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REVIEW PAPER

Production and physico-chemical properties of biochar and its impact on phosphorous release for soil improvement: A review

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Abstract

Through a process known as pyrolysis, biomass of various biological origins is thermally decomposed to produce biochar, a solid carbon-rich substance. Biochar has enormous potential to cut greenhouse gas emissions, sequestering carbon in the soil, revitalizing depleted soils, and reducing the dependence on chemical fertilizers in agricultural practices. Furthermore, it improves the soil's physical, chemical, and biological properties while raising healthier plant growth. As a result of these attributes, there is a growing interest in integrating its utilization in agriculture, soil and land rehabilitation, and strategies aimed at mitigating climate change. The impact of biochar application can range from neutral to highly beneficial, contingent upon several factors, such as the source of the raw materials, the conditions during carbonization, the frequency and method of application, as well as the quantity applied. A suitable niche that biochar can provide for soil bacteria can lead to an improved pattern of growth and proliferation. The vital mineral phosphorus (P), which is usually lacking in plant nutrition, must be managed sustainably in order to preserve soil fertility and crop yield over the long term. Biochar may also help to improve P availability in soil by providing habitat and carbon supply to phosphate solubilizing bacteria (PSB) which can solubilize P compounds of low solubility. Integrated application of biochar and PSB can therefore, be exploited as ecofriendly strategy for the enhancement of PSB activity in soil to mobilize higher P for increased plant productivity. In conclusion, this review suggests that improving soil chemical properties by adding biochar not only requires consideration of biochar application rates and chemical properties but also the local soil environmental factors, especially soil initial pH and sand content of the soil, should be considered.

Keywords: Biomass feedstock, Carbon sequestration, Microorganisms, Pyrolysis, Soil Phosphorus, Soil health, Waste biomass

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Introduction

An organic carbon byproduct called biochar is created when waste biomass is pyrolyzed without the presence of oxygen. Storage of biochar in soil is a viable method for carbon sequestration since it is highly resistant to microbial degradation in soils (Baldock & Smernik 2002; Lehmann, 2007; Glaser et al., 2009). Additionally, by enhancing the physicochemical characteristics of soil, biochar incorporation can increase crop productivity (Sohi et al., 2010). As a result, it is receiving a lot of interest as a technique for improving soil and sequestering carbon to increase crop output. Because the physicochemical characteristics of biochar vary depending on the type of feedstock and pyrolysis circumstances (Chia et al., 2015), it should be highlighted that the incorporation of biochar in agricultural soils does not always result in increased crop yields (Spokas et al., 2012). The physicochemical characteristics of biochar also influence its ameliorating effects. Additionally, each soil has a different set of physicochemical characteristics that need to be improved or remedied. Therefore, the types of feedstock and pyrolysis temperatures should be chosen to produce a biochar that is specifically designed to enhance particular soil qualities. Designing selected biochars to repair or enhance particular soil qualities requires an understanding of how feedstock choice and pyrolysis conditions affect the physicochemical properties and elemental compositions of biochar (Novak et al., 2014).

Phosphorus chemistry in soil

As the thirtieth chemical element in nature (Emsley, 2000), P exists as an orthophosphate form surrounded by four O atoms. In general, its quantity in natural water is low (Némery & Garnier, 2016) and anthropogenic activities via loading P to water have been known as the major source of eutrophication in aquatic ecosystems (Turner et al., 2012; Turner & Condron, 2013). Regardless of its abundance on land surface, the processes of nutrient dynamics and ecosystem development lead to P discharge into soil solutions (Elser, 2012; Jarvie et al., 2013; Sharpley et al., 2013). P is thus transformed successively through physicochemical, biochemical, and biological pathways during soil development stages (Sims & Pierzynski, 2005), which occur between soil, vegetation, and microorganisms (Fig. 1). Soil also plays an important role in P cycling in terrestrial ecosystems (Dorioz et al., 2006). Besides, its forms are determined via several factors such as soil pedogenesis extent, type, parent material, and management practices (Sharpley & Tunney, 2000). As well, its release in nature occurs through the weathering of primary minerals (mainly apatite) derived from parent materials during soil development (Shen et al., 2011). Paedogenesis can further result in transformations of primary minerals into secondary ones, producing a build-up soil organic matter (OM) (Smeck, 1985). Hence, P transformations appear through intensive cycling processes. The main mechanisms of P cycling are thus as follows: soil sorption-desorption (Zaimes & Shultz, 2002), immobilization-mineralization, and precipitation-dissolution (Fig. 1).

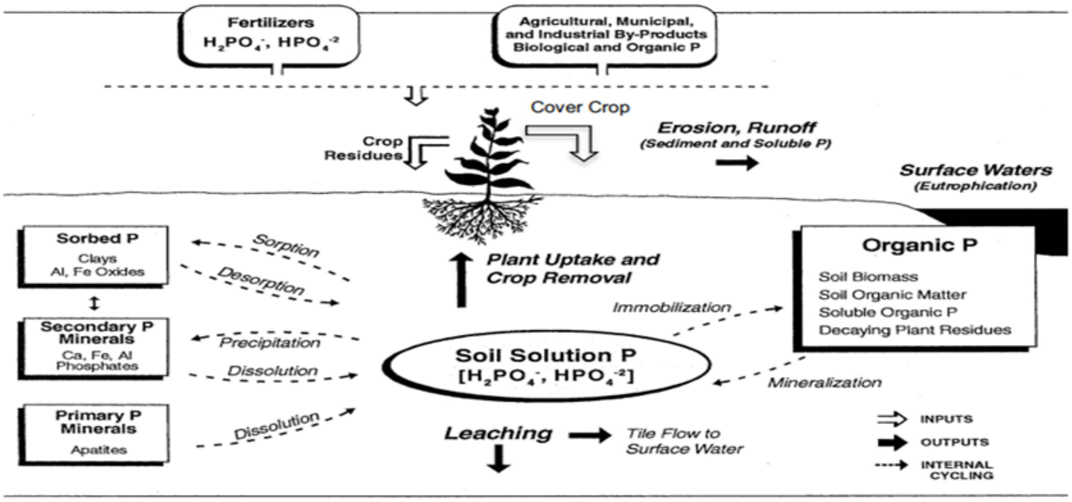

Fig. 1 Cycling of terrestrial phosphorus (Pierzynski et al., 2000).

Phosphorus forms in soil

Total phosphorus (TP) quantity can change between 0.02 and 0.5 % in soils (Cao et al., 2012). However, less than 1% of TP fraction is available for plant growth and development (Pierzynski et al., 2005). Organic P (Po) and inorganic P (Pi) are also known as the main forms of soil P, combined with mineral elements such as iron (Fe), aluminium (Al), and calcium (Ca) (Arai & Sparks, 2007; Shen et al., 2011). P concentration gradually increases via Po and Pi in soil solutions; however, a small quantity of P is bioavailable for plants (Shen et al., 2011). According to pH ranges, the ionic P form is as follows: dihydrogen phosphate (H_2PO_4-: pH 2.1-7.2), hydrogen phosphate (HPO_4^{-2}-: pH 7.2-12.0), and phosphate (PO_4^{-3}: pH >12.0) (Kruse et al., 2015). Generally, dissolved particles (>0.45µm) are known as ionic P forms (Haygarth et al., 1997). Nevertheless, colloids (bound with P) can govern P mobilization since they constitute a great segment of dissolved P in water-soil ecosystems (Filella et al., 2006; Jarvie et al., 2012; Missong et al., 2016). Pi is also mostly bound with clay elements and Fe/Al/Ca (Sims & Pierzynski, 2005). Hydroxyapatite and apatite are thus the main Pi in alkaline soils, while P is linked with Fe/Al in acidic soils (Arai & Sparks, 2007). Therefore, bioavailability, solubility, and forms of Pi are controlled via soil properties for instance textures, pH ranges, and Fe/Al/Ca concentrations, as well as soil OMs (Richardson et al., 1994).

Soil phosphorus dynamics

Initially, water-soluble form of P transfers in solutions as orthophosphate ions by the application of phosphates in soils (Arai & Sparks, 2007). Afterwards, P can be taken via plants and/or microorganisms, precipitated by Ca carbonates, or lost by surface or subsurface runoff (Kruse et al., 2015). P sorption from soil surfaces is the major pathway of orthophosphate ion decrement, which transforms into inorganic minerals (Shen et al., 2011), indicating P sorption and precipitation (namely, P fixation). The sorption capacity is mainly governed by the number of soil constituents, the type of soil particles, and the quantity of accessible sites (Reddy et al., 2008). The precipitation process also makes the greatest stable bond on the surfaces of soil particles. By adsorbing phosphate ions, the concentration of phosphate ions enhances, which can precipitate during solid phases (Weihrauch & Opp, 2018). In all types of soils, sorption and precipitation occur at various pH ranges (Shen et al., 2011). Conversely, the relative quantity and type of the sorbed P generally vary based on OM, soil type, pH range, and clay content (Arai & Sparks, 2007).

Soil phosphatase activities

Soil enzyme activity is a biological index of soil quality (Zhang et al., 2012). Soil phosphatase is also a general term that can catalyse the hydrolysis of organophosphates (such as phosphate monoester, phosphate diester, etc.) and phosphoanhydrides (e.g., pyrophosphate). Besides, soil phosphatase is a kind of extracellular enzyme secreted by plant roots or microorganisms (of note, it is generally believed that plant roots can only produce acid phosphatase, while alkaline phosphatase is secreted by microorganisms or protozoans in soils). It is mainly used to catalyse Po mineralization such as triphosphate, phosphodiester, phosphate monoester, etc. to Pi in soil. Based on soil phosphatase types, there are mainly phosphomonoesterase, phosphodiesterase, phosphotriesterase, and pyrophosphatase. According to optimal soil pH range, phosphomonoesterase can be divided into acid phosphomonoesterase (ACP), alkaline phosphomonoesterase (ALP), and neutral phosphomonoesterase. Soil phosphatase is also an adaptive enzyme, whose activity is quite different under various physical and chemical conditions of soils (such as pH range, substrate concentration, and temperature) (Wang, 2012a). For example, the ACP is greater than that of ALP when pH range of soils is less than 7.0. As well, both microorganisms and plants discharge phosphatase to the exterior environment of cells and decompose less available P in soils to meet the needs of plants for nutrients such as P when the substance of readily available P in soils is low (Nannipieri et al., 1990). In addition, different agricultural management practices can significantly shape soil phosphatase activities (Zhang et al., 2012). From the perspective of the substrate types for catalytic hydrolysis, soil phosphatase is also a specific enzyme, which can hydrolyze specific P compound substrates to become a target phosphate. Generally, its activity is positively associated to the application amount of organic fertilizer materials, which can directly estimate decomposition and transformation rates of soil Po and biological effectiveness of Po. Therefore, soil phosphatase activity can be employed as a significant biological index of the quality of soil (Zhang et al., 2012).

Colloidal phosphorus in soil

P mobility and loss in soil occur between solid and aqueous phases (Heathwaite et al., 2005). Colloids (1-1000 nm) are also identified as the 3rd mobile aspect (Stamm et al., 1998) since they can dramatically enhance the movement and transport of sorb contaminants due to their great specific surface area and mobility (Hens & Merckx, 2002). In aquatic environments, phosphorus (P) moves significantly between particulate P (PP) and dissolved P (DP) forms. Dissolved P can combine with macro-particles, demonstrating further movement (Hens & Merckx, 2002). The CP actions also distinguish between PP and DP, probably attributed to physicochemical characteristics (Heathwaite et al., 2005). The colloidal phosphorus (CP) also plays an expressive role in transferring P in soil and water milieus (Buesseler et al., 2009). Compared with larger particles, colloidal substances can migrate further in aquatic ecosystems (O'Melia, 1980; Baalousha et al., 2005). Therefore, the study of CP can have a significant effect on P efficient utilization and loss control.

Factors influence colloidal phosphorus

As one of the P migration forms in soil solutions, CP occurs for 13-95% of TP in soil solutions (Hens & Merckx, 2001). Ionic strength, pH range, and electrolyte composition (especially C ion concentration) can even significantly affect the stability of colloids and the migration of colloidal suspensions (Kretzschmar et al., 1993; Kretzschmar et al., 1999). However, organic C can increase the aggregation of surface soil particles, giving rise to the release of colloids (Celi et al., 2001). Compared with monovalent cations, divalent ones have a stronger impact on the inhibition of colloidal release and further increase the aggregation of colloidal suspensions. As well, some substances adsorbed on soil particles shape the migration and transportation of the colloids (Kretzschmar et al., 1999). P adsorption will thus reduce the surface load of its adsorbent (Celi et al., 1999). Therefore, the Fe/Al oxides on the surface of the initial cation may inhibit P adsorption.

Effect of phosphorus saturation on colloidal phosphorus

P application causes the mobilization of colloidal iron oxide (FeO). Similarly, studies by Siemens et al. (2008) had indicated that P adsorption could lead to CP release in batch experiments of two P-enriched human-made soils. They had also proposed that the existence of critical P saturation could mark the change node of CP release rate from the soil. Ilg et al. (2008) had further pointed out that P saturation had an increasing linear trend. Compared with orthophosphate, inositol hexaphosphate could promote the migration of the colloids. Hence, the addition of organic materials (namely, biochar) to soil might escalate the migration of soil colloid more than that of mineral fertilizer with orthophosphate as the main component. Excessive fertilization can also lead to P accumulation in solid phase, which may raise the content of DP and CP in the runoff. Thus, the increase in P saturation might compound P concentration of CPs and accelerate their release. Therefore, increased CP concentration may be the result of changes in adsorption equilibrium caused by growth in dissolved P concentration.

Effect of pH on colloidal phosphorus

CP has been proved as one of the main contributors to eutrophication. As well, CP release depends on the adsorption of soil colloid and its ability to release P, both of which affected by pH ranges. In this sense, Liang et al. (2010) had reported that CP migration would increase in both high and low pH environments. At lower pH, CP release was mainly caused by inorganic constituents. At the pH range, there is additionally an intense association among CP content and water-dispersible colloid, implying that water dispersive colloid is the carrier of CP. Simultaneously, CP concentration may be related to P concentration in CPs. Increasing the concentration of DP and adsorption equilibrium may thus lead to a growth in P concentration in CPs. There was also a substantial association between soluble P and CP (Ilg et al., 2005).

Biochar production and properties

Biochar is a kind of substance rich in carbon (C) elements, as a type of black C. It is a highly aromatic and refractory solid substance produced by pyrolysis of plant biomass at various temperatures under anoxic or completely anaerobic conditions (Fig. 2). During pyrolysis, the carbonaceous substances in hemicellulose, cellulose, and lignin can gradually undergo dehydrogenation and deoxidization, and then proceed in the direction of aromatic C and graphite structure C. Attributable to the characteristics of great specific surface area and strong stability, biochar can further provide nutrient supply, increase soil C sink, reduce greenhouse gas emissions, and give rise to multiple effects after its application into soils (Lehmann, 2007), which has attracted many researchers' attention (Manya, 2012; Cayuela et al., 2014). Compared with the direct application of biomass raw materials to soils, pyrolysis of biomass raw materials to prepare biochar before application to soils may noticeably diminish the polycyclic aromatic hydrocarbons (PAHs) bioaccumulation and heavy metals and enhance the biomass of plants. The utilization of biochar and endophyte in soils can further promote the growth of soybean under heavy metal stress and augment its yields (Waqas et al., 2014a).

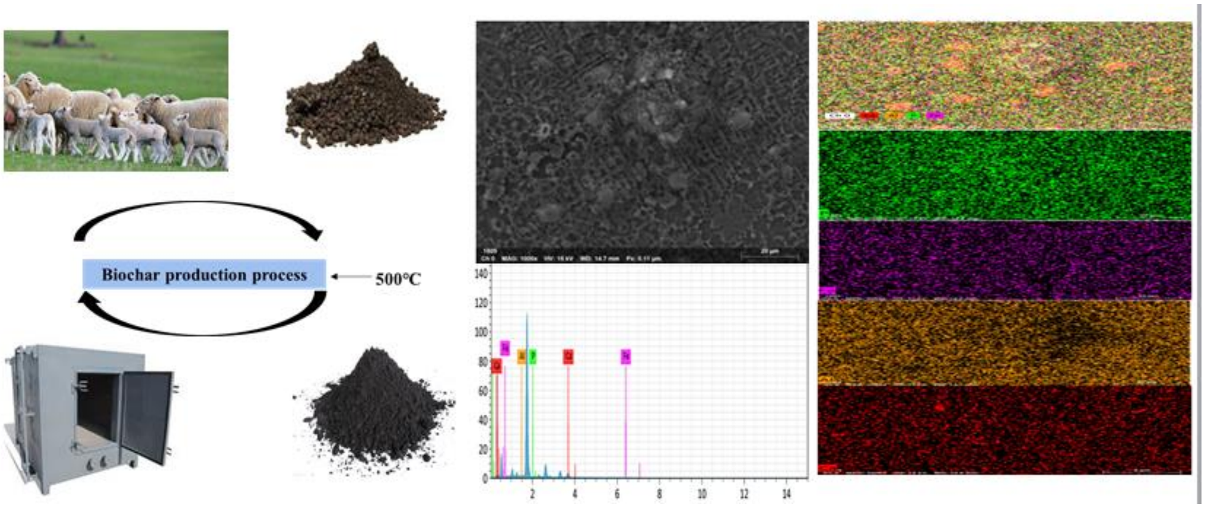

Fig. 2 Schematic picture illustrating various stages of biochar production

Most of raw constituents for preparation of biochar come from agricultural and forestry residuals. Too much excrement is also being produced in the process of livestock breeding. In 2003, data showed that 3.190 billion tons of faeces were produced in China's livestock and poultry breeding industry, which was 3.2 times of the industrial solid waste (Wang et al., 2007). The manure of livestock and poultry is usually composted and then decomposed to be used as an organic fertilizer. In the face of such a huge amount of livestock manure, if it is not consumed and disposed in time, it may seriously affect water, soil, and atmospheric environments around farmlands and accelerate the risk of eutrophication. How to treat and use excrement from livestock and poultry breeding effectively has thus become a research hotspot in environmental science (Sun et al., 2018).

Physico-chemical properties of biochar

At present, the physical and chemical characteristics of biochar are different from each other. First, raw materials used for the preparation of biochar are different in various studies; secondly, there is still lack of a standard unified process for the preparation of biochar via pyrolysis in the world; thirdly, methods developed for this characterizing and analysing of biochar are not also the same in various studies. Accordingly, several physical and chemical properties of biochar are as follows:

Total carbon

Evaluating C in biochar, some researchers have also expressed that total C and organic C should be treated differently (Atkinson et al., 2010). At present, in the study of biochar, the content of total C has been frequently only concerned, while the content of organic C has been rarely studied. However, some scholars have pointed out that organic C in biochar may be a better indicator. This is because, under the condition of high-temperature pyrolysis, biochar contains more carbonate due to the existence of high ash content. This will overestimate the ratio of hydrogen (H)/C, C/N, and O/C, which represent the aromatization degree of biochar. The total C content in biochar also fluctuates greatly (36-94%), and the maximum amount of organic C from raw materials fixed in biochar can reach 50% (Sohi et al., 2010).

Ratio of C/N

C/N ratio is denoting the ability of biochar to release N elements. Generally, the C/N ratio of animal faeces is considered acceptable when it is 20: 1 because higher C/N ratio means that microorganisms can more easily fix N elements. Plants can also easily use C/N ratio when it is 12: 1 (Stevenson & Cole, 1999). Lately, the C/N ratio has substantially fluctuated, ranging from 8 to 1500 in biochar (Mutanda et al., 2011; Enders et al., 2012), which shows that biochar can fix soil N element.

Ash content

The ash in biochar is composed of crystalline, semi-crystalline, and amorphous inorganic minerals and OMs. These ash components are the products of the thermochemical reaction of minerals in biomass raw materials. Different pyrolysis temperatures, heating rates, and constant temperature residence times can thus have significant effects on the ash content of biochar. Through pyrolysis, biomass can further produce a variety of minerals, mainly including silicates, carbonates, phosphates, sulfates, oxides, halides, etc. and the common P minerals are $Ca^3(PO_4)_2$, $FePO_4$, K_3PO_4, and $Mg^3(PO_4)_2$ (Vassilev et al., 2013). Organic C components in biochar can also bridge inorganic minerals through chemical bonds, and the formation of nanocrystalline minerals plays the role of a C scaffold during pyrolysis (Thy et al., 2013).

Specific surface area

Generally, when the surface area of biochar samples is measured by Brunauer Emmett Teller (BET), N_2 or CO_2 is selected as the single-layer physical adsorption gas, and the temperature of adsorption is selected as the existence temperature of liquid nitrogen (77 K). Many works have shown that the specific surface area of biochar is at least two orders of magnitude larger than that of soil samples, and generally, there is a considerable positive association among the specific surface area of biochar and pyrolysis temperature (Tsai et al., 2012; Meng et al., 2013). For some biochar samples, the correlation is not obvious when prepared at high pyrolysis temperature, which likely because of the destruction of microporous structure on the surface of biochar at high temperature and the formation of molten materials.

Porosity

The porosity of biochar refers to biochar particles that are not filled with solid (Brewer et al., 2014). The pores of biochar mainly consist of macropores and micropores. The macropores (> 2 nm) come from the material with vascular bundle structure. In contrast, the micropores come from the bubble bladder structure for instance residence time, pyrolysis temperature and rate, throughout the pyrolysis process (Downie et al., 2009). As there are all kinds of pores in biochar samples, so far, there is no technology that can accurately measure the average distance between pores.

Surface morphology

The morphology is a preliminary characterization of the size, shape, and structure of biochar samples. The morphology of biochar is usually only for the surface of biochar, which depends on biomass raw materials and pyrolysis temperature. Generally, the surface morphology of biochar is rarely like that of porous biochar.

Soil conditioners

Soil conditioners refer to the substances applied in soils to build up their physical, chemical, or biological properties. Such conditioners are mainly used to build up soil structure, to regulate soil pH, to improve soil water status, and to prevent soil nutrient loss (Lucas et al., 2014). The sources of soil conditioners are various. According to the main components, soil conditioners utilized in agriculture can be as follows: natural soil conditioners (Alghamdi et al., 2018) such as bentonite, natural gypsum, and montmorillonite powder; synthetic soil conditioners (Ai-Ping et al., 2011), e.g., polyacrylamide (PAM) and superabsorbent hydrogel (Pushpamalar et al., 2018); and by-products and wastes supplied in the process of industrial and agricultural production, such as phosphogypsum, alkali residue, and fly ash (Feng et al., 2017). Polymer technology has further provided a technic to coat P fertilizers with hydrophilic compounds (Hanafi et al., 2002) or to combine them with superabsorbents (Dergunov et al., 2009; Bortolin et al., 2012) to modify their utilization (Marcela et al., 2018). Superabsorbent hydrogels have also gained more attention as a kind of polymer with a three-dimensional (3D) cross-linked network with H-bonds, hydrophilic functional groups, and high-quantity aqueous solution retention that can enhance water holding capacity (WHC) following fertilizer retention capacity in soils (Seetapan et al., 2011) to govern the release of fertilizers (Ullah et al., 2015; Martin et al., 2019) used in agriculture (Puoci et al., 2008). Superabsorbent polyacrylamide hydrogel

(SPH) is also being applied in agriculture (Mikkelsen., 1994; Laftah & Hashim, 2011; Ghobashy et al., 2018) as a soil erosion inhibitor due to its high molecular weight (Charoenpanich, 2013), resulting in slow-release water and fertilizer, containing amine and carboxylic functional groups (Ghobashy et al., 2018). Moreover, PAM is capable of enhancing soil aggregation (Chao-Yin et al., 2012), water stability, infiltration (Sojka et al., 2003), and even decreasing P mobility (Jiang et al., 2010; Szogi et al., 2012). In this sense, anionic polyacrylamide (PAM)/superabsorbent polymer hydrogel (SPH) can provide applicable management to minimize soil runoff and erosion, and may inhibit the release of soil water and nutrients (Sojka et al., 2007). Application of divalent cations in the PAM/SPH solution or the soil surface can be a proper method to stabilize soil structure in an effective manner (Shainberg et al., 1990; Laird, 1997), owing to the linkage between negatively charged groups of PAM/SPH or soil surface, and positive charge of the cation. Likewise, gypsum can provide Ca^{+2} as a source to the soil surface that may be a cation bridging sorption PAM from particles of soil effectively (Laird, 1997), and resulting in adsorption of PAM/SPH in soils due to electrolytes of divalent cations between P (negatively charged) and PAM/SPH, and consequently, less P release and water pollution. Additionally, Favaretto et al. (2012) had indicated that gypsum application could be an appropriate management practice to decrease water pollution by P.

Conclusion

Global threats including climate change, land degradation, environmental contamination, and water shortages lead to economic, social and environmental damage. Biochar has the capability to serve as green environmental amendment and can improve soil fertility and sustainability in various ecosystems. Higher surface area coupled with higher charge density make it highly reactive to affect physical, chemical and biological properties of soil. Biochar application increases the biological activities of soil by creating favorable habitat for microorganisms in soil and save them from predators leading to increase in abundance and diversity microbial community. Biochar can also serve as soil conditioner that has potent ability to provide favorable niche for microbes to mineralize and solubilize both organic and inorganic P for higher plant uptake and productivity. However, quality and efficiency of biochar to affect soil health and plant growth varies greatly depending upon pyrolysis temperature, feedstock material, age of produced biochar at application. Future research should be planned to evaluate field efficiency and economic feasibility of biochar application under different agro-climatic conditions.

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