials mainly focuses on materials such as straw, rice husk, and sawdust (Min et al. 2020; Oginni et al. 2020). Ligand exchange is a process by which low molecular weight organic acids, such as oxalic acid, citric acid, and tartaric acid, can increase phosphorus release in soil. These organic acids directly replace the existing ligands on the surface, facilitating phosphorus release. Additionally, the interaction between anions and aluminum can influence soil phosphorus release (Lazo et al. 2017; Yin et al. 2018). Aluminum can stimulate the release of low molecular weight organic acids from plant roots, influencing phosphorus release dramatically. Specifically, aluminum ions can attach to a specific location on anion channel proteins, encouraging the outflow of organic acids via anion channels (Kar et al. 2021).

The molecular structure and dissociation degree of standard molecular weight organic acids and the stoichiometric ratio of mineral elements in biochar govern the influence of low molecular weight organic acids on phosphorus release in biochar (Zhang et al. 2020b). Hydrogen bonding makes the deprotonation of acetic acid form a complex with dissolved hydrogen phosphate ion or dihydrogen phosphate (Clarholm et al. 2015; Wu et al. 2020). The hydrophobic methyl of acetic acid is exposed outside the compound, lowering phosphate's water solubility. Tartaric and citric acids are multivalent anions that can be exchanged with phosphorus in biochar after deprotonation. The trivalent/divalent metal-to-phosphorus ratio is high. The impact of glycolic acid on biochar phosphorus release can be disregarded, as it lacks exposed hydrophobic functional groups and only possesses one deprotonation carboxyl group. Furthermore, high-density protonation or hydroxylation of biochar lowers the stimulation of low molecular weight organic acids on phosphorus release by increasing steric hindrance at high acidic or alkaline pH values (Zhang et al. 2020b). It serves an essential guiding role in boosting the use efficiency of biochar in soil fertilization by regulating the low molecular weight of organic acids in soil.

In summary, low molecular weight organic acids are abundant in soil settings and are advantageous for effectively utilizing biochar in soil development. The molecular structure and dissociation degree of standard molecular

**Table 7** Different organic acid types' effects on phosphorus release from other types of biochar

Biochar raw materials	Organic acid type	Research contents	References
Furfural residue	Acetic acid, malic acid, citric acid	Investigate the influence of low molecular weight organic acids on biochar aging and the release of related inorganic elements	Liu et al. (2017)
Distillers grains	Tartaric acid, citric acid, oxalic acid	Biochar loaded with metal oxides was made from Chinese Baijiu distiller's grains, and the mechanism of phosphorus adsorption and regulated release were examined under various conditions	Liu et al. (2022b), Liu et al. (2020a; b)
Corn straw	Oxalate	An investigation into the combined effect of biochar and oxalic acid on the dissipation of polycyclic aromatic hydrocarbons	Li et al. (2019)
10 types of biochar with different stoichiometric ratios of mineral elements	Acetic acid, glycolic acid, tartaric acid, citric acid	This study aims to elucidate the mechanism of the effect of low molecular weight bioacids on phosphorus release in biochar	Zhang et al. (2020b)
Sewage sludge	Acetic acid, quinic acid, benzoic acid, oxalic acid, mucic acid, malic acid, succinic acid, maleic acid, phthalic acid, trans aconitic acid, citric acid, kojic acid	The ability of 12 low molecular weight organic acids to release phosphorus from sewage sludge biochar was investigated	Paul et al. (2021)

Low molecular weight organic acids predominate in soil solutions and are mostly produced from plant root secretions. Organic acids of low molecular weight are found in abundance in nature. Organic acids with typical molecular weights play an essential role in the fate of nutrients in soil/minerals. The molecular structure of low molecular weight organic acids may uniquely affect phosphorus release in biochar



weight organic acids and the stoichiometric ratio of mineral elements in biochar govern the influence of low molecular weight organic acids on phosphorus release in biochar. Furthermore, high-density protonation or hydroxylation of biochar lowers the stimulation of low molecular weight organic acids on phosphorus release by increasing steric hindrance at high acidic or alkaline pH values.

### Slow and controlled phosphorus release from engineered biochar

Engineering biochar can potentially reduce the bioavailability and leaching rate of heavy metals and organic contaminants in soil and water systems through adsorption and other physicochemical interactions (Qiu et al. 2022). The highly stable aromatic and porous structure of biochar, coupled with the relatively large surface area, makes biochar an excellent soil conditioner. Biochar exhibits efficient nutrient absorption and transfer, improving soil fertility, microbial community, water-holding capacity, and carbon fixation (Hussain et al. 2017; Yang et al. 2021c). Mineral clay can be co-hydrolyzed with biomass before being impregnated into the biochar framework. Mineral clay, particularly montmorillonite, is widely employed in the adsorption and removal of contaminants from wastewater due to the layered structure, the cation exchange capacity, and the large surface area contained. Biochar, particularly in adsorption capacity, can combine the properties of mineral clay to display superior performance (Lin et al. 2023b).

Biochar and tailored biochar are mainly used as adsorbents and nutrient carriers rather than as packing materials in producing slow-release fertilizers (Wang et al. 2022a, b). Although biochar is more stable and releases nutrients more slowly than regular fertilizers, the process is still preliminary. Two factors influence the effectiveness of nutrient delivery, nutrient utilization efficiency, and environmental contamination. The first is to match nutrient supply to plant demand, and the second is to keep nutrient availability constant. The use of water-soluble phosphorus fertilizer in the field of fertilization affects the effectiveness of plant phosphorus absorption because phosphorus leaches and is carried to groundwater and/or enters water bodies through surface runoff (Ge et al. 2023). Therefore, slowly releasing phosphorus from applied fertilizers helps to reduce phosphorus losses and prevent water pollution.

Biochar has a large specific surface area, porosity, and the presence of diverse functional groups, which makes it a suitable substrate for slow-release and controlled-release fertilizers (Rashid et al. 2021). Slow-release/controlled-release fertilizers provide nutrients as micro-soluble compounds or capsules, making them more effective on plants. Using slow-release/controlled-release fertilizers can

improve the synergistic effect of nutrients while reducing stress and particular toxicity resulting from traditional fertilizers. Slow-release/controlled-release fertilizers can be applied once, giving nutrients for the growing season and lowering agricultural operating costs (Gwenzi et al. 2018). Slow-release biochar fertilizers can boost nitrogen consumption efficiency and crop productivity while also influencing the soil microbial ecosystem, increasing many soil bacterial species (Liao et al. 2020). Phosphorus-adsorbed biochar, used as a slow-release fertilizer, aids in establishing long-term phosphorus cycling routes.

The production technique and substrate determine the classification of controlled-release/slow-release biochar-based fertilizers. Barriers are classified into three types, inorganic/mineral, polymer/organic, and ultra-absorbent fertilizers. The most typical cladding materials for controlled-release/slow-release fertilizers are sulfur, dolomite, bentonite, diatomaceous earth, zeolite, and gypsum. Polymer coatings on the surface of fertilizer particles have been shown to prevent phosphorus loss by delaying nutrient release rates, enhancing phosphorus usage efficiency, and lowering environmental contamination (Kassem et al. 2022). Especially using hydrogel absorbent polymer as coating, nutrients, and water can be gradually released. Then effective nutrient and water supply can be achieved (Oladosu et al. 2022).

In summary, Biochar's porous nature and many functional groups on the surface allow it to successfully contain more nutrients. The nutrient release rate of biochar-based slow-release fertilizers is 2–4 times slower than typical fertilizers like urea or superphosphate. Future studies should employ biochar alteration to regulate phosphorus and other nutrient discharge. Furthermore, research on phosphorus-adsorbed biochar as a slow-release fertilizer is preliminary, and the possible dangers that biochar-based fertilizers may bring should be considered.

### Effect of biochar type and application rate on phosphorus release

Phosphorus release is affected by the type of biochar used. Table 8 shows how different forms of biochar affect phosphorus release and adsorption. Biochar made from excrement often has a higher phosphorus concentration than biochar made from grass or wood. Plant-derived biochar, on the other hand, has a more extensive elemental carbon content than fecal biochar (El-Shahawy et al. 2018). Furthermore, biochar derived from excrement or poultry manure contains more nutrients. It has a higher pH value and specific surface area than biochar derived from high cellulose raw materials such as wood. All other biochar demonstrated a considerable beneficial response to phosphorus availability in agricultural soil, with animal dung

**Table 8** Effect of various biochar raw materials on phosphorus adsorption and release

Biochar raw materials	Research contents	Research results	References
Hardwood, poultry waste	Determine the effects of adding broad-leaved wood biochar and poultry waste biochar in different proportions on the adsorption and release of phosphorus from two different soils	The impact of using biochar to improve phosphorus adsorption and release in a soil largely depends on the phosphorus retention characteristics of the soil itself rather than the characteristics of biochar	Dari et al. (2016)
Wheat straw, hardwood, willow	Compare the effect of raw material types on the phosphorus adsorption effect of biochar, and learn how salinity affects phosphorus adsorption by different biochar	As the phosphorus concentration in the aqueous solution increases, phosphorus adsorption by straw biochar and hardwood biochar increases. In contrast, the phosphorus adsorption by willow biochar shows an opposite trend	Dugdug et al. (2018)
Wood, straw	The effects of two forms of biochar on the phosphorus adsorption process of five distinct soil and plant phosphorus absorption types were investigated	Compared with straw biochar, wood biochar reduced total phosphorus uptake, possibly due to the simultaneous phosphorus release and adsorption processes reducing the available phosphorus of plants in soil treated with wood biochar. In contrast, straw biochar significantly increased total phosphorus uptake in phosphorus-deficient soil environments	Borno et al. (2018)
Poultry manure, sugarcane straw	Biochar was created from sugarcane straw and poultry manure, doped with magnesium chloride, and pyrolyzed at various temperatures to evaluate the maximal phosphorus adsorption capacity and ability to release absorbed phosphorus	Doping magnesium chloride enables two types of biochar to acquire the ability to adsorb phosphorus. Poultry manure biochar has a high adsorption capacity for phosphorus, while sugarcane straw has a low adsorption capacity for phosphorus	Novais et al. (2018)
Taro straw, corn straw, Cassava straw, fir straw, banana straw, Camellia shell	Six magnesium-loaded biochar varieties were created to investigate total phosphorus adsorption in aqueous solutions	The adsorption of total phosphorus on six different forms of biochar is closely proportional to the loaded magnesium concentration	Jiang et al. (2019)
Corncoobs, rice husks	For desorption, investigate the effects of corn cob and rice husk biochar on phosphorus adsorption in typical plinthic-A and plinthic acrodox-B, as well as neutral soil quartzipsamment-C	The effect of biochar on phosphorus adsorption is affected by the raw material used, the temperature of pyrolysis, and the equilibrium pH value. On the other hand, phosphorus desorption is less affected by raw material type and more dependent on pyrolysis temperature, pH, and initial phosphorus concentration	Eduah et al. (2019)
Coffee straw, eucalyptus bark	Evaluate the optimization of two types of biochar in phosphate fertilizer at different temperatures	Coffee straw biochar can successfully increase phosphate fertilization optimization, maximizing phosphorus accumulation for aboveground plant parts throughout the experimental procedure	Fonseca et al. (2020)
Longleaf pine, red oak, hard maple	Investigate natural and magnesium oxide-modified biochar's microstructure, physicochemical parameters, and phosphorus adsorption properties	The original hard maple biochar and red oak biochar absorbed more phosphorus than the long-leaved pine biochar, while the magnesium oxide-modified biochar absorbed 11 times more phosphorus than the original biochar	Oginni et al. (2020)

The phosphorus adsorption capacity of biochar is influenced by the type of source material used. Animal feces have been found to exhibit higher phosphorus adsorption capacity compared to crop residues when used as feedstock for biochar production. Untreated biochar generally shows minimal adsorption effect on phosphorus. However, biochar modified with metal nanoparticles often demonstrates improved phosphorus adsorption and release effects compared to the original biochar

outperforming biological waste and crop residues outperforming crop residues (Glaser and Lehr 2019). Cui et al. (2016) found that the adsorption effect of untreated biochar on phosphorus was almost zero. Novais et al. (2018) once again confirmed that untreated biochar had almost no

adsorption effect on phosphorus and indicated that poultry manure biochar had a high adsorption capacity for phosphorus. Sugarcane straw, on the other hand, had a low phosphorus adsorption capability. The researchers investigated the adsorption impact of six different biochar raw

materials treated with magnesium on total phosphorus (Jiang et al. 2019). The results revealed that the phosphorus adsorption impact of this biochar is mainly determined by the amount of magnesium carried.

Biochar from animal, agricultural, and crop waste responded positively to plant-available phosphorus in biochar-treated soil. The animal residue group, which included various types of excrement and animal bones as biochar raw materials, demonstrated a solid favorable response to phosphorus efficacy (Haider et al. 2022; Purakayastha et al. 2019). Because the total phosphorus content in livestock manure produced each year is much higher than that in phosphate fertilizers produced worldwide, converting waste into biochar seems to be an effective method to reduce the use of mineral phosphate fertilizers (Lun et al. 2018). There is no effect on phosphorus bioavailability observed for biochar derived from wood, and it will not increase the phosphorus available to plants in the soil (Glaser and Lehr 2019). In addition, the diversity level of wood biochar is shallow. Therefore, it seems that it is not considered an ideal candidate for phosphate fertilizer, and further research is needed to determine whether there are other potential advantages.

According to the study, it has nothing to do with the raw materials used in manufacturing biochar. When the use of biochar generated at a temperature of 600 °C exceeds 10 megagram/hectare, the phosphorus availability of agricultural soil is greatly increased (Glaser and Lehr 2019). However, to define the threshold of application amount, it is necessary to consider not only the increase in nutrient supply following the addition of biochar but also the potential influence of leaching. Several studies have found that phosphorus leaking from biochar-enhanced soil may cause water contamination (Blanco-Canqui 2019; Xie et al. 2021). Contrary to this study's findings, there are reports that biochar can potentially adsorb orthophosphate and organic phosphorus molecules, reducing phosphorus leakage in the soil (Chen et al. 2018c). As a result, more research on the effect of biochar on phosphorus leaching in soil is required. The advice for the ideal application amount must consider the application amount's response to plant growth, and studies have shown that adding biochar harms plant growth. The biomass will decrease when the application amount exceeds 60 megagrams/hectare (Baronti et al. 2010) and 120 megagrams/hectare (Mia et al. 2014),

In summary, the type of biochar material has a strong relationship with phosphorus emission. Biochar made from phosphorus-rich raw materials can supply more accessible phosphorus to plants than phosphorus-deficient raw materials, possibly from biochar. A weak but substantial link exists between application rate and plant-accessible phosphorus in biochar-treated soil.

## Limitations and future research directions

### Limitations of phosphorus-loaded biochar in plant production

The diverse range of biomass feedstocks, biochar production techniques, phosphorus loading methods, and application conditions lead to significant variations in the composition, adsorption capacity, release kinetics, and soil-dependent behavior of phosphorus in biochar. In addition to considering agronomic and economic efficiency, it is crucial to consider other factors when utilizing phosphorus-loaded biochar for plant growth. This section aims to discuss the limitations associated with the long-term use of phosphorus-loaded biochar in agronomy, addressing potential concerns that may arise. Previous research has demonstrated the promising potential of using various biomasses as raw materials to produce phosphorus fertilizer from biochar, irrespective of the initial nutrient content in the feedstocks. Waste-based biomass, in particular, has emerged as a key focus in recent studies, driven by waste reduction and utilization factors. The utilization of waste-based biomass offers several advantages. Firstly, when nutrient-rich wastes are employed as feedstocks, valuable nutrients can be reclaimed from solid waste sources. This reclamation prevents environmental pollution that could occur through the leaching or direct discharge of these nutrients into the environment.

Additionally, waste-based biomass contributes to sustainable waste management practices by reducing the waste generated and optimizing biochar-derived phosphorus fertilizer. On the other hand, many studies, including Ahmad et al. (2018), Frišták et al. (2018), Yang et al. (2021b), Chen et al. (2022), Qi et al. (2022a), and Sha et al. (2023), have reported the ability of the phosphorus loaded biochar to adsorb heavy metals from waste streams and/or immobilize heavy metals in the soil through precipitation, electrostatic attraction, and complexation, which consequently reduce the plant uptake of a water-soluble and exchangeable fraction. Nonetheless, there are unneglectable health and environmental concerns about the deployment of biochar-based phosphorus fertilizer produced from wastes as the chemical composition of the biomasses could vary from one source to another, leading to uncertainty in the potential toxicity of when applied in the soil.

Wang et al. (2021b) utilized a co-pyrolysis approach to produce biochar from a combination of sewage sludge and cotton stalks with a 1:1 mass ratio. The pyrolysis process was conducted at a temperature of 650 °C for 1.5 h. The study's findings revealed that biochar generated through pyrolysis at temperatures below 750 °C exhibited effective retention of heavy metals. This favorable outcome can be

attributed to the volatility of cadmium at temperatures as low as 600 °C and the degradation of copper, zinc, lead, nickel, and chromium at temperatures of 600 °C and above. It is worth mentioning that Figueiredo et al. (2021) observed that higher pyrolysis temperatures, surpassing 600 °C, have additional benefits. These elevated temperatures not only enhance the biochar's phosphorus adsorption capacity, facilitated by increased porosity and improved phosphate diffusion (Wang et al. 2020b), but also promote the conversion of the soluble fraction of phosphorus to the insoluble fraction. Therefore, the optimum pyrolysis temperature could be selected based on soluble phosphorus release capacity and heavy metal retention adequacy. As explained, high pyrolysis temperatures could be disadvantageous for heavy metal immobilization due to the high oxygen-containing group removal Yuan et al. (2021), which is also essential for heavy metal fixation in the long-term biochar application on the soil. A significant amount of oxygen-containing groups in biochar facilitates the immobilization of heavy metals through complexation during aging. However, this high oxygen content hinders phosphorus adsorption due to repulsive forces and low affinity between phosphorus and biochar.

Oxygen-containing groups in biochar play a crucial role in the immobilization and stability of heavy metals. The choice of feedstock influences the stability of heavy metals within biochar. As mentioned earlier, lignin is highly thermally stable, and biomass with a high lignin composition tends to yield better biochar due to the lower content of volatile oxygen-containing groups. However, the absence of oxygen-containing groups in lignin-based biomass can result in the poor performance of the resulting biochar in terms of heavy metal adsorption and stabilization. Moreover, according to Yuan et al. (2021), lignin-derived biochar is highly resistant to oxidation, often occurring during aging. Hence, biochar is not designed for heavy metal immobilization for long-term application on the soil. The authors also discussed the aliphatic carbon content as another factor to consider. Woody biomasses are rich in aliphatic carbon, which is more susceptible to oxidation than the relatively stable aromatic groups. The presence of phosphorus-loaded biochar could enhance the affinity and immobilization of heavy metal cations, primarily due to the increased phosphate content. This finding is consistent with previous literature that supports the improved performance of phosphorus-loaded biochar in the adsorption and immobilization of heavy metals (Ahmad et al. 2018; Frišták et al. 2018; Palansooriya et al. 2022; Qi et al. 2022a; Sha et al. 2023; Yang et al. 2021b).

Recent studies have indicated that the particle size of biochar has both positive and potentially adverse effects on phosphorus and heavy metal adsorption. While the effect on phosphorus adsorption is generally positive, the impact

on the stability of adsorbed heavy metals appears to vary, leading to discrepancies in the findings across different studies. Referring to the results of Fahmi et al. (2018), the leachable amount of lead in fine empty fruit bunch-derived biochar (particle size less than 50 µm) was lower compared to coarse biochar (2 mg). Specifically, in synthetic rainwater at 1–6 cycles and 1% application rates, the recorded values for lead in fine biochar were 136.77, 73.90, 1.07, 0.13, 1.92, and 0 µg. In contrast, the values for lead in coarse biochar were 230.73, 111.65, 6.20, 1.30, 0.15, and 0.52 µg. The difference in particle size had a less significant impact on the leachability of cadmium, with variations ranging from 0.05 to 8.21 µg. In contrast to the previous study, Gu et al. (2023) found that the bioavailability of cadmium, specifically the acid-extractable and reducible fraction, increased as the biochar particle size decreased. When the particle size of biochar was reduced from macro size (above 1 µm) to nano size (below 0.001 cm), the acid-extractable fraction increased from 3.93, 3.76, 2.56, and 2.14% to 4.94, 4.81, 4.27, and 2.64%, respectively, at pyrolysis temperatures of 300, 400, 500, and 600 °C. Similarly, the reducible fraction also increased from 3.93, 3.76, 2.56, and 2.14% to 4.94, 4.81, 4.27, and 2.64% at the respective temperatures. Moreover, the residual fraction of cadmium decreased from 68.9, 73.31, 81.86, and 86.76% to 52.82, 63.99, 66.04, and 75.87% as the biochar particle size decreased. However, an increase in pyrolysis temperature from 300 to 600 °C led to converting a significant portion of the heavy metals to the residual form, accounting for 17.86–23.05%, consistent with the previous discussion.

Using chemicals for biochar property activation, such as potassium carbonate, can lower the leaching risk of heavy metal cations in soil based on the environmental risk assessment (Wang et al. 2021b). Still, the stability of heavy metal immobilized on biochar surface in the long-term application shall be assessed, considering the variable field conditions and the potential toxicity that could be exerted by biochar-based phosphorus fertilizers derived from toxic wastes through desorption from the biochar surface, considering the high retention of heavy metals in the biochar during pyrolysis. The possibility of increased soil heavy metal content caused by the addition of biochar with high heavy metal retention was demonstrated by Zhang et al. (2021a), who revealed that the increase of 6.20–248 µg cadmium per kilogram of soil at the top 10 cm with the application rate of 1–40 megagrams biochar, which had 7.63 mg cadmium per kilogram, on 1-hectare land. Heavy metal desorption from biochar can be triggered by the change in biotic and abiotic factors, which include soil pH variation as the most significant factor of biochar-metal heavy stability. Abiotic factors could greatly alter biochar quality, leading to a lower heavy metal immobilizing ability under field conditions than the laboratory results.



Although studies have proven the ability of biochar to elevate the soil pH in a one-year application, this effect is temporary due to the abiotic factors that weaken the biochar effect and contribute to the soil pH reduction over a longer course, which include proton addition due to acid rain and rhizosphere, carbon dioxide adsorption forming carbonates, and low molecular-weight organic acid formation from organic carbon during biochar aging (Yuan et al. 2021). The field experiments in past studies revealed the negligible effect of biochar addition to counter soil acidification caused by acid rain (Yuan et al. 2021). Soil acidification promoted by microorganism-synthesized organic acid in biochar-treated soil could result in a protonated biochar surface (Gong et al. 2019; Qin et al. 2021). Besides, biochar surface protonation by substituting heavy metal cations with protons over a long application period is inevitable under acidic conditions (Qin et al. 2022). According to them, the reducing effect of biochar application in terms of heavy metal bioaccessibility of edible vegetable parts is also uncertain, as indicated by the lack of trend in the heavy metal bioaccessibility concerning the harvest times of edible plant parts. Redox potential is also a determining factor of soil pH and heavy metal mobility in soil. The effect of phosphorus-enriched biochar was, as explained, positive on the immobilization of lead in the paddy field, demonstrated in the study by Yang et al. (2021b).

The release of dissolved organic matter possibly induces the dissolution of heavy metal oxide. Using biochar in soil could increase the dissolved organic matter content, contributing to the migration of heavy metal pollutants in soil and leading to the potential risk of groundwater pollution. Referring to Zhang et al. (2020c), over 90 days of incubation under flood conditions, the dissolved organic matter increased by 57.5% in the soil amended by the maize straw-derived biochar produced at 450 °C, which the increased soil alkalinity could also promote by the biochar amendment. The elevation of total organic carbon followed that of dissolved organic matter content in the soil, favoring metal binding with the dissolved organic matter. Due to the high mobility of the dissolved organic matter, downward mitigation of heavy metals and nutrients in the soil is occasioned. However, this depends on the affinity of heavy metal cations to the dissolved organic matter. The risk of nickel and zinc leaching into groundwater is bigger than cadmium, attributed to the greater affinity of the two elements to the dissolved organic matter (Zhang et al. 2020c).

Dissolved organic matters have different effects on mitigating different heavy metal species. The distinct immobilization mechanism of various heavy metal species by biochar, which is caused by differences in the hydrolysis constant, solubility product constant, and the hydrated radius (Yuan et al. 2021), resulted in the opposite effect of

the dissolved organic matter on the heavy metal mitigation, as depicted by the increased lead and decreased cadmium in the water-soluble organic fraction produced through complexation with the dissolved organic matters despite the reduction of exchangeable fraction in soil (Fan et al. 2020). Yuan et al. (2021) reported that the immobilization of zinc differs from cadmium, lead, and copper in response to precipitation during the biochar aging process. Zinc requires less precipitation to become immobilized due to the larger hydrated size, higher first hydrolysis constant, and higher solubility product constant. As a result, zinc demonstrates higher stability even under reduced pH conditions during the aging process of biochar. Besides, the study by Feng et al. (2021b) showed the ability of wheat straw and cow manure-derived biochar to selectively adsorb dissolved organic matter in the soil. The amount of dissolved organic matter released by the high-temperature biochar, particularly at 600 °C, accounted for only 11–17% of the adsorbed soil dissolved organic matter, which is also lower than the released dissolved organic matter from the lower-temperature biochar produced at 300 °C, indicating the benefits of high pyrolysis temperatures to limit the dissolved organic matter release during the biochar application on the soil.

Applying phosphorus-loaded biochar on alkaline soil might not necessarily counter the problem of heavy metal leaching from the biochar during aging despite soil alkalinity fixing the heavy metals in their insoluble inorganic forms. This is because the other potential pathway of heavy metal leaching is the decomposition of biochar organic matter facilitated by soil microorganisms, which is more likely to occur at high pH and release the bounded heavy metals in the form of soluble complexes (Yuan et al. 2021). Biochar stability in terms of the resistance to decomposition by microorganisms can be enhanced by higher carbonatization degree and compact aromaticity. Still, previous research also revealed the extensive degradation of biochar structure, where aromatic carbon is transformed into oxygen and carbon-alkyl groups, except for stable carbon, occurs within 2 years of application (Wang et al. 2021c). Notably, phosphorus-loaded biochar could possess a selective heavy metal immobilization effect. Qi et al. (2022a) reported heavy metal adsorption selectivity of their fabricated biochar fertilizer. Remarkably, the removal of lead(II) ions was found to be more favorable in contrast to that of copper(II) and cadmium(II) ions. This is due to inhibited adsorption of copper ions and cadmium(II) ions posed by lead(II) ions. Hence, it is crucial to consider the specific types of heavy metal contaminants in the soil when applying biochar-based phosphorus fertilizer for soil remediation.

The addition of phosphorus fertilizer based on biochar to the soil affects soil alkalinity and the bioavailability of



heavy metals. This increase in alkalinity, particularly when the pH rises above 6.5, may lead to a depletion of essential micronutrients crucial for healthy plant growth and productivity. It is important to consider and monitor the effects of increased soil alkalinity on soil micronutrient levels when utilizing biochar-based phosphorus fertilizers (Arwenyo et al. 2022). However, as previously discussed, the effect may diminish as the pH improvement is not permanent due to biochar aging. While phosphorus-loaded biochar could enhance the phosphorus availability in soil for plant growth, potassium, and magnesium demands rise simultaneously (Arwenyo et al. 2022), and therefore, the effect of the biochar on the source of magnesium and potassium in soil shall also be a consideration. As stated by Li et al. (2020a) and Luyima et al. (2021), there is a need to study the impacts of the application of phosphorus-loaded biochar as fertilizer in large-scale plant production on the dynamics of not only phosphorus but also other macronutrients and micronutrients, which is mainly driven by the inconsistency in the relevant researches.

In recent studies, the most prolonged experiment duration of heavy metal adsorption by phosphorus-loaded biochar is approximately 2 months using metal chloride solutions as the solute media. There is a lack of studies that focus on the effect of phosphorus-loaded biochar on heavy metal desorption and mitigation via the formation of organic complexes, especially for the application on soil over 1 year. The immobilization effect of biochar last for 2–3 years and, occasionally, 5 years (Wang et al. 2021c), compared to the half-life of the biochar, which is at least 100 years. While using phosphorus-loaded biochar in agricultural soil can offer advantages such as improved plant growth and carbon sequestration, it is essential to carefully evaluate the risks associated with heavy metal desorption and mitigation during the biochar aging process. These risks include potential plant contamination and secondary environmental pollution. Therefore, a thorough assessment should be conducted before considering the large-scale application of phosphorus-loaded biochar in field settings.

Agronomic phosphorus use efficiency, which is related to plant productivity but also cost efficiency, is one of the factors that might limit the widespread application of biochar-based phosphorus fertilizers for plant production. Morais et al. (2023) synthesized a phosphorus-loaded biochar from the coffee husk via pyrolysis at 300 °C and 10 °C/min for 0.5 h by using Araxá phosphate rock as the phosphorus source, as well as magnesium chloride and serpentinite rock for cation modification. Triple superphosphate has a higher initial phosphorus release amount and availability than biochar-based fertilizer, which leads to a higher crop yield. The differences were recorded as 51 and 59% for nitric acid-treated and modified biochar,

respectively. Accumulation of phosphorus in plant shoots due to applying the mineral fertilizer was noticed. Their results may imply the lower agronomic efficiency of biochar-based phosphorus fertilizer than mineral fertilizer. However, the agronomic efficiency of biochar-based phosphorus fertilizer greatly relies on the choice of feedstocks, the production process conditions, and the plant requirements.

Concerns about transferring antibiotics and antibiotic resistance genes to soil and crops through applying organic biochar as fertilizer have been raised due to the significant environmental impacts and health concerns. Referring to Polianciuc et al. (2020), the application of antibiotics helps the growth of antibiotic-resistant bacteria and the development of antibiotic-resistance genes in consumers. Humans exposed to antibiotics through infections by antibiotic-resistant pathogenic bacteria could have higher health risks due to the increased ineffectiveness of medicine and treatment. This was proven based on the statistical data reported in the past, as stated in their study, particularly the increased mortality caused by infections of antibiotic resistance bacteria. Serwecińska (2020) further elaborated on the effects of antibiotics on living organisms. The effects include adopting and horizontal transferring antibiotic-resistance genes in microbial communities, disturbance to plant physiochemical activities, including photosynthesis, growth, and germination through uptake from the contaminated soil, and other ecotoxic effects exerted on living organisms in aquatic and terrestrial environments.

The biological activity of antibiotics depends on pH, moisture, soil properties, organic carbon content, microbial properties, and a bioavailable fraction (Polianciuc et al. 2020; Serwecińska 2020). Biotic degradation of antibiotics relies on types of microorganisms and fundamental environmental parameters. In contrast, antibiotics' abiotic decomposition can occur through hydrolysis, redox reaction, or photodissociation, triggered by satisfied physiochemical and environmental properties. There are multiple pathways of antibiotics resulting in environmental pollution and harm to humans, flora, and fauna. These mainly comprise the direct disposal of wastewater and sewage sludge as well as the application in livestock and plant production. Antibiotics are active in the excretion of humans and animals and, therefore, have a high potential to contaminate the environment through wastewater, manures, and biosolids (Serwecińska 2020). Animal farming and plant growth are two major entry routes of antibiotic and antibiotic resistance genes to the environment, food chain, and humans. As Koch et al. (2021) discussed, farmers use antibiotics on animals through their feeding primarily to boost production capacity and efficiency.

Antibiotics also can be found in fertilizers and pesticides for similar reasons. Antibiotics help prevent diseases, reduce plant and animal mortality, and trigger faster growth. However, the application of antibiotics in animal farming and plant production leads to increased microbial resistance to antibiotics and the production of bacteria strains with antibiotic-resistance genes. Recent studies discussed the risk of antibiotics entering the environment and food chain through organic fertilizers. Zhou and Yao (2020) revealed through their experiment that the use of composted manures from cows, chickens, and sheep, as well as earthworm casts as soil fertilizer, is effective in leaching antibiotic resistance genes even though composting induces antibiotic and antibiotic resistance genes reduction in the produced fertilizers. Leaching of antibiotic resistance genes is highly probable due to the direct application of composts made from wastes as organic fertilizers as well as their effluent water, leading to soil and food contamination (Huang et al. 2023; Sanz et al. 2022). This raises a great question on the contribution of biochar-based fertilizers derived from manures and sewages in the entry of antibiotic resistance genes to soil and the food chain. Importantly, comparing results in the recent research might not yield a clear conclusion on this matter.

Zhou et al. (2019b) produced an organic fertilizer by applying composted pig manures and biochar derived from the composted manures in the soil to study the release of antibiotic-resistance genes. Based on their experiment results, incorporating biochar in the organic fertilizer decreased the level of antibiotic resistance genes in soil and the uptake of the mobile fraction by plants, leading to lower health risks than direct application of composted manures. The pyrolysis process caused the former at 400–450 °C, which eliminated the antibiotic resistance gene content in the organic fertilizers. At the same time, the latter was attributed to the biochar adsorption of mobile fraction in soil. Still, they stated that other factors, such as pesticide adsorption by biochar applied in soil, could affect the efficiency of antibiotic resistance gene adsorption.

Similarly, the positive effect of biomass pyrolysis in the antibiotic resistance gene reduction was reported in the study by Zhang et al. (2023b), who produced a phosphorus-loaded biochar derived from antibiotics fermentation residues with high calcium and iron content through impregnation and adsorption in phosphorus-rich wastewater. They reported that pyrolysis could eliminate vancomycin and antibiotic resistance genes at more than 300 and 400 °C, respectively. Excellent adsorption of phosphorus from wastewater was also exhibited by the produced biochar, which was recorded as 74.3 g of phosphorus per kilogram biochar, suggesting the potential role of the material in wastewater remediation and agricultural application.

Conversely, the positive correlation between biochar use and antibiotic leaching in soil was reported by Zhang et al. (2020a). They fabricated biochar with corn cobs, corn stems, and walnut shells. The biochar was used to remediate antibiotic-polluted soil from mixing soil and contaminated chicken manure composts. According to their results, abiotic dissipation of antibiotics in soil could be affected by the short-term application of the biochar in soil, indicated by the inconsistent result of different types of antibiotics. The leaching risk of ofloxacin, enrofloxacin, ciprofloxacin, and sulfonamides increased, except for sulfaclozine and sulfadimethazine. This could be caused by the reduced active sites due to the adsorption of dissolved organic matter, implying the effect of other factors on antibiotic adsorption. They also mentioned the potential impact of biochar aging on the biochar-antibiotics interaction, leading to the necessity of future studies on this issue.

Masura et al. (2022) studied the adsorption and desorption of antibiotics and nutrients by biochar derived from paper mill sludge and oak wood, where human urine consisting of various nutrients, including phosphorus, nitrogen, and potassium, as well as antibiotics, was used as the source of biochar enrichment via adsorption. They reported that a pH below 5 favors the adsorption of antibiotics more than nutrients from wastes and vice versa. The maximum phosphorus adsorption capacity of paper mill sludge-derived biochar at 400 °C and -derived biochar at 900 °C was reported as 96.15 and 84.82 g/kg, respectively, but, with greater phosphate adsorption capacity, that of antibiotics are lower. Chemical bonds tend to be stronger and harder to dissociate than physical ones, resulting in a lower tendency of aluminium desorption in water than phosphates. Desorption of different types of antibiotics is noticed but in a wide range, where trimethoprim that was poorly adsorbed had the highest desorption efficiency, recorded as 92.6%, while azithromycin-biochar was the most stable, indicated by the low desorption efficiency, which was 3.3%. Furthermore, they also stated the need for further investigation on the amount of leached antibiotics on human health and the environment, although the desorption capacity differs with adsorption mechanisms.

The promising role of biochar in nutrient and antibiotics recovery from various wastes is evident due to biochar's excellent adsorption ability. However, recent studies lack validation on the stability of the adsorbed antibiotics on biochar with the introduction of different abiotic factors. The risk of leaching mainly arises from the antibiotics and resistance genes remaining in biochar-based fertilizers, which are highly dependent on the choice of phosphorus source and feedstock. Pyrolysis at high temperatures, particularly above 400 °C, could remove the antibiotics and resistance genes from biochar derived from antibiotic-rich

biomasses through dissipation. Notably, the discussion on the risk of antibiotic and resistance genes in studies focusing on producing and applying phosphorus-loaded biochar has been scarce.

Using biochar loaded with phosphorus can effectively improve soil fertility and moisture retention, reducing soil acidity and promoting crop growth (Zhang et al. 2022c; Zhao et al. 2018). Biochar loaded with phosphorus can also reduce the absorption of heavy metals by adsorbing heavy metals to reduce lead and cadmium in the soil, thereby reducing the risk of heavy metals to people. In the study conducted by Cui et al. (2022), several findings were reported regarding the implications of biochar loaded with phosphorus. Firstly, it was observed that phosphorus on the surface of biochar can dissolve into water, leading to soil eutrophication. Secondly, applying biochar loaded with phosphorus in extreme environments can result in soil salinization. Finally, using contaminated raw materials for producing biochar loaded with phosphorus can lead to secondary contamination of the environment.

The primary concern associated with biochar loaded with phosphorus is the release of phosphorus from the biochar surface into water bodies, leading to eutrophication (Wang et al. 2023). According to Sun et al. (2018b) survey, phosphorus-containing biochar contains 0.2–73.0 g/kg of phosphorus, of which 15–11,600 mg/kg of bioavailable phosphorus, which may be available for algae or large plants, the remaining phosphorus will be fixed in biochar. According to Bao et al. (2023), irrigation is the conventional method of agricultural watering, where substantial amounts of water come into contact with biochar loaded with phosphorus. This contact leads to the release of phosphorus from the surface of the biochar into the water. When water-affected biochar loaded with phosphorus is present, there is a rapid release of phosphorus that surpasses the demands of plants and soil conservation. As a result, the dissolved phosphorus in water can contaminate water sources through processes such as soil erosion and infiltration, ultimately contributing to water body eutrophication. Xu et al. (2021) mentioned that biochar loaded with phosphorus releases phosphorus concentrations exceeding 10 mg/L, significantly surpassing the National quality standard for surface water in China, set at 0.4 mg/L.

Additionally, Xu et al. (2023) discovered that excessive phosphorus entry into water bodies stimulates the rapid proliferation of green algae and cyanobacteria. These organisms consume dissolved oxygen in the water, which leads to oxygen depletion and produces toxic gases, including hydrogen sulfide. Consequently, the overgrowth of algae and cyanobacteria and oxygen depletion can result in mass mortality of fish and other aquatic organisms.

Biochar loaded with phosphorus may salinize soil and affect plant growth in freezing and thawing environments. In the course of plant growth, many factors cause acidification of the earth, precipitation, and concentration of calcium, magnesium, potassium, and other alkaline salt groups in the soil, resulting in acidification of the ground, and when people overuse uric acid can also lead to acidification of the ground (Shi et al. 2023a, b). Furthermore, Shi et al. (2020) found that manganese and aluminum ions in acidified soils fix phosphorus elements, so crops cannot absorb them. Large quantities of manganese and aluminum ions can affect crops by rejecting the absorption of iron ions, calcium ions, and magnesium ion nutrients as nutrients enter the crop. Still, this approach has been shown to pose a more significant problem in parts of the world where the earth is salinized and soil is formed to inhibit plant growth further. The freeze–thaw cycle promotes aggregates' fragmentation and accelerates biochar aging, where strong alkaline weak acids accelerate the precipitation (Sui et al. 2022). These strong alkaline weak acids produce large amounts of hydroxide, raising the pH of the soil, while the cations in biochar increase the salt content of the soil (Khadem et al. 2021). Over time, the salt in the biochar can be fixed by the soil particles leading to salinity and the soil forming a plate. Phosphorus in the phosphorus-containing organisms will be extracted from the earth by microorganisms, thus producing large amounts of phosphate in the ground, further exacerbating the salinization of the earth. Therefore, biochar loaded with phosphorus is not used in regions that are relatively extreme temperatures.

The raw materials for preparing biochar loaded with phosphorus are also very demanding. People need to select raw materials when preparing biochar loaded with phosphorus. Usually, people use a straw to produce biochar loaded with phosphorus because straw contains a lot of carbon and nitrogen. However, heavy metals in contaminated land can quickly accumulate in rice. In China, for example, nearly 30 billion tons of straw are produced annually, and a large proportion of straw is contaminated with cadmium (Shen et al. 2019). If people use high-temperature cracked contaminated straw made of biochar directly in the soil, organic matter in biochar is volatile due to high temperature, and cadmium content has not changed, so the presence of cadmium in biochar loaded with phosphorus can easily be transferred to the soil, causing secondary contamination of the earth (Zong et al. 2022). According to the survey, 41% of the cadmium in biochar made from contaminated materials is interchangeable, which poses a significant risk to plants and humans. Therefore, screening raw materials for biochar or removing pollutants using unique treatments when using contaminated biomass is necessary. Table 9 analyzes the different

**Table 9** Prevailing approach of treating contaminated biochar through pyrolysis and modification

Biomass	Treatment	Temperature	Characteristic	References
Contaminated rice straw	Add sodium hydroxide solution to adjust pH to 10	300–500 °C	As the pyrolysis temperature increases, the bioavailability of cadmium in biochar decreases. This proves that the exchangeable cadmium decreases as the pyrolysis temperature increases	Zong et al. (2022)
Plant stems	Making plant stems' pH 6.76	400 °C, 500 °C, 600 °C, 700 °C	The cadmium's chemical morphology in different plants' repaired residues was analyzed using various extraction methods. The results show that plants do not readily use cadmium in biochar when the pyrolysis temperature exceeds 600 °C	Zhang et al. (2020)
Ramie Stem	Dry to constant weight in a 60 °C thermostat box	300 °C, 400 °C, 500 °C, 600 °C, 700 °C	Carbonization is a viable way to stabilize metals in biochar, reducing their fluidity and bioavailability	Gong et al. (2019)
<i>Oiltea camellia</i> shells	<i>Oiltea camellia</i> shells are mixed with silicon dioxide crystals and then adjusted pH to 3–7 using hydrogen chloride and sodium hydroxide	500 °C	The conversion of heavy metals between sodium hydroxide solutions and contaminated biochar is used to extract heavy metals from biochar, which can be reused	Cai et al. (2021)
<i>Sedum plumbizincicola</i>	The high concentration of zinc cadmium is mixed with <i>Sedum plumbizincicola</i> to be heated in a furnace	350 °C, 400 °C, 650 °C	The leaching rate and bio efficiencies of cadmium and zinc in biochar produced by pyrolysis have always been significantly lower than the solid residues from asphyxiation. Pyrolysis is more suitable for the heat treatment of biochar than asphalt	Zhang et al. (2021a; b)
Bamboo, wood, coconut shell, corn core, corn stalk, and sludge	The pH value of the filter is controlled at 7	800 °C	Biochar has an optimal adsorption capacity of 456.2 mg/g for cadmium and twice as much for commodity biochar	Sun et al. (2023)

The table provides insights into the effects of various treatment conditions on biochar. Based on the information presented, conventional methods aim to prevent plant absorption of heavy metals by converting them into residues within biochar. This involves employing different temperatures, treating contaminated biochar with acids or alkaline substances, and modifying the biochar to enhance the retention of heavy metals. The table highlights the need for distinct treatment approaches for different types of biomasses, resulting in varied characteristics of the produced biochar. These findings emphasize the importance of tailoring the treatment process to the specific biomass to optimize the properties and performance of the resulting biochar

methods of treating contaminated biochar and summarizes the results of the biochar treatment.

This section examines the limitations of phosphorus-loaded biochar by addressing the loss of phosphorus from biochar in water, the risk of soil salinization under extreme weather conditions, and the potential drawbacks associated with phosphorus-loaded biochar's use. While the current application of phosphorus-loaded biochar in plant growth is relatively well-established and cost-effective, studying phosphorus-loaded biochar's limitations and exercising caution is crucial.

In summary, the limitations of biochar-based phosphorus fertilizer stem from the potential leaching and migration of heavy metals, disturbances in soil nutrient dynamics, leaching of antibiotic resistance genes, and agronomic efficiency for field application. Future research should prioritize studying the application of biochar-based phosphorus fertilizers under field conditions and assessing the risks of secondary pollution, mainly when derived from highly polluting biomass sources such as sewage and animal waste. This focus will promote sustainable, safe, and environmentally friendly practices in plant production.

## Potential environmental impacts of biochar use

The potential environmental impacts of the biochar production process and the long-term application shall not be neglected in the assessment of the sustainability of this technology, which is the focus of this section. Concerning lignocellulosic material-derived biochar, sufficient and stable biomass input is needed at a bigger scale of application, which could promote large-area land use for the cultivation of targeted biomasses and thus promote deforestation. Cutting indigenous forests is carried out to fulfill the need for more land for cultivation, the expansion and building of manufacturing and industrial facilities, the development of new residential areas, and the construction of infrastructures (Njora et al. 2022). The adverse impact of the forest conversion to low-input agricultural land was revealed by De Blécourt et al. (2019), who studied the cultivation of beans, pearl millet, maize, sorghum, and groundnuts in the west of Namibia and Zambia, where fertilizers were occasionally used to counter low yield of biomass. Removing the forest raises the rate of organic matter decomposition, resulting in the loss of organic carbon and nitrogen, bounded the organic matter at a depth of 40–100 cm, especially for the old fields. Still, nitrogen loss is also attributed to agriculture's combustion activities that induce organic nitrogen's volatilization. The loss of magnesium up to the depth of 40 cm was detected, where that of 0–20 cm was the most pronounced in the old fields. Cultivation induces the depletion of organic carbon content in soil due to the continuous removal of nutrients from the soil by the crops, where the organic matter is decomposed by bacteria, which is promoted by the release of plant root exudates (Chaplot and Smith 2023).

Additionally, the study by Warren et al. (2020) shows that part of the reduction of organic carbon matter in the topsoil, which is at a depth of 0–15 cm, is attributed to the dilution into a larger volume of soil as the cultivation depth increases. Thus, the loss of nutrients and organic carbon in the topsoil becomes more evident with longer cultivation duration. Although pieces of the literature showed the formation of a new state of organic carbon equilibrium after one year, this was not reported in the study by De Blécourt et al. (2019), which implies the long-term effect of land conversion on the soil nutrient and carbon stocks is yet to clarify. The research by Davari et al. (2020) shows that deforestation followed by dry farming for 60 years could lower the organic matter content associated with macro-aggregates at a depth between 0 and 60 cm. Due to the depleted organic carbon stock and nitrogen concentration in topsoil, plant production is expected to drop due to the decreased soil fertility (De Blécourt et al. 2019). Moreover, fertilizer used to counter nutrient and organic

carbon loss in the soil, which follows deforestation, lacks sustainability, considering the potential environmental impacts of biochar-based fertilizer application and forest clearance. Chaplot and Smith (2023) suggested that prevention of the loss of soil organic matter, which causes the emission of carbon dioxide, is impactful in overcoming land degradation and climate change.

Deforestation for agricultural use and settlement plays a great part in global issues, including carbon emission and soil erosion. Deforestation accounted for 15% of the world's carbon emissions based on the Global Forest Goals report in 2021 (Njora et al. 2022). Deforestation for agricultural use released 11.7 gigatons of carbon which is 35 times that of settlement between 2010 and 2018, while agricultural land use also accounted for approximately 33% of the overall soil erosion rate per hectare of deforested land (Hu et al. 2021). Deforested land or agricultural soil is vulnerable to soil erosion due to limited water-holding capacity (Cirella and Iyalomhe 2018), the loss of watersheds, and the weakened soil structure, leading to extreme runoff. With more soil entering the adjacent water bodies, the capacity of the water bodies at the lower course is expected to decrease, which further increases the severity of flooding in areas adjacent to rivers and streams. In the study by (Popa et al. 2020), there is a positive correlation between deforestation and flood risk, indicated by the simultaneous increase of the flood risk with the deforestation rate and deforested area, while flash flood in middle and upper catchment basins, which is brought by the climatic conditions including large runoff volume, is the result of deforestation in the past 20 years. Removing large forests also promotes water cycle disturbance, which Leite-Filho et al. (2019) and Dos Reis et al. (2021) reported. Leite-Filho et al. (2019) noted two drawbacks of forest clearance on rainfall patterns and frequency in Southern Amazonia. Firstly, the probability of dry weather rises simultaneously with the degree of deforestation. Besides extended dry spells, one percent of deforestation raises 0.12–0.17 days of rainy season onset delay. Agriculture, including those practicing double cropping, is expected to experience increased impacts since there is a strong dependence on crop growth and the yield on weather and regional climate. Dos Reis et al. (2021) revealed that ranching and agricultural land maintenance heavily contribute to forest fires in the Autazes of the Amazon. Environmental impacts of forest fires comprise loss of carbon sinks, soil erosion, habitat destruction, water and air pollution, and carbon emission, in addition to various health effects, particularly on the eyesight and respiratory system.

When evaluating the sustainability of biochar technology, life cycle assessments are essential references, which shall cover the environmental impacts of biochar



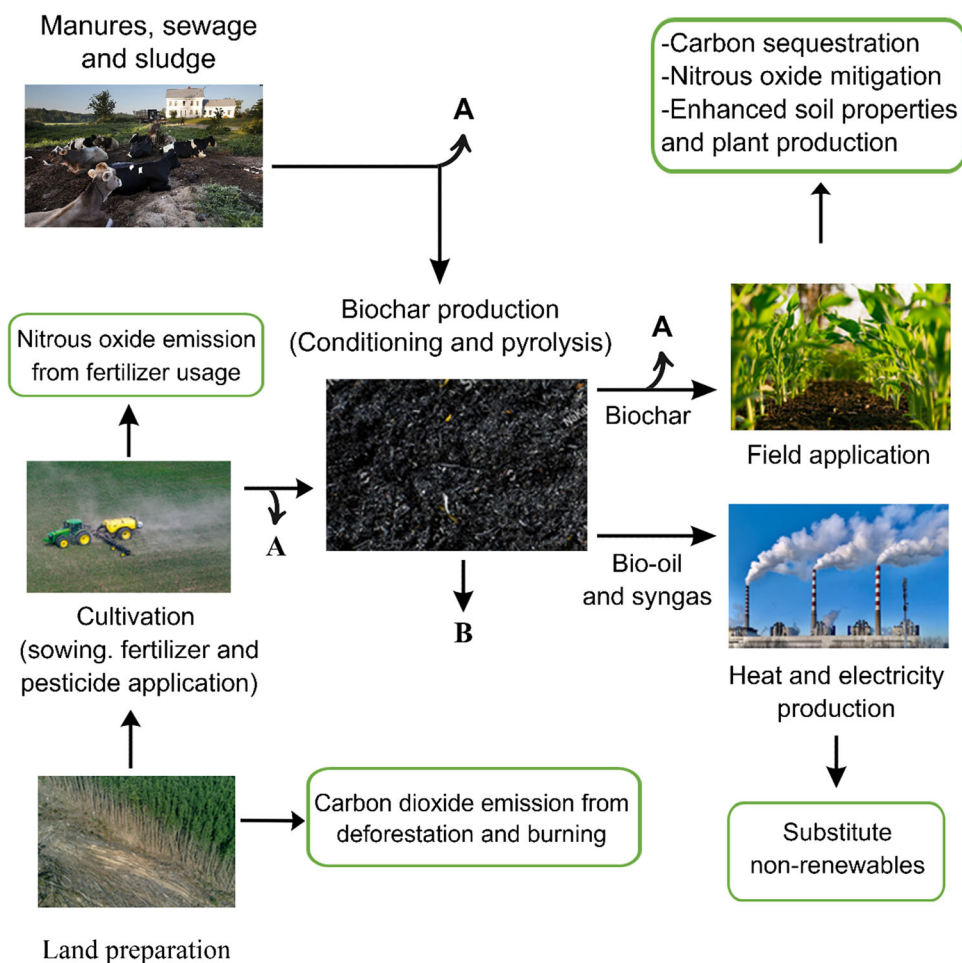
production from beginning to end application, including land preparation, harvest, pre-treatment, handling and transportation of raw materials and products, production of biochar, and field application. A simplified system for a life cycle assessment is illustrated in Fig. 8.

Life cycle assessments were conducted by Brassard et al. (2018), Robb and Dargusch (2018), Thers et al. (2019), Rajabi Hamedani et al. (2019), and Yang et al. (2021a). The life cycle analysis of switchgrass-derived biochar by Brassard et al. (2018) considered a 16-year perspective. It covered a system comprising agricultural land preparation, switchgrass cultivation, which includes the production of seeds, usage of pesticide and fertilizer, and other works of preparing harvested biomasses, handling and conditioning of the biomasses, biochar production via pyrolysis, and biochar application as a soil amendment for wheat agriculture. The measured parameters are carbon sequestration, greenhouse gas emission reduction, and by-product valorization, which includes bio-

oil and syngas as alternative energy sources to replace non-renewables. Two scenarios were shaped, which differed in the residence time and the pyrolysis temperatures; wherein the second scenario, longer residence time and higher pyrolysis temperatures led to greater energy consumption to produce the same biochar as the first scenario.

All processes before biochar application on soil are contributors to greenhouse gas emissions. Referring to Brassard et al. (2018), the reduction of greenhouse gas emission with the application of biochar produced at a longer residence time and a higher pyrolysis temperature is greater than that of a shorter residence time and lower temperature, which were recorded as 2561 and 2110 kg greenhouse gases per megagram biochar, respectively. However, the former has a larger greenhouse gas emission due to the larger cultivation scale, which increases the required land area, fuel used for transportation, handling and conditioning biomass, and pyrolysis. Surprisingly, among the different stages, fertilizer usage was reported as

**Fig. 8** Life cycle assessment of biochar production. The life cycle of biochar encompasses various stages, including agricultural land preparation, cultivation, feedstock transportation, biomass conditioning, pyrolysis, biochar transportation and spreading, and field application. Each stage contributes to greenhouse gas emissions and environmental impacts, with notable factors being land preparation, cultivation, biochar production, and transportation. Applying biochar in the field not only aids in carbon sequestration and mitigating nitrous oxide emissions but also enhances soil properties and promotes plant growth. Additionally, the valorization of bio-oil and syngas as alternatives to non-renewable resources further reduces carbon dioxide emissions



**A:** Carbon dioxide emission from transportation

**B:** Carbon dioxide emission from drying, size reduction, and pyrolysis

the biggest greenhouse gas contributor, which accounted for 63%, while that of pyrolysis ranged between 20.2 and 20.3% of the overall emissions. This could be attributed to the emission of nitrous oxide from soil. Overall, both scenarios have a negative net emission of greenhouse gases. Enhancing the carbon content in biochar and improving the energy efficiency of the pyrolysis unit are crucial factors to consider in achieving effective carbon sequestration and reducing energy demands.

Robb and Dargusch (2018) examined biochar's financial viability and carbon footprint derived from oil palm empty fruit bunches. They compared two scenarios: one focused on increased crop production with constant inputs of fertilizer and biochar, and the other aimed to achieve the same productivity with reduced fertilizer requirements. The financial viability analysis included aspects such as feedstock sourcing, pyrolysis, feedstock, biochar transportation, and the effectiveness of biochar on crops. On the other hand, the carbon footprint assessment considered a broader system boundary, encompassing agricultural land preparation, cultivation, milling, pyrolysis, transportation and shipping, implementation, and the impact on crop production. Their study showed that, on average, every scenario considered had a net carbon dioxide emission of  $-489$  kg per megagram of biochar produced. However, it is essential to note that this data did not account for emissions associated with land transformation. When the potential carbon dioxide emissions from land transformation, specifically from forests and peat forests, were included, the net emissions increased to  $+2087$  and  $+4742$  kg per megagram of biochar produced.

Nevertheless, using oil palm empty fruit bunches as feedstocks for biochar production instead of their current application as organic fertilizer could help avoid an average of  $102$  kg of carbon dioxide emissions per megagram of biochar produced. Regarding financial viability, the authors highlighted that the choice of shipping method, feedstock price, and transportation distance were crucial factors influencing the biochar market. Based on data from previous studies and biochar producers in Australia, they also reported a low breakeven point, averaging  $266$  USA dollars per megagram.

Thers et al. (2019) focused on the assessment of greenhouse gas emissions, particularly carbon dioxide and nitrous oxide, in the life cycle of biochar, where baling, biomass and biochar transportation, pyrolysis, biochar application, and efficiency in gases emission reduction were included. Their study also considered the production of biochar from oilseed rape straws at two different pyrolysis temperatures, which are  $400$  and  $800$  °C. They reported that in 100 years, the biochar produced at  $800$  °C could avoid 86.7% of the carbon dioxide emission through carbon sequestration, which is higher than that of biochar

produced at  $400$  °C with a carbon sequestration effect of 71.5%. The result obtained for the 20-year perspective contrasted with 100-year perspective, where an increase in greenhouse gas emissions was reported, and this can be caused by the little carbon sequestration effect during biomass harvest activities in 20 years compared to 100 years. The development of nitrous oxide mitigation through biochar application was negligible. They emphasized the definition of marginal electricity, which dramatically impacts the biochar life cycle analysis result. In the case where the use of natural gas is used for electricity production, net greenhouse gas emissions became  $+171$  and  $+111$  kg per megagram for pyrolysis at  $400$  and  $800$  °C, respectively, which in comparison to wind power, the net value increased by a factor of 7.

The life cycle assessment of a 20-year perspective conducted by Rajabi Hamedani et al. (2019) focused on pig manure and willow-derived biochar. The system boundaries included the preparation of dried thick pig manures and willow woodchips, transportation of biomass, pyrolysis, transportation of products, and biochar application in replacement of nitrogen, phosphorus, and potassium fertilizers. Similarly, bio-oil and syngas are valorized to substitute natural gas for electricity production. Carbon removal of  $2063$  kg and  $472$  kg per ton of biochar produced was recorded for willow and pig manure-derived biochar, respectively. In fact, the former has a more significant impact on carbon removal due to the production process's higher energy demand and biochar's higher carbon stability. Furthermore, willow cultivation consumes larger land space which may contribute a bigger portion to the overall emission. Nevertheless, both biomasses effectively mitigate global warming, as the net negative carbon dioxide emissions indicate. Carbon sequestration accounted for the most considerable carbon dioxide emission reduction, followed by substituting non-renewables for heat and electricity generation and the depleted demand for mineral fertilizers.

Another important finding is that there was an increase in the primary energy usage in the life cycle of pig manure-based biochar, recorded as  $10,820$  megajoules per ton biochar, owing to the energy intensity of the pre-treatment process, particularly the drying process. Likewise, by valorizing bio-oil and syngas, primary energy usage was lowered by  $18,109$  megajoules per ton of willow-based biochar. The willow-derived biochar life cycle is expected to result in greater environmental impacts, owing to the significant fertilizer and machine used during cultivation and wood chip production.

Yang et al. (2021a) conducted a comprehensive life cycle assessment with a time horizon of 100 years. They established a system boundary encompassing various stages, including crop residue management, biomass and

biochar transportation, pyrolysis, product spreading, soil application, and the valorization of bio-oil and syngas in electricity production. It is worth noting that the study excluded the cultivation of specific crops such as grain, tuber, bean, cotton, hemp, oil crop, and sugarcane, focusing instead on collecting residues. The authors examined the electricity consumption associated with collecting residues and product spreading, while transportation was evaluated for diesel fuel usage. They considered several factors related to carbon sequestration, plant production, fertilizer usage, nitrous oxide emissions, and the organic carbon content in the soil.

Based on the findings of Yang et al. (2021a), the production of 1 ton of crop residues could result in the generation of approximately 337.83 kg of biochar. The study identified four major contributors to the overall carbon emissions in the biochar life cycle: pyrolysis, biomass collection, product spreading, and transportation. These stages were estimated to emit 392.4, 75.66, 78.74, and 0.88 kg of carbon, respectively. Furthermore, syngas and bio-oil were found to have the potential to avoid approximately 725.15 kg of carbon dioxide emissions. In contrast, biochar application in the field was expected to sequester around 743.83 kg of carbon per ton of biochar applied, resulting in a net negative carbon dioxide emission of 921.39 kg per ton. Regarding nitrous oxide emissions, the study projected a decrease of 0.01 kg per ton annually. At the same time, nitrogen, phosphorus, and potassium fertilizer usage were expected to decrease by 0.1, 0.02, and 0.01 kg per ton, respectively.

Overall, the life cycle assessments show the potential of biochar as a soil amendment to realize carbon sequestration and mitigate the global warming effect, indicated by the net negative carbon dioxide and greenhouse gas emissions. A notable finding is that the degree of contribution in carbon dioxide emission at different stages of biochar production varies in different literature since the definitions of system boundaries and scenario settings are dissimilar. Thus, there is a need to standardize scoping and system boundary definition, including the life cycle duration, to easily compare different feedstocks and processes. Another problem is that land transformation, which involves deforestation and biomass burning, was not included in the scope of most life cycle assessments discussed. The exclusion of land transformation could underestimate the global warming impact of biomass cultivation, as demonstrated by Robb and Dargusch (2018). However, it is essential to note that the long-term effects of biochar application on agricultural soil, including the potential impact of land transformation, require further validation. While biochar has shown promise in carbon sequestration and soil improvement, the specific interactions between

biochar, soil, and the environment over extended periods must be carefully studied and validated.

The global warming effect of the biochar life cycle may have been underestimated due to assumptions regarding the complete substitution of fossil energy with syngas and bio-oil in heat and electricity production. Technological and economic considerations, policy support, incentives, energy efficiency, and industrial awareness influence the feasibility and implementation of these substitutes. Furthermore, due to repeated cultivation processes involving biochar application, there is a lack of comprehensive assessments regarding the potential changes in nitrous oxide emissions and soil properties, including organic carbon and nutrient content. It is essential to consider these factors' long-term effects and dynamics to fully understand the environmental impact of biochar use. In addition, the production of wastewater during the biochar production process and the emission of polluting gases containing sulfur, chlorine, and nitrogen during biomass combustion should not be overlooked. These factors can have significant environmental implications that must be properly assessed and managed.

To provide a more accurate assessment, life cycle assessments of biochar should ideally cover at least 100 years. This is necessary to account for the effects of biochar aging, which has emerged as a concern in recent studies due to biochar's potential impact on soil pH, dissolved organic content, and the leaching of soil contaminants from biochar. Biochar is often used to purify water sources and adsorb impurities in water; It can also act directly on the soil, allowing biochar to absorb heavy metal elements from the soil to form phosphate that plants cannot absorb. This reduces the absorption of heavy metals by plants and the effects of heavy metals on human health (Wu et al. 2022). However, these effects can all be attributed to the direct impact of biochar on nature, and the potential effect of biochar on the environment still needs to be analyzed from biochar's physical and chemical properties.

Biochar loaded with phosphorus can positively affect the environment by culturing related favorable flora. Cadmium now accumulates in the soil because plants in farmland need phosphorus to help them grow. However, Zhang et al. (2023c) mentioned that nitrogen absorption by soil and crops could only reach 15–30% of the total amount. At the same time, the rest of the phosphorus is lost with a series of activities, such as rainfall and irrigation. Li et al. (2020c) noted that cadmium could cause phosphate to form insoluble precipitation and thus cause the plant challenging to absorb. However, cadmium is a highly toxic pollutant that lasts long in the soil and quickly accumulates. Wu et al. (2022) suggested that using phosphorus-soluble bacteria improves soil phosphorus's effectiveness

by releasing mineral solvents, secreting extracellular enzymes, and degrading the substrate. Rahman (2020) mentioned that phosphorus-soluble bacteria have excellent phosphate dissolution capacity (155.30 mg/L in 48 h). At the same time, phosphorus-containing biochar combined with phosphorus-melting bacteria reduced cadmium content by 25.90–43.46% in crops. In this way, biochar can help people change from a chemically regulated environment to a biologically managed environment while reducing the harm of heavy metals to crops and humans and increasing the utilization of phosphorus in the soil.

When biochar made from agricultural waste is used in soil, biochar, as a carbon reserve, can last a long time in the ground while reducing the decomposition efficiency of soil organic matter and increasing crop yields. Blanco-Canqui et al. (2020) observed that agricultural fields treated with 11,820 kg per hectare of biochar in 2011 showed an increase of 9300 kg per hectare in carbon content by 2017 compared to new biochar. Eltigani et al. (2022) suggested that the production of biochar can be understood as the secondary use of agricultural waste, and fuel and reactants are agricultural waste, not only promoting the material cycle of waste but also the heat generated during the reaction process can be used.

Phosphorus-loaded biochar plays a crucial role in facilitating material circulation. Phosphorus, an essential nutrient for plant growth and a key element for all life on earth, is often a limiting factor in agricultural systems. However, as phosphorus is a non-renewable resource, the global production of approximately 6.9 billion tons of phosphate is not sustainable in the long term. At the current consumption rate, phosphorus reserves could be depleted within 300–400 years (Ban et al. 2023). Therefore, Zhang et al. (2022a; b, c, d) mentioned that it is crucial to promote the material cycle of phosphorus and reduce the waste of phosphorus in use. Biochar adsorption of phosphorus in water combined with phosphate to form phosphate and biochar composites, the material can enhance the adsorption capacity of biochar. At the same time, phosphate is considered one of the most promising reagents for biochar modification because of phosphate's low cost and strong affinity to heavy metal ions (Zhang et al. 2021b). Biochar can not only circulate phosphorus elements in nature but can also be used with phosphate-forming composites in the adsorption process of heavy metals (Zhang et al. 2022c). Ahmad et al. (2018) proposed that the adsorption capacity of copper with phosphoric acid-modified biochar was significantly increased by 12–44 times, while the adsorption capacity of cadmium was increased by 4–13 times. The fixed efficiency of phosphate-modified biochar for copper and cadmium increased by 69.8 and 55.4%, respectively.

The studies indicate that biochar positively impacts the environment and possesses significant potential as a low-

cost and high-efficiency adsorbent. It has a promising market for various applications. Biochar can be utilized for cultivating specific plant species, contributing to ecosystems' biological control. Additionally, selecting agricultural waste as feedstock for biochar production allows for using biochar as a heat source during the reaction process. Biochar's adsorption properties enable the recycling of non-renewable substances in nature, and this recovery process is cost-effective and widely acceptable.

In summary, uncertainties in the properties of biochar influence the potential environmental impacts associated with biochar's application. To minimize these impacts, conducting intensive studies under field conditions is crucial to ensure consistent performance. Additionally, there is a need to establish standardized guidelines for scoping and defining system boundaries in the life cycle assessment of biochar. This should include considering all relevant events and factors that can have an environmental impact, such as greenhouse gas emissions, global warming potential, the release of polluting gases, and other potential effects on living organisms. By addressing these aspects comprehensively, we can better understand and mitigate the environmental implications of biochar application.

### Future research directions for phosphorus-loaded biochar

Recent studies have highlighted the efficacy of various phosphorus-loading methods for biochar and the benefits of applying phosphorus-loaded biochar in soil. These benefits encompass soil fertilization, enhanced plant growth, carbon sequestration, and environmental remediation. However, there are limitations within these studies that hinder the validation of field applications. Further research is necessary to address these limitations, which this section discusses.

Future investigations using phosphorus-loaded biochar should prioritize optimizing the production method for improved energy and material efficiency. Currently, the dominant production method for biochar is slow/intermediate pyrolysis, which requires a substantial amount of heat input, thereby contributing to energy consumption. Moreover, the recommended pyrolysis temperatures exceeding 600 °C are necessary to produce biochar with high carbon stability and enhanced heavy metal removal and immobilization capabilities. However, this also necessitates a higher input of feedstocks and energy to attain the desired yield and quality. Alternative techniques such as hydrothermal carbonization and torrefaction show promise regarding energy conservation and cost reduction. These methods involve lower processing temperatures and enable the recycling of wastewater. However, their application in agricultural soil is limited due to the relatively high heavy



metal content compared to biochar. This discrepancy may be attributed to the significantly lower processing temperatures typically used, which generally range from 260 to 350 °C.

Nonetheless, Fei et al. (2019) and Song et al. (2023) demonstrated the reduction of heavy metal retention in hydrochar by removing the elements from the hydrochar to the liquid products. In a study conducted by Song et al. (2023), it was observed that the hydrothermal carbonization of sunflower straws at 200 °C, coupled with a 2% hydrochloric acid pre-treatment, resulted in significant removal of zinc, cadmium, copper, and lead. The maximum removal percentages for these heavy metals from the hydrochar to the liquid product were reported as 99, 99, 94, and 87%, respectively. The removal efficiency of heavy metals exhibited an upward trend with increasing processing temperatures and acid concentrations. Similarly, Fei et al. (2019) studied reducing heavy metal content in hydrochar derived from sewage sludge. The processing temperature ranged from 150 to 300 °C, reducing zinc, copper, lead, cadmium, and nickel concentrations in the hydrochar. The heavy metal content in the hydrochar was 457–728, 131–210, 77.2–109, 1.80–2.44, and 28.8–40.8 mg/kg of hydrochar, respectively. In comparison, the pyro-char produced at higher temperatures of 350–550 °C exhibited higher concentrations of these heavy metals. The increased concentrations in pyro-char were attributed to the more rapid volatilization and mass loss during the pyrolysis process. The relatively lower processing temperatures used in hydrochar production were not sufficient to volatilize most heavy metals due to their high sublimation temperatures. The lower concentration of heavy metals in the hydrochar can be explained by differences in the mechanisms involved. In hydrochar production, the heavy elements are removed and transferred to the liquid product, reducing their retention in the hydrochar itself. In contrast, pyro-char exhibits higher heavy metal retention due to immobilization on the material surface. This indicates a lower risk of heavy metal leaching from the hydrochar, highlighting hydrochar's potential as a more environmentally friendly option.

Fei et al. (2019) reported that the available phosphorus, alkali-hydrolyzable nitrogen, and potassium content were 0.270–0.735, 1.58–6.87, and 0.256–0.873 g/kg hydrochar. The phosphorus retention in the hydrochar was lacking compared to the pyro-char. Phosphorus loss is primarily caused by volatilization during pyrolysis, which differs from hydrothermal carbonization, which eliminates nutrients via dissolution, volatilization, and degradation. In pyrolysis, available phosphates can be effectively transformed from water-soluble to labile form, which comprises the mineral-bounded phosphates due to higher processing temperatures. This property is significant in the production

of slow-release phosphorus fertilizer as the greater labile pool could increase the longer duration of phosphorus release, reduce the fertilizer need, and improve the phosphorus use efficiency. This feature, however, could be absent in the hydrochar since a large portion of phosphorus is maintained in the exchangeable form. However, no comparison of the efficiency of pyro-char and hydrochar is doable because of the missing kinetics data of phosphorus release from hydrochar in water and organic acids in laboratory and field conditions.

Although Cui et al. (2020a) demonstrated the efficiency of hydrochar in reclaiming phosphorus from phytoremediators, particularly wetland plants, no assessment was carried out on the efficiency of phosphorus release from the enriched-biochar when applied on soil, which is essential for the characterization and performance evaluation of biochar-based phosphorus fertilizer. Other recent studies, including Xia et al. (2020) and Zheng et al. (2021), focused on hydrochar for heavy metal-polluted soil remediation. Xia et al. (2020) reported that the maximum heavy metal bioavailability reduction efficiency of amino-functionalized pinewood sawdust-derived hydrochar produced at 220 °C, which are 15.5, 52.2, and 96.2%, while the leaching risk of the said heavy metals were also lower in the hydrochar-amended soil, recorded as 30.4, 31.3, and 98.1% for cadmium, lead, and copper, respectively. The immobilization mechanisms involving the added amino groups, which are complex bases, successfully improved the heavy metal affinity and complexation with the metal cations, especially lead(II) ions, which are complex acids. Zheng et al. (2021) used the nitric acid-modified wheat straw-derived hydrochar produced at 220 °C to remediate heavy metal-contaminated agricultural soil, and they reported the significance of acid modification in enhancing the specific surface area and oxygen-containing groups, which resulted in the increase of cadmium adsorption efficiency from 4.23 to 46.18 g/kg using 15% nitric acid-modified hydrochar and raw hydrochar, respectively. The primary mechanisms of heavy metal removal involved are electrostatic interaction, complexation, cation exchange, and pi bond coordination. However, the increase in the heavy metal cation-binding groups, including amino groups and oxygen-containing groups, which are also inherently more abundant in hydrochar than pyro-char due to the former lower processing temperature, might not be beneficial for phosphorus loading with external sources such as inorganic and organic phosphate-containing materials due to the increasing repulsive force between phosphates and the hydrochar surface.

The environmental impacts of a phosphorus loading method are also crucial in advancing sustainable agriculture, following Piash et al. (2022). The most studied way to enhance phosphorus content in a nutrient-deficient material



phosphorus loading method is adsorption and chemical modification, which involve the use of toxic or potentially environment-polluting phosphorus sources and chemical modifiers, including inorganic phosphate solution, municipal wastewater, and alkali metals, the wastewater produced from the biochar loading process could cause water pollution if not treated properly. The environmental friendliness of different loading methods was often overlooked in recent studies. On the other hand, optimizing phosphorus loading shall consider various forms of phosphorus (Li et al. 2020a) and soil properties (Piash et al. 2022). The study of the phosphorus release kinetics and use efficiency shall be biochar production feedstock, soil, and crop-specific. The study direction shall shift to the application for the cultivation of essential crops under field conditions to determine the optimum loading ratio of phosphorus and dosage of enriched biochar according to the plant-soil-biochar interaction.

Biochar is a very stable material that can last in the soil for a long time, which, as mentioned, could reach 100–1000 years of the material half-life. Hence, there is an uncertain risk of phosphorus-loaded biochar in the soil after a long usage period, including reversible heavy metal desorption and antibiotics leaching, which arises with the effect of various abiotic and biotic factors on the soil pH and dissolved organic matter. Notably, the experiment conducted using phosphorus-loaded biochar under either laboratory or field conditions for at least 1–2 years is scarce despite a long period of study needed to validate the efficiency in the past studies.

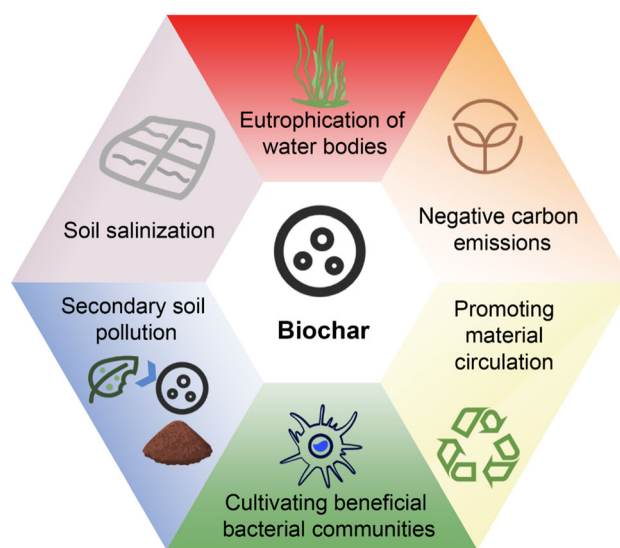
Besides, future studies should focus on experiments in different field application scenarios dependent on the environmental conditions, including moisture level, temperature, and soil pH, because the environmental conditions could influence the adsorption and desorption of biochar matrix. Therefore, there is a lack of studies focusing on the effect of phosphorus-loaded biochar applied as soil amendment under field conditions. Experiments under the actual plantation conditions could provide information and validation on the performance of phosphorus-loaded biochar in terms of phosphorus availability, phosphorus use efficiency, and plant growth responses in the field (Arwenyo et al. 2022; Qi et al. 2022a; Wali et al. 2022; Yang et al. 2021b; Zhao et al. 2022), and thereby eliminating the inconsistency, uncontrollability, and unpredictability of biochar behavior in soil. The minimum study of a 2-year perspective is recommended since the loss of biochar integrity and soil alkalization effect reportedly happen within this duration.

Another crucial variable to be evaluated under field conditions is cation holding reversibility (Wali et al. 2020), especially for long-term application, and this is particularly important to avoid heavy metal leaching and mitigation,

especially when the use of phosphorus-enriched biochar to fertilize and remediate heavy metal-contaminated soil simultaneously is promoted in the recent studies, which provide a lack of confirmation on the effectiveness of heavy metal immobilization during biochar aging.

Moreover, the selectivity of the heavy metal immobilization effect, as explained previously, is also another consideration in the field application of phosphorus-loaded biochar because some heavy metal cation species, such as zinc, have a higher stability and lower desorption tendency due to the more reliable immobilization mechanisms, namely cation exchange, and precipitation. Also, feedstock choice, a determining factor of retained heavy metal amount in the biochar due to the high initial content, shall be considered. Notably, past studies demonstrated the promising usage of phytoremediators as the feedstock to synthesize phosphorus-loaded biochar (Ahmad et al. 2018; Cui et al. 2020a), and hence, more verification on phosphorus release efficiency and environmental risks is needed. The direction of future research shall advance toward improving the reusability and recyclability of the biochar enriched with heavy metal contaminants after field application (Zhou et al. 2023).

Addressing the existing limitations and exploring potential applications of phosphorus-loaded biochar is essential. Figure 9 provides an overview of biochar's current limitations and positive environmental impacts. Future research should focus on expanding phosphorus-loaded



**Fig. 9** Limitations of biochar use and positive environmental impacts. The chart highlights the ecological risks associated with improper use of biochar, including water eutrophication, land salinization, and secondary pollution. On the other hand, biochar has the potential to positively impact the environment by promoting material circulation, reducing harmful carbon emissions, and supporting beneficial flora. The chart emphasizes the importance of proper biochar production and application management to mitigate these risks

applications to maximize benefits while minimizing cost and resource waste.

Use microorganisms to bind to the carbon surface of phosphorus-containing organisms, thereby reducing phosphorus loss from phosphorus-containing organisms as water flows. Bao et al. (2023) found that the most significant limitation of using biochar loaded with phosphorus is that when it comes into contact with water, phosphorus in biochar is lost, causing secondary pollution of the environment. At the same time, phosphorus on the surface of biochar is significantly less reusable because it is lost in aqueous solutions. Therefore, they proposed to use microorganisms to fix phosphorus on the surface of biochar. Ding et al. (2019) stated that the fixed steps of microorganisms on the surface of biochar are reversible attachment, irreversible attachment, synthesis of extracellular polymer substances, and formation of mature biofilms. The biofilm produced by microorganisms on the surface of biochar can well fix phosphorus in biochar. For microbial selection, fecal *Aspergillus* was chosen as the study object. Rashid et al. (2022) mentioned that fecal *Aspergillus* is commonly found in sludge in wastewater treatment and exhibits strong resistance to heavy metals. Fecal *Aspergillus* is, therefore, suitable for the adsorption of heavy metals in soil on surfaces with biochar. At the same time, *Aspergillus* can obtain the nutrients needed for growth and reproduction by degrading the unstable composition and aromatic structure of biochar, so *Aspergillus* can quickly multiply on the surface of biochar to form a biofilm to more steadily inhibit phosphorus loss (Qi et al. 2022b). According to Wang et al. (2023), fecal *Aspergillus* decreased the solubility of phosphorus in biochar loaded with phosphorus by 84.96%. Conversely, the efficiency of uranium removal from nuclear wastewater by the same biochar was nearly 100%. However, there are some limitations to this approach. *Aspergillus* may cause functional groups inside biochar to dissolve, reducing their reusability and resulting in a waste of resources.

Biochar loaded with phosphorus can also be combined with pesticides and other substances to improve pesticides use efficiency. Singh et al. (2022a; b) found that biochar could increase the duration of pesticide effects on the soil by increasing the soil's adsorption and delaying dissipation. Wu et al. (2019b) found that the half-life of oxyfluorfen in biochar-modified soils is faster than in biochar-free soils. This is due to biochar's high specific surface area and microporous structure, which provides ground with more pesticide adsorption sites, demonstrating that biochar loaded with phosphorus enhances the fixation of pesticides in soil (Hafez et al. 2020). Gao et al. (2023) mentioned that biochar loaded with phosphorus could increase crop yields by carrying different kinds of pesticides and by controlling

their rate of decomposition to orientate the changes in the flora in the soil by cultivating microbes conducive to crop growth and by reducing microbes harmful to crops. Wang et al. (2022a; b) added biochar to the soil to control atrazine, reducing the atrazine residual percentage from 90.71 to 44.60% and the degradation half-life from 13.3 to 121.6 days. By combining pesticides with biochar loaded with phosphorus, pesticide use efficiency can be effectively increased, and the environmental impact of pesticides due to soil erosion is somewhat avoided. People can further orientate the microbiota by studying the effects of pesticides on microbes in the soil.

Sludge is increasingly being considered as a potential raw material for biochar production. In traditional biochar preparation, biomass is typically converted into powdered form and mixed with a binder before pyrolysis, known as carbonization. However, this method has the drawback of potentially clogging the existing biochar pores, which reduces biochar's active surface area and hampers effectiveness. Addressing this issue is crucial to enhance the performance of biochar as an adsorbent or soil amendment. Sun et al. (2023) mentioned that sludge is an unavoidable by-product of wastewater treatment plants, producing up to 130,000 tons annually. In addition, most sewage sludge is only landfill and needs to be effectively reused. However, for biochar, there is a large amount of carbon-containing organic matter in the sludge, but also a large number of highly viscous extracellular polymers, which can be used as in situ adhesives to prepare high-density biochar particles (Yang et al. 2022c). Of the high density of biochar it produces, Liu et al. (2020a; b) applied biomass wastes are introduced as water moderators and pore formers to increase their surface area and adsorption capacity. Therefore, with sewage sludge as a binder, water source, carbon source, and magnetic source, biomass waste is a slower water agent and porous agent—modular biochar with high adsorption capacity (Yin et al. 2021). Sun et al. (2023) noted that biochar made from sludge had an optimal cadmium adsorption capacity of 456.2 mg/g. The biochar produced had magnetic and particle properties, making it easy to collect.

In summary, the widespread implementation of phosphorus-loaded biochar still faces several challenges that need to be addressed, including validation under field conditions and mitigating potential environmental risks. Future research efforts should focus on optimizing the phosphorus loading process by exploring different phosphorus sources, feedstocks, and loading techniques. Field trials are essential to validate the effectiveness of phosphorus-loaded biochar tested in the laboratory under real-world conditions. The prospects for biochar are promising, as it holds the potential to enhance human well-being. Biochar can benefit significantly by broadening biochar's

applications, utilizing environmental shaping abilities, and enriching the soil for enhanced crop productivity. Additionally, carefully selecting raw materials can contribute to cost reduction and material recycling, enhancing biochar's overall efficacy.

## Conclusion

Inorganic fertilizers containing phosphorus promote plant growth in agriculture, but their use can lead to environmental pollution, reduced crop yields, and eutrophication of water bodies. This review discusses the key topics related to phosphorus-loaded biochar, employing computational chemistry and machine learning to optimize the application of phosphorus-loaded biochar in sustainable agriculture. The adverse environmental impacts of traditional fertilizers are examined, including their inefficiency and detrimental effects on soil health and biodiversity. Biochar production and loading techniques are elucidated, covering various production methods and phosphorus sources for loading biochar. Characterization methods for loaded biochar are also discussed. The mechanisms of phosphorus release from biochar are explored, encompassing the physical and chemical properties that influence the release and the microbial and root-mediated processes involved. Factors affecting phosphorus release, biochar modification, and the impact of organic acids on the release are analyzed. The review also highlights the benefits of slow and controlled phosphorus release from engineered biochar and investigates the influence of biochar type and application rate on phosphorus release. Limitations associated with using phosphorus-loaded biochar in plant production are identified, leading to discussions on future research directions in this field.

Biochar can effectively adsorb inorganic salts and heavy metals from pesticides, offering a low-cost and easy-to-use treatment option. Biochar production methods include pyrolysis, gasification, and low-temperature carbonization, with pyrolysis being the most commonly used. Phosphorus-loaded biochar enhances adsorption capacity and efficiency, utilizing urban sludge and animal feces as phosphorus sources to promote solid waste recycling. Pyrolysis conditions affect biochar's properties, including functional group type, cation exchange capacity, and pH, which impact phosphorus release. Bacterial contraction can further increase biochar's retention capacity. While physical, chemical, and biochemical modifications can enhance biochar's adsorption capacity, they may require significant time. Optimizing organic acids and employing machine learning to improve phosphorus bioavailability from biochar in climate-smart agriculture is necessary. Integrating computational chemistry with experimental data enhances

understanding of phosphorus bioavailability. Although phosphorus-loaded biochar promotes substance circulation and heavy metal absorption, caution should be exercised due to potential toxicity and variation in chemical composition from biomass sources. Future research should focus on the field application of biochar-based phosphorus fertilizers, assessing risks of secondary pollution, particularly when derived from highly polluting biomass sources. This approach will promote sustainable, safe, and environmentally friendly practices in plant production.

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## Declarations

**Conflict of interest** The authors declare no conflict of interest.

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