



Contents lists available at ScienceDirect

Chemosphere

journal homepage: [www.elsevier.com/locate/chemosphere](http://www.elsevier.com/locate/chemosphere)

## Effects of environmental conditions on the release of phosphorus from biochar

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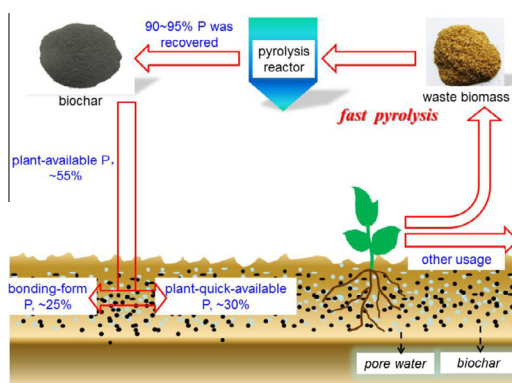
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### HIGHLIGHTS

- A novel method to mitigate the P depletion crisis by reuse of biochar was proposed.
- The environmental factors influencing the P release were investigated in detail.
- The mechanism of the release of different P species from biochar was provided.

### GRAPHICAL ABSTRACT

The biochar-water system was adopted as a model to investigate the effect of environmental factors (e.g., P species, retention time, coexisting anions, and nutrient salts) on P release. The results revealed that about 55 wt.% P could be released in 3–4 d, and the P release rate could be controlled by adjusting the environmental factors. The coexisting anions can enhance the P release due to the effect of ion exchange competition. The introduction of Hoagland nutrient solution led to the decrease in the release of P for the formation of precipitates between dissolved P and excessive  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ .



### ARTICLE INFO

#### Article history:

Received 24 April 2013

Received in revised form 11 July 2013

Accepted 17 July 2013

Available online xxx

#### Keywords:

Biochar  
Phosphorus release  
Kinetics  
P species  
Hoagland nutrient

### ABSTRACT

Biochar, the byproduct from fast pyrolysis of waste biomass, is widely used as a soil conditioner. The phosphorus in biochar is not only a P source for plant growth, but also an important factor caused the eutrophication of water. Here, the effects of environmental conditions on the release of different P species from biochar in a biochar-water system were investigated. About  $2.2 \text{ mg g}^{-1}$  P in the form of inorganic orthophosphate and pyrophosphate was released from a raw biochar (contained  $4.7 \text{ mg P g}^{-1}$ ) at initial pH of 9.0 in the initial 8 h. The release of orthophosphate was significantly enhanced from  $0.64$  to  $1.35 \text{ mg g}^{-1}$  by the coexisting anions of  $\text{Cl}^-$ ,  $\text{NO}_3^-$  or  $\text{SO}_4^{2-}$  due to the effect of ion exchange competition, while the release of pyrophosphate ( $\text{P}_2\text{O}_7^{4-}$ ) was not influenced by the introduction of anions which might be attributed to the formation of stable complexes. The introduction of Hoagland nutrient solution led to the decrease in release of P due to the formation of precipitates between dissolved P and excessive  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ .

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### 1. Introduction

Large quantities of crop residues, such as rice husk, cornstalk, and straw, often disrupt the next year's crop, and their treatment

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and disposal are still a thorny issue. Burning of crop residues is a prevalent method in the world. However, the burning of residues may generate the problems of air pollution, impairment of human health, emissions of green house gases, serious fine dust problems, and even the change of circulation and monsoon patterns (Gustafsson et al., 2009; Haefele et al., 2011). Instead of burning residues directly in field, processing crop residues in fast pyrolysis systems to produce biofuels and biochar is an effective strategy for both energy production and disposal of crop residues (Williams and Nugranad, 2000; Liu et al., 2011; Zeng et al., 2011; Zhang et al., 2013).

Biochar is recognized as a promising material for soil remediation and it has not been utilized sufficiently up to now (Bridgwater and Peacocke, 2000; Laird, 2008; Mohammad et al., 2013). The physical structure, e.g., porous and high surface area, of biochar is beneficial to increasing air (oxygen) content, enhancing water storage capacity and improving living condition of microorganisms in soil (Lehmann et al., 2006; Atkinson et al., 2010). The inorganic compounds, e.g., the compounds of N, P, K and Ca, in biochar could provide nutrient elements to the plants (Tan and Lagerkvist, 2011).

Various large-scale fast pyrolysis apparatuses have been established by industries, such as Red Arrow Products Co. (50 t d<sup>-1</sup>), Wisconsin, USA, BTG Co. (50 t d<sup>-1</sup>), and The Netherlands. The massive produced biochar usually contains 0.2–0.8% of P. Compared with other elements, P in biochar has received more concerns. On the one hand, P is a non-renewable resource and irreplaceable in crop growth and development (Seyhan, 2009), and the reserves of phosphorus-rock will become depleted in 30–100 years with the severe loss of P in agricultural fields and the very slow recycle rate of P by natural force (Weikard and Seyhan, 2009). P in biochar can be a potential P source to mitigate the coming “P crisis (depletion)”. On the other hand, the leakage of P would bring about serious eutrophication of water body. Thus, methods of reusing and recovering P deserve more investigations than before (Cordell et al., 2009). However, most studies on biochar used as a soil conditioner are just focused on its function as a P retention or increasing the amount of bio-available P in soil after fertilizing (Chan et al., 2008; Laird et al., 2010). Precious few literatures reported that biochar itself may be a potential P source (Silber et al., 2010; Cao and Harris, 2010). The release of different species of P from biochar under different environmental conditions is still unclear up to now.

A full understanding of P migration from biochar to soil porewaters is a necessary step for fully utilization of P in biochar and decrease of P leakage. Thus, more studies need to be conducted to understand the characteristics of P species in biochar, the kinetics of P release in soil porewaters, and the effects of porewater environment on P release. The main objective of this work is to investigate the mechanism of the release of different P species in biochar under various environmental conditions (retention time, coexisting anions, and nutrient elements) in a biochar-water system. To this end, we chose a rice husk biochar as a model to explore: (1) the P release kinetics of biochar in water; (2) the effects of coexisting anions and nutrients on P release; (3) the effect of P species on P release; and (4) the mechanism of transformation and translocation of P in biomass-biochar-porewater system.

## 2. Materials and methods

### 2.1. Preparation of biochar

The biochar produced from Anhui Yineng Bio-Energy Co., China, was obtained from pyrolysis of rice husks at 723–823 K for 1–2 s. The yields of bio-oil, biochar, and gas are about 50, 35, and

15 wt%, respectively. The biochar samples were grounded to pass a 120-mesh (125 μm) sieve, then stored under ambient conditions for the subsequent experiments.

### 2.2. General properties of biochar

Specific surface area of biochar was determined by nitrogen adsorption–desorption isotherms, obtained at 77 K by a Micromeritics Gemini apparatus (ASAP 2020M+C, Micromeritics, Co., USA). The pH of point of zero charge (pH<sub>pzc</sub>) for biochar was determined following the method described by Dastgheib et al. (2004). Proximate analysis was conducted according to the American Society for Testing and Materials (ASTM) D1762-84. Ultimate analysis was determined on an elemental analyzer (VARIO EL III, Elementar Inc., Germany). The chemical compositions of biochar were determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES, Optima 7300 DV, Perkin Elmer Co., USA). The biochar samples were prepared in KBr (1 wt%) and pressed into pellets, and characterized using Fourier transform infrared spectroscopy (FTIR, EQUINOX55 IR spectroscopy, Bruker, Germany). Spectra were collected in transmittance, in a range of 400–4000 cm<sup>-1</sup> at resolution of 4 cm<sup>-1</sup> and 16 scans.

### 2.3. Analysis of <sup>31</sup>P-NMR samples

Two samples extracted with H<sub>2</sub>O and EDTA–NaOH were prepared for <sup>31</sup>P-NMR analysis. 5 g of biochar and 100 mL of water or 0.25 M NaOH/0.05 M EDTA solution was mixed and shaken for 16 h at 298 ± 3 K. The mixture was centrifuged at 4000 rpm for 30 min, and the supernatant was collected and lyophilized for 3 d. The lyophilized samples were then re-dissolved in D<sub>2</sub>O and 1 M NaOH for <sup>31</sup>P-NMR analysis (Turner et al., 2003). Solution <sup>31</sup>P NMR spectra were obtained using a Bruker AVANCE AV III 400 MHz spectrometer operating at 162 MHz and 297 K. Spectra were recorded using a 30° pulse width, a total acquisition time of 1.5 s and broadband proton decoupling. 1024 scans were collected to obtain acceptable signals. Chemical shifts were measured relative to an external standard of 85% H<sub>3</sub>PO<sub>4</sub>. The NMR spectra were analyzed by NMR software (MestReNova v 6.1.1–5475).

### 2.4. Determination of orthophosphate and total phosphorus

The orthophosphate concentration was determined by the molybdate-ascorbic acid method. The samples for total P determination were digested with potassium persulfate at 393 K for 30 min, to convert both the polyphosphate and the organic phosphate to orthophosphate. Then, the digested samples were determined using the molybdate ascorbic acid method. The P content in biochar was determined by the molybdate-ascorbic acid method after digesting the sample in concentrated H<sub>2</sub>SO<sub>4</sub>/HClO<sub>4</sub> at 473 K for 1 h.

### 2.5. Kinetic analysis

1.0 g of biochar and 100 mL of water were added into each Erlenmeyer flask, the flasks were then shaken at 180 rpm, 298 ± 3 K on a reciprocating shaker. The samples were withdrawn at appropriate time intervals. The mixture was filtered with a 0.45 μm membrane immediately. The concentration of orthophosphate and total P of the filtrate was then determined. The P release amount of biochar  $q$  (mg g<sup>-1</sup>) was calculated from the following equation:

$$q = \frac{C_i V}{m_b} \quad (1)$$

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