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Research Article

Citric acid acidification of wheat straw derived biochar for overcoming nutrient deficiency in alkaline calcareous soil (Case of Phosphorus)

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Keywords: Acidified wheat straw biochar; Phosphorus adsorption; Phosphorus availability; Low phosphorus soil; Sustainable agriculture

Abstract

Phosphorous fixation in soils is a serious concern worldwide, and biochar is gaining attention daily due to its potential benefits for improving the agronomic benefits of applied phosphorus. The present study aims to enhance understanding of the phosphorus transformation process in a deprived sandy soil following biochar amendments (no-acidified wheat straw biochar and chemically modified (acidification with 0.01 M $C_6H_8O_7$) along with or without phosphorus at 250 mg kg^{-1}. A 54-day pot experiment was conducted with two biochar levels of 4%, 8% (w/w), and control, and two phosphorus levels (without or with phosphorus). The results indicate that the integration of acidified wheat straw biochar with phosphorus resulted in increased available phosphorus in the soil. We conclude that incorporating acidified wheat straw biochar is a promising practice to potentially improve phosphorus availability in deprived soils. Further research is needed to explore site-specific phosphorus management for sustainable crop production.

Introduction

Phosphorus (P) is an irreplaceable element that has no substitute to sustain life on Earth [1]. Most importantly, it is obtained from limited phosphate rock resources [2]. In the soil, the available phosphorus of plants is relatively low because most of the phosphorus is usually combined with calcium (Ca) and magnesium (Mg) in calcareous soils, and combined with iron (Fe) and aluminum (Al) in acid soils, resulting in a decrease in the availability of phosphorus in this plant [3]. The fixed phosphorus in the soil is prone to runoff loss, leading to the eutrophication of freshwater bodies [4]. Therefore, under acidic and alkaline soil conditions, a large amount of phosphate fertilizer (> 90%) becomes unavailable, and the effectiveness of phosphorus in farmland systems becomes the primary limiting factor limiting phosphate fertilizer [5].

Exploring advanced phosphorus recycling technologies and management strategies is inevitable. These technologies and management strategies can provide phosphorus in the form available to plants and reduce the loss of available phosphorus to meet the increasing demand for phosphorus and food [6]. One option to promote phosphorus management in alkaline soils is to use biochar, a carbon-rich solid product at high temperatures, by exposing organic waste (such as wood chips, crop residues, or fertilizers) under anaerobic conditions [7]. Applying biochar to the soil can replace or partially reduce the use of inorganic phosphate fertilizers and may be one of the lowest costs, most efficient, and most sustainable methods to save P resources and prevent P pollution [8].

A recent Meta study with 108 pairwise comparisons of peer-reviewed studies on biochar effects on *p* availability in varying soils suggested that: P availability was increased by a factor of 5.1 and 2.4 in acidic (pH < 6.5) and neutral (pH 6.5 - 7.5) soils, respectively and no significant effect was observed in alkaline soils [7]. Thus, the biochar amendment effects on

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p availability are inconsistent and regulated by changes in soil chemical properties, specifically soil pH.

Recently, biochar feedstock/biochar modifications have been proposed to produce biochar with superior characteristics and improve its agronomic benefits [9]. However, chemical modifications using Citric Acid (CA) are not well studied. Therefore, improving our understanding of the potential effects of citric acid-modified biochar on *p* processes in soil and plant bioavailability in agricultural systems is mandatory.

The current study aimed to evaluate how biochar produced from wheat straw, and their chemical modification, treated with 0.01 N - Citric Acid and *p* application (control: no *p* application or yes, *p* applied at 250 mg kg^{-1} soil affect *p* availability under alkaline soil condition.

Materials and methods

Biochar production and properties

The wheat straw was collected from a wheat field at Ouargla (31°58′ N latitude; 5°20′ E longitude), Southern Algeria. Wheat straw was crushed into powder and dried to constant weight at 65 °C in a thermo-ventilated oven and then pyrolyzed in a muffle furnace at atmospheric pressure by applying 400 °C for 1^h 30 under limited oxygen conditions in a 250 - c. The detailed preparation process of acidified wheat straw biochar (AWSB) described above is shown in Figure 1. Before analysis, the resulting biochar materials were grounded and sieved through a 250 μm square-mesh sieve. pH and electrical conductivity (EC) were measured in distilled water at a 1:10 biochar to water mass ratio after shaking for 30 min according to ASTM D1762-84 2007 [10]. Biochar Organic Carbon Content (OC) was determined by the Walkley-Black method. The samples were digested in sulfuric acid to determine the total *p* in biochar. Later, the *p* concentration was measured by using a using spectrophotometer at 882 nm [11].

Experiment location, soil sampling and incubation study

A pot incubation experiment was carried out at the experimental station of the Scientific and Technical Research Center for Arid Areas (CRSTRA), Algeria. Before beginning the experiment, a preliminary survey, and field observation were performed using maps and previous research to get basic information on soil types in the study area based on calcareous contents and textural class. The top 0 – 30 cm composite soil samples were collected, belonging to one of the major soil types in the study area (southern Algeria) i.e., Calcid (Aridisol) located at 32°56′26″ N, 5°28′18″ E. Sub-samples were collected using a soil auger. One composite sample of each soil type was prepared by mixing the different soil sub-samples. The composited soil samples were air-dried, ground to pass through a 2 mm sieve, and transported to a laboratory for experimentation. The soil was sandy, neutral, calcareous ($CaCO_3$ ~ 15%) and poor in organic matter as well as in available P. The incubation experiments included ten treatments, and each treatment was carried out with 100 g portions of the air-dried soil packed uniformly in plastic cups. In eight treatments, each soil was amended with one of the biochars produced: acidified

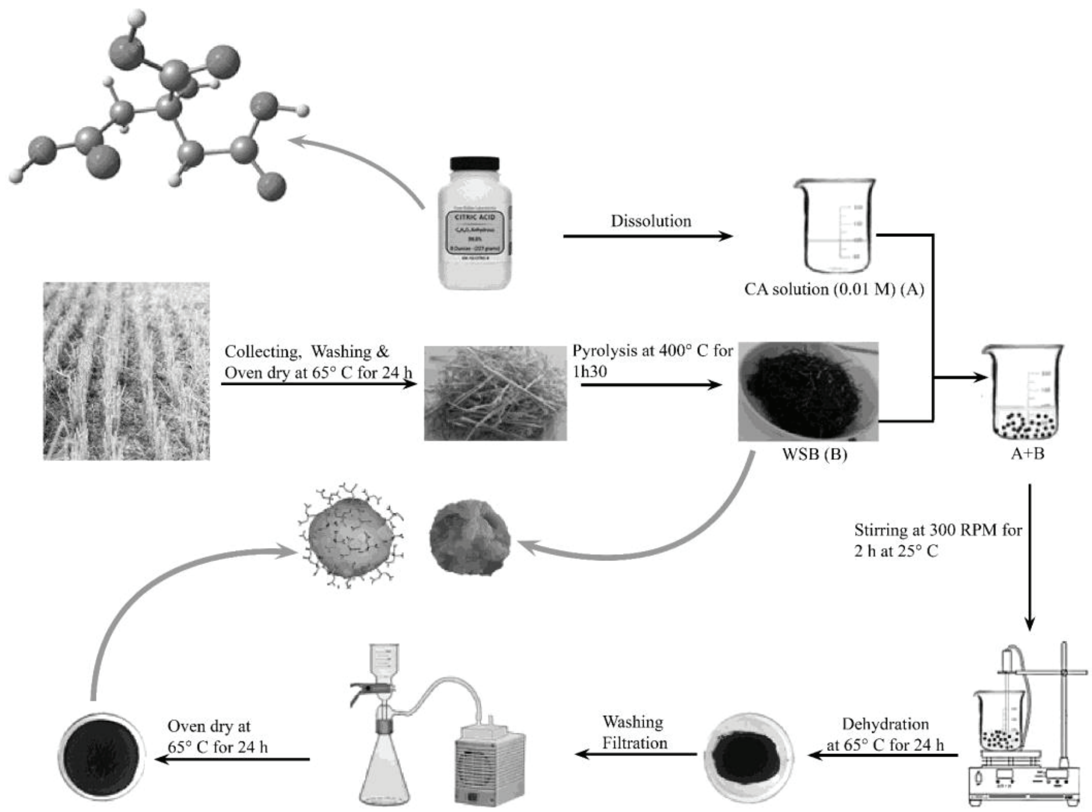

Figure 1: Scheme for the preparation of CA-modified biochar.

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or no-acidified biochar at rates of 4%, and 8 % (w/w) of initial soil in dry weight, with or without the addition of KH_2PO_4 at a *p* rate of 250 mg kg^{-1} soil. Two controls were included without biochar input, one with the unfertilized soil and the other with only KH_2PO_4 were included. The different treatments used were as follows (Table 1). In the experimentation, two replicates of each treatment were prepared, randomly placed, and incubated in the laboratory at an ambient temperature of 25 ± 2 °C and 80% soil moisture (v/w) for 9, 18, 27, 36, 45 and 54 days. At the end of each incubation period, samples (~20 g) were removed from each plastic cup and analyzed for available *p* (Olsen-P). Olsen - *p* was extracted with 0.5N $NaHCO_3$ [12] and concentration was measured by the colorimetric molybdate-ascorbic acid method [13].

Data analysis

Statistical analysis was performed using Statsoft Statistica Software, 10th Edition (Statsoft, Tulsa OK). Average and stranded deviation were calculated. In addition, Duncan's multiple range test, which combines means of similar values into ordered homogenous groups, was applied.

Result and Discussion

The wheat straw that was charred at 400 °C yielded alkaline biochar (pH = 8.9), rich in OC (55.4%), moderately low in available P (9 mg kg^{-1}), and total P (68.64 mg kg^{-1}). However, a higher EC value was found (26.12 dS m^{-1}), indicating the existence of water-soluble salts. In this experiment, the CA modification/ amelioration of biochar focused on enhancing P availability and its half-life in low-P soils. It is demonstrated that applying 4% – 8% biochar significantly increased both *p* availability in studied soil. All biochar treatments individually or combined with or without phosphorus input significantly increased the available *p* in studied sandy soil. When compared with the control, the content of available P in soil samples increased significantly ($p < 0.001$) after amendment with WSB compared with the controls without biochar amendment (Table 2). The addition of biochar alone without *p* amendment increases the availability of *p* in soil. Our results are similar to previous studies which indicated that adding biochar increases *p* availability even without adding *p* [14]. Numerous researchers have reported that adding biochar to calcareous soils may or may not increase the availability of *p* [15]. Other studies found that adding biochar to calcareous soil did not affect soil *p* availability [16]. In general, the role of biochar in nutrient availability in calcareous soils is not well understood [17].

In the current study, the amount of soil available *p* in AWSB1 and AWSB2 amended treatments is higher compared to the control (without biochar input) and even compared with WSB treatments (Figure 2). This could probably be attributed to the acidification of soil/biochar by citric acid which can compete strongly with P for adsorption sites by blocking phosphate sorption sites on soil, thereby reducing phosphate adsorption [18]. Many studies have found that organic acids limit P sorption due to site competition and metal complexation [19-21]. Organic acids have the potential to dissolve Ca-P and compete with phosphate for adsorption sites on soil particle surfaces, increasing the availability of P [22,23]. Furthermore, organic supplements increase biological and enzyme activity in the soil, increasing P availability via dissolved organic carbon [24]. The soil under study was extremely calcareous, and calcium-bound *p*, which is weakly associated with calcium (Ca), was the most abundant fraction in calcareous soils due to the high

Table 1: Treatment details used for the experimentation.

Treatment	Acronym
Control, no *p*	CK
Control	CK+P
Non-Acidified wheat straw biochar, 4%, no *p*	WSB1
Non-Acidified wheat straw biochar, 4%, 250 mg *p* k^{g-}1	WSB1+P
Non-Acidified wheat straw biochar, 8%, no *p*	WSB2
Non-Acidified wheat straw biochar, 8%, 250 mg *p* kg^{-1}	WSB2+P
Acidified wheat straw biochar, 4%, no *p*	AWSB1
Acidified wheat straw biochar, 4%, 250 mg *p* kg^{-1}	AWSB1+P
Acidified wheat straw biochar, 8%, no *p*	AWSB2
Acidified wheat straw biochar, 8%, 250 mg *p* kg^{-1}	AWSB2+P

Table 2: Evolution of soil available P of different treatments during the incubation time.

Treatments	Incubation times (days)					
	9	18	27	36	45	54
CK	2.22±0.62^{d}	23.11±3.47^{b}	19.035±4.43^{b}	10.40±5.44^{e}	7.06±0.06^{e}	8.18±0.31^{a}
CK+P	10.31±2.53^{d}	35.22±3.22^{f}	29.70±7.17^{b}	29.42±3.82^{d}	19.92±4.45^{a}	13.29±0.40^{a}
WSB1	42.12±4.06^{abc}	17.65±2.67^{ae}	52.52±5.52^{a}	40.88±5.03^{ad}	29.14±1.98^{c}	13.96±0.54^{b}
WSB2	71.89±1.89^{b}	61.54±1.18^{b}	73.33±3.91^{c}	52.44±3.13^{a}	45.94±4.83^{a}	44.09±1.11^{a}
WSB1+P	51.2±1.2^{bc}	47.07±1.74^{cd}	64.45±1.16^{f}	49.40±0.55^{c}	45.91±0.89^{d}	51.80±2.16^{de}
WSB2+P	74.15±4.15^{ac}	73.85±1.67^{de}	87.45±3.27^{ad}	69.29±2.38^{b}	64.05±2.45^{b}	99.25±0.98^{bc}
AWSB1	54.02±4.02^{a}	65.63±1.27^{a}	68.49±2.22^{de}	40.13±1.68^{bc}	57.00±1.62^{d}	38.36±6.18^{e}
AWSB2	70.06±0.06^{abc}	54.09±2.22^{c}	104.62±1.42^{ac}	70.76±0.03^{ab}	76.07±3.71^{b}	60.38±1.45^{cd}
AWSB1+P	74.44±4.44^{e}	70.91±1.27^{g}	83.33±5.33^{g}	60.64±5.35^{g}	74.69±3.49^{f}	65.67±1.14^{f}
AWSB2+P	102.24±2.24^{a}	97.29±0.27^{a}	126.56±3.63^{e}	84.53±0.55^{c}	89.24±2.80^{c}	88.16±7.27^{g}
F-values and level of significance for treatments						
Incubation times	33.141***					
Treatments	206.341***					
Incubation Times × Treatments	5.232***					

Values represent mean of two replicates ± SD. Values followed by different letters are significantly differences among each other as determined by the DMR test ($P < 0.05$).
***Stands significant at $P < 0.001$.

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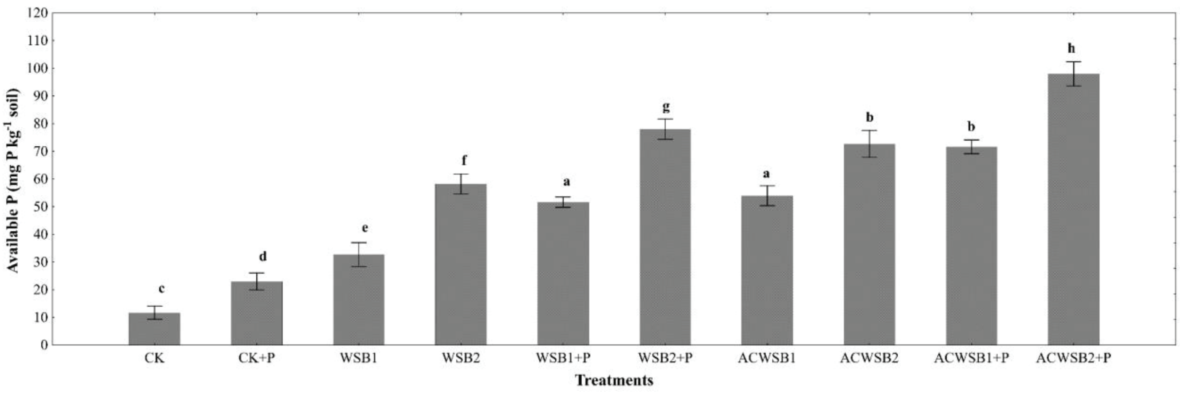

Figure 2: Effect of wheat straw biochar acidification (yes/no) and phosphorous application (no application or 250 mg *pkg*$^{-1}$ soil) on *p* availability under alkaline condition. Bars represent means ± S.E and values followed by different letters are significantly differences among each other as determined by the Duncan's test (*P* < 0.05).

Ca^{2+} content, thus reducing *p* availability [25-27]. The low pH of the soil plays a vital role in the dissolution of immobilized soil *p* [28]. The addition of organic acids to the soil caused an immediate pH drop and the extent of pH decrease depended on both soil type and organic compound [23]. Organic supplements reduce Ca-P by dropping soil pH caused by organic acids [29], indicating the importance of organic amendments in enhancing P availability and its plant uptake. According to [30], decreasing soil pH (6.5) will increase the mobility of fixed soil *p*. In the case of low soil pH, the activity of H^+ will decompose the bond of calcium and phosphorus in the calcareous soil. Breaking the bond between calcium and phosphorus leads to the dissolution and availability of phosphorus in the soil [31]. In addition, *p* is also part of the biochar structure [32]. As observed in the AWSB of this study, lowering the pH of biochar also increases the release of phosphorus from the biochar into the soil solution [33]. Biochar improves *p* availability in calcareous soils mainly due to changes in soil microbial community [6,34]. Indirect application of biochar can also promote the secretion of phosphomonoesterase by soil microorganisms, thereby enhancing the mineralization of soil [6]. According to [35], applying biochar can increase the cation exchange capacity (CEC) of the soil by 20%. The CEC is an indirect measure that can increase nutrient retention rate by reducing its leaching loss. The modification of various biosorbents (such as biochar) by citric acid may change its quality by introducing additional carboxyl groups on its surface [36], thereby increasing the availability of soil and nutrients availability [37].

Conclusion

Results of the incubation experiment showed that the acidification of biochar exerted a positive effect by enhancing the availability of soil *p*. A greater Olsen's *p* availability was obtained with acidified biochars instead of non-acidified ones. The capacity for a reduction in *p* adsorption and increase in *p* availability appears to follow the order of AWSB treatments > WSB treatments > control treatments. This indicates that treating biochar with an acidifying agent such as citric acid is effective enough to reduce the rate of orthophosphate conversion to an unavailable form. However, field experiments must further confirm these findings over the long term, considering the possible adverse effects of biochar application at high rates.

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