**Recovery of phosphate from aqueous solution by magnesium oxide decorated magnetic
biochar and its potential as phosphate-based fertilizer substitute**

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Abstract

The present study deals with the preparation of a novel MgO-impregnated magnetic biochar (MMSB) for phosphate recovery from aqueous solution. The MMSB was evaluated against sugarcane harvest residue biochar (SB) and magnetic biochar without Mg (MSB). The results showed that increasing Mg content in MMSB greatly improved the phosphate adsorption compared to SB and MSB, with 20% Mg-impregnated MMSB (20MMSB) recovering more than 99.5% phosphate from aqueous solution. Phosphate adsorption capacity of 20MMSB was 121.25 mg P/g at pH 4 and only 37.53% of recovered phosphate was desorbed by 0.01 mol/L HCl solutions. XRD and FTIR analysis showed that phosphate sorption mechanisms involved predominately with surface electrostatic attraction and precipitation with impregnated MgO and surface inner-sphere complexation with Fe oxide. The 20MMSB exhibited both maximum phosphate sorption and strong magnetic separation ability. Overall, phosphate-loaded 20MMSB significantly enhanced plant growth and could be used as a potential substitute for phosphate-based fertilizer.

Keywords : Phosphate; adsorption; MgO-impregnation, magnetic, biochar; fertilizer

1. Introduction

Phosphate is an essential nutrient that is known to be primarily responsible for eutrophication, because excessive utilization of phosphate resources for chemical fertilizer production and widespread runoff from agricultural applications have increased the phosphate levels in surface waterbodies. This has become major problematic issue around the world especially in United State and China (Conley et al., 2009; Pei et al., 2015). As low as 0.02 mg/L phosphate would lead to uncontrolled growth of algae, which causes the reduced water oxygen content and the production of toxins particularly in shallow lakes, estuarine and coastal marine regions, leading to fish kills and harm to wildlife (Conley et al., 2009; Pei et al., 2015). On the other hand, while being the most important incentive element of the problem, phosphorus (P) reserves in nature are limited. Phosphorous reserves are expected to run out quickly with the ever-increasing application of phosphate-based fertilizers for agronomic production (Gilbert, 2009). Therefore, it is crucial to develop ecofriendly technologies to prevent eutrophication and simultaneously manage the phosphorus shortage crisis; reclaiming phosphorus from phosphate-enriched aqueous medium has been recognized as a key strategy (Desmidt et al., 2015). Among available conventional technologies for phosphorus recovery from the aqueous medium, adsorption has believed to be one of the most effective methods, owing to its high selectivity, easy operation and cost-effectiveness (Loganathan et al., 2014). However, the problems associated with the high cost, low renewability, difficult disposal after use hinder the wide application of traditional adsorbents (activated carbon and anion exchange resins) especially in developing countries (Nguyen et al., 2014). In addition, available literature in this field has focused primarily on phosphate recovery from sewage sludge or sludge ash, e.g. via dissolution and precipitation methods with the formation of struvite (He et al., 2013; Ye et al., 2014). Today,

great attention has paid to the development of new potential low-cost adsorbents from agricultural wastes, microbial biomass, industrial by-products, natural minerals and engineering particles for phosphate recovery (Huang et al., 2015; Nguyen et al., 2014; Loganathan et al., 2014; Xie et al., 2015; Ye et al., 2015; Jung and Ahn, 2016; Takaya et al., 2016). Although several earlier studies reported the potential uses of montmorillonite (Chang et al., 2016), iron oxides (Giménez et al., 2007), zeolite (Jiang et al., 2013), pumice (Karimaian et al., 2013), coir pith (Krishnan and Haridas, 2008) and red mud (Ye et al., 2015) for phosphate recovery, these adsorbents worked only for wastewater treatment under certain environmental conditions and required huge quantities (Jung and Ahn, 2016; Nguyen et al., 2014), which made them not cost-effective.

Recently, biochar has been used as a potential adsorbent for pollutant remediation due to its various beneficial properties like low cost, environment friendly, excellent stability, high porosity, easy preparation and operation (Tan et al., 2015; Jeong et al., 2012; 2016). As a result, research has focused on the application of biochar for the phosphate recovery (Yao et al., 2013) and reduction of greenhouse gases emission, while improving soil physical and chemical properties, and increasing soil fertility (Ahmad et al., 2014). However, biochar with predominantly net negatively-charged surface has made it exhibit only limited ability to absorb anionic pollutants (Chen et al., 2011). On the other hand, it is known that some metal elements (Al, Fe, etc) in biomass-based adsorbents play an important role in the adsorption of anionic pollutants (Loganathan et al., 2014), although the metal outflow in biomass tissue is a major limitation. Consequently, some novel biomass based biochar impregnated with AlCl_3 , MgCl_2 , LaCl_3 , or FeCl_3 salts have been prepared with the aim to improve its adsorption capacity for negative ions (Arcibar-Orozco et al., 2012; Yao et al., 2013; Zhang and Gao, 2013; Wang et

al., 2015). Thus, it is logical to produce an intended metal oxide functionalized biochar for efficient anionic pollutants recovery (Arcibar-Orozco et al., 2012; Chen et al., 2011; Zhang and Gao, 2013). However, powder carbon based adsorbents, including powdered active carbon, graphene, carbon nanotubes and biochar, are difficult to be separated from the aqueous solution after use (Chen et al., 2011). While the addition of magnetic iron oxide into these adsorbents through chemical co-precipitation or post grafting methods could recover the used adsorbents by magnetic separation (Arcibar-Orozco et al., 2012), the manufacturing process of these kinds of magnetic adsorbents is complicated because many sequential steps are involved including precursor material preparation, activated carbon oxidation, and iron grafting (Liu et al., 2013). In addition, the traditional magnetic medium grafting process increases the cost of the adsorbent (Chen et al., 2011). Since the effectiveness of the anionic pollutant adsorption is closely related to the amount of functional sites loaded, dispersion, affinity and surface accessibility of the activated sites within the adsorbent matrix (Arcibar-Orozco et al., 2012; Liu et al., 2013), the preparation of carbon based adsorbent with higher pollutant adsorption affinity through simple and low cost procedures needs to be explored (Chen et al., 2011; Liu et al., 2013).

The aim of this investigation was to develop an Mg-contained magnetic biochar (MMSB) for the recovery of phosphate from aqueous solution and evaluate its application as phosphatic fertilizer. For this purpose, locally available harvest trash biomass of sugarcane was pyrolyzed at 550°C after being impregnated with ferrous chloride and magnesium chloride salt solution. The performance and adsorption mechanism for phosphate recovery from water solution, and subsequently the efficiency of phosphate-sorbed biochar as a phosphatic fertilizer were examined.

2. Materials and methods

2.1. Materials collection and biochar preparation

The sugarcane harvest residue (SHR) biomass used in this study was collected from Louisiana State University AgCenter Sugar Research Station at St. Galniel (LA, USA) and was cut into <5 cm small pieces and sequentially washed by deionized water (DW) (18.2 MΩ) to minimize the presence of dust followed by oven drying at 55°C for overnight. The dry residue biomass was crushed by a high-speed rotary cutting mill, passed through a screen smaller than 0.12 mm and used for biochar preparation. Ferrous chloride, magnesium chloride, sodium phosphate monobasic monohydrate, sodium hydroxide, nitric acid, sulfuric acid, and hydrogen peroxide of analytical grade were purchased from Fisher Scientific (Pittsburgh, PA, USA). All chemical solutions were prepared using DW.

The MMSB was prepared following an impregnation and pyrolysis combined procedure. Briefly, 50 grams of SHR were first added to a flask containing 500 mL ferrous chloride solution to soak the material. After 6 h shaking at room temperature, the mixture was transferred into an oven at 80°C until the supernatant vanished and then dried at 120 °C for 3 h. The 500 mL of magnesium chloride solution in desired concentrations were added and shaken in a constant temperature oscillator at 120 rpm for 6 h. After that, the mixtures were heated at 80°C until the supernatant vanished, and finally once again dried at 105°C for 3 h. Before biochar preparation, each dried mixture was transferred into a porcelain crucible and placed in a muffle furnace under N₂ flow of 400 mL/min for 30 min to remove air from the system. After that, the mixture in the muffle furnace was heated with temperature rate of 10°C/min and maintained the temperature at 550 °C for 1 h under N₂ flow of 200 mL/min (Jeong et al., 2016). The resulting biochar products were gently crushed and passed through < 0.12 mm nylon sieve, washed and oven dried at 105 °C for 6 h before characterization. Biochars with and without magnesium salt addition were

made respectively. For convenience, SB were used to label the biochar without Mg and Fe, MSB were used to assign the magnetic biochar, and x MMSB were used to express Mg contained magnetic biochar with x representing the Mg content in percent.

2.2. Sample characterizations

Infrared spectra of biochar samples were observed using a Nicolet iS50 Fourier transform infrared spectrometer (FTIR) (USA). XPS (X-ray photoelectron spectroscopy) was performed on a Kratos AXIS Ultra DLD spectrophotometer with an Al K X-ray source (1486.6 eV of photons) (Japan). The contents of C, H and N in the samples were characterized using an elemental analyzer (Elementar Analysen systeme GmbH, Germany). The Mg and Fe content in biochar samples were measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES, SPECTRO Plasma 3200, Germany) after samples being digested with concentrated sulfuric acid and hydrogen peroxide. The magnetization curve of the product was obtained using a PPMS-9T vibrating sample magnetometer (VSM) (Quantum Design, USA) with an applied field between -15,000 and 15,000 Oe at 298K. Pore and surface characteristics of samples were measured by N₂ adsorption at 77 K using a V-Sorb 2800P analyzer (App-one, China). The BET surface area (S_{BET}) and average pore radius (APR) were evaluated by multipoint BET analysis of adsorption data points with relative pressures of 0.05-0.3 by BJH method. The total pore volume (TPV) was estimated from a single N₂ adsorbed point at a relative pressure of about 0.99. The microscopic features and morphology of the samples were characterized using a field emission gun scanning electron microscopy (FEG-SEM, JEOL 6335F, Japan) equipped with an energy-dispersive X-ray (EDX) spectroscopy and a transmission electron microscopy (JEOL 200CX TEM, Japan). X-ray diffraction (XRD) analysis was also carried out to identify any crystallographic structure in the

1 samples using a computer-controlled X-ray diffraction meter (Philips Electronic Instruments,
2 Mahwah, NJ, USA).

3 *2.3. Batch adsorption tests*

4 Batch experiments were conducted to examine the adsorption efficiency of SB, MSB and
5 MMSB for the recovery of phosphate from aqueous solutions. Adsorption experiments were
6 designed to investigate phosphate adsorption as a function of Mg content and aqueous pH, as
7 well as desorption study and organic pollutant adsorption evaluation. In a typical experiment,
8 0.05 g of adsorbent was added to a polyethylene centrifuge tube containing 20 mL of 50 mg/L
9 solution diluted from a 1000 mg/L phosphate stock solution. The pH of the solution was adjusted
10 between 3.0 and 10.9 using 0.1 mol/L HNO₃ and NaOH before the centrifuge tubes were placed
11 in a shaker operating at 120 rpm and 23.0±0.2 °C. All the experiments were performed in
12 triplicate. After overnight mixing, sample was filtrated through a 0.22 µm GE cellulose nylon
13 membrane filter. Concentration of phosphate in the filtrate was analyzed using a Thermo
14 Scientific EVO 60 spectrophotometer (USA) at wave length of 880 nm as recommended by the
15 EPA. The adsorption capacity (q_e , mg/g) of the sorbent material for P was calculated by mass
16 balance as expressed in Equation (1).

$$17 \quad q_e = V(C_i - C_e)/m \quad (1)$$

18 where C_i and C_e are the initial and equilibrium concentration of phosphate in solution (mg/L),
19 respectively; V is the volume of solution (L) and m is the sorbent mass (g).

20 *2.4. Sorption isotherms*

21 Our previous experiment showed that SB and MSB had very limited phosphate ability, while the
22 MMSB, especially 20 MMSB has excellent phosphate ability. Hence, in the phosphate
23 adsorption isotherm study, 20 MMSB was selected as adsorbent. Adsorption capacities of 20

MMSB for phosphate were examined at pH 4 with phosphorus concentration varied from 5 to 500 mg/L at 23.0 ± 0.2 °C as the procedures described in the batch experiment. Two isotherm models were used to simulate the experimental data and the governing equations can be written as:

$$\text{Langmuir model, } q_e = KQC_e/(1+KC_e) \quad (2)$$

$$\text{Freundlich model, } q_e = K_f C_e^n \quad (3)$$

where K and K_f represent the Langmuir bonding term related to interaction energies (L/mg) and the Freundlich affinity coefficient ($\text{mg}^{(1-n)}\text{L}^n/\text{g}$), respectively; Q denotes the Langmuir maximum capacity (mg/g); C_e is the equilibrium solution concentration (mg/L) of the sorbate and n is the Freundlich linearity constant.

2.5. Desorption study

For the desorption study, 0.10 g adsorbent was added into a 50 mL centrifuge tube with 40 mL solution (50 mg/L phosphorus), and the mixture was properly shaken on a shaker at 120 rpm for overnight. After adsorption, the phosphate-loaded adsorbent was separated from the solution through centrifuge and the supernatant analyzed for phosphate using spectrophotometric procedure described as above. For desorption, the phosphate-loaded adsorbent was added with 10 mL of desorption reagent and shaken for 4 h, the supernatant was separated and again detected to calculate the desorption amount. The desorption rate was calculated by dividing desorption amount with adsorbed amount.

2.6. Pot experiments

The soil samples were collected from the campus of Northwest A&F University with sampling depth of 0~20 cm. The soil samples were air dried in laboratory and grounded to pass through 2 mm nylon sieve after discarding the plant residues. The physico-chemical properties of

the soil samples were: pH 8.66, 45.22% clay particle (<0.01 mm), 1.12 g/kg organic matter, 265 $\mu\text{S}/\text{cm}$ electrical conductivity, 1.05 g/kg total nitrogen, 2.38 mg/kg $\text{NH}_4^+\text{-N}$, 5.62 mg/kg $\text{NO}_3\text{-N}$, 11.6 mg/kg Olsen-P and 173.6 mg/kg available K. Pot experiments were conducted based on a procedure previously described by Li et al. (2015). In doing so, pots (height 12 cm, bottom 7 cm and mouth 10 cm) were washed using DW before experiment. The SB and phosphate-loaded 20MMSB samples were added into the soil at 1% wt application rates, respectively. In case of control treatment, only soil was added in the pot. Pots containing 200 g treatment soil and control were incubated for 7 days at $\sim 60\%$ field capacity. Then ten seeds of *ryegrass* were planted per pot and growth experiment was carried out in a greenhouse with controlled temperature (18~20 $^{\circ}\text{C}$) and humidity (55~60%). After 21 days, plant heights of ryegrass seedlings were recorded and harvested. The aboveground dry biomass weights were determined following oven drying at 55 $^{\circ}\text{C}$ for 24 h.

3. Results and discussion

3.1. Characterization of adsorbents

Elemental composition and textural properties of the prepared samples are given in Table 1. The carbon content decreased from 66.28% to 26.23% with Mg content increasing from 0.44% to 21.07%, indicating that there was a blend of carbon and magnesium in the sample. The BET surface area analysis revealed the S_{BET} of SB and MSB were 24.59 m^2/g and 92.54 m^2/g , respectively. The increasing S_{BET} was attributed to the impregnating of sugarcane residue biomass powder by iron and magnesium salts solution before pyrolysis. For the salts like FeCl_3 , ZnCl_2 and MgCl_2 were often used as carbon activating agents in order to produce more pores and higher surface area (Liu et al., 2013). After the magnesium introduction, the S_{BET} of MMSB decreased from 118.03 m^2/g to 27.22 m^2/g with the Mg content increasing from 2.12% to 20.47%

1 in MMSB. With the increasing Mg content, the *TPV* of the samples increased from 0.038 cm³/g
2 to 0.343 cm³/g and *APR* increased from 1.78 nm to 4.32 nm proved these reasons. This could be
3 explained by the fact that with the metal salt content continuously increasing, some larger pore
4 was probably produced or the surface of the biochar was possibly covered by the metal oxides
5 formation during the salts dehydration process (Yao et al., 2013), resulted S_{BET} decrease.

6 The magnetization properties of the samples were tested by determining the magnetization
7 response at room temperature, and the results are shown in Fig. 1. A magnet, with the saturated
8 magnetization of MSB and 20MMSB was determined to be 42.86 emu/g and 35.35 emu/g,
9 respectively. MSB and 20MMSB can easily attracted by a magnet, while SB had no magnetic
10 response at all. Even after immersing in water for 5 months, the MSB and 20MMSB could still
11 be effectively recollected by a magnet (see Fig. S1 of SI), confirming the excellent magnetic
12 abilities of MSB and 20MMSB in aqueous solution. To determine whether there is any
13 dissolution of Fe or Mg from the MSB and 20MMSB during adsorption process, 0.05g samples
14 of respective MSB and 20MMSB were immersed in 20 mL DW with pH 3.0 and 11.0 for 24 h,
15 respectively. Analysis of the supernatant showed that Fe and Mg were strongly bound in the
16 biochar matrix with undetectable dissolution of Fe or Mg in the supernatant (data not shown),
17 indicating excellent stability of MSB and 20MMSB samples in acid and alkali solution.
18 Therefore, it is possible to apply magnetic separation technique to separate powdered magnetic
19 Mg-contained biochar after actual use.

20 The surface morphological features of SB, MSB and 20 MMSB were characterized by SEM
21 and EDX analysis. In general, the particles of SB showed smooth surface and sharp edges and
22 corners, while the surfaces of MSB and 20 MMSB particles were very coarse and some metal
23 oxides covered in the surface homogeneously (see Fig. S2a-c of SI). Further, the 20 MMSB

showed extremely high EDX peaks for carbon, oxygen, magnesium and iron, all of which are typical elemental composition of the salts used in impregnating SHR (Fig. S2d of SI). Silicon, a common element within sugarcane residue, was also found in EDX pattern of 20 MMSB sample. On the other hand, the TEM images clearly revealed that Fe_3O_4 particles in size around 12-40 nm were embedded into the carbon matrix of MSB sample while additional MgO and $\text{Mg}(\text{OH})_2$ crystals were grown to cover the surface of 20 MMSB sample, which were confirmed by XRD analysis (see Fig. S3a-d of SI).

The formation of the iron and magnesium oxides could be explained by the fact that during the pyrolysis process at 550°C , the metal-preloaded sugarcane residue powder was thermally decomposed and biomass turned into solid carbonaceous particles. The produced volatile components are swept out by the N_2 gas continuous supply, while the ferric and magnesium salts might undergo a drastic dehydration process. The specific formation of Fe_3O_4 was likely through the reaction sequence of $\text{FeCl}_3 \rightarrow \text{Fe}(\text{OH})_3 \rightarrow \text{FeO}(\text{OH}) \rightarrow 2\text{Fe}_3\text{O}_4$ with gases HCl , H_2O , and CO_2 released from the respective reactions. On the other hand, MgO and $\text{Mg}(\text{OH})_2$ were formed through the steps of $\text{MgCl}_2 \rightarrow \text{Mg}(\text{OH})_2 \rightarrow \text{MgO}$ with gas forms of HCl and H_2O produced and released. Similar results were also observed during carbonizing the ferric chloride soaked sawdust (Liu et al., 2013), ferric and ferrous chloride impregnated orange peel powder (Chen et al., 2011) and MgCl_2 preloaded sawdust (Liu et al., 2013).

3.2. *Effect of Mg content and solution pH on phosphate adsorption*

The effect of MgO impregnation on the phosphate adsorption of magnetic biochar was affected by Mg content (see Fig. S4 of SI). While the SB exhibited very low phosphate adsorption capacity (<0.05 mg P/g) due to its negative charged surface, the MSB with the introduction of Fe_3O_4 MSB improved the phosphate adsorption capacity to 2.47 mg P/g. This

increased adsorption capacity of MSB was greater than that of the magnetic biochar made from orange peel (Chen et al., 2011) as well as that of a cotton stalk biochar loaded with ferric oxide particles (Ren et al., 2015), indicating the characteristic advantage of the SHR biomass. On the other hand, after further inoculation of Mg oxides into the MSB with increasing Mg content, MMSB showed continued increase in the sorption ability with the highest phosphate sorption at more than 19.92 mg P/g observed in the 20MMSB (Fig. S3 of SI). This result was in agreement with that of MgO-biochar composites derived from Mg-accumulated tomato tissues, which also had strong affinity for aqueous phosphate (Yao et al., 2013). Nonetheless, our study clearly indicated that magnetic biochar with greater Mg content removed higher percent of phosphate from the solution. For this reason, 20MMSB samples were selected for subsequent evaluation.

The effect of solution pH on the sorption of phosphate to 20MMSB is displayed in Fig. 2. Phosphate adsorption amount gradually decreased from 19.9 mg/g to 4.7 mg/g with pH varied from 3.0 to 10.9, respectively. Several authors already reported that lower pH value favors the phosphate adsorption onto many types of metal oxides-containing adsorbents (Krishnan and Haridas 2008; Xie et al., 2015; Ye et al., 2015). Such negative impact of pH on phosphate adsorption could be well interpreted in terms of phosphate species distribution and surface property of the adsorbent (Nguyen et al., 2014). In our experimental condition, phosphate predominantly existed in anionic forms of HPO_4^{2-} or H_2PO_4^- over the pH range of 3.0 to 10.9 (Fig. 2). For 20MMSB, at lower initial pH solution, the presence of Fe and Mg oxides would be protonated into FeOH^+ and MgOH^+ forms, resulting an increase in the solution pH (pH final in Fig. 2). The existing FeOH^+ and MgOH^+ groups might act as the active sites for HPO_4^{2-} or H_2PO_4^- adsorption through electrostatic interaction process. Hence, the increasing pH would lead to the change of the positively-charged surface gradually into negative due to the

deprotonation effect, resulting in electrostatic repulsive interaction decreased between the negative charged surface and phosphate anions (Giménez et al., 2007; Ren et al., 2015), and decreasing amount of phosphate adsorption.

3.3. Adsorption isotherm and desorption

The batch data for phosphate adsorption with 20MMSB were fitted using the Langmuir and Freundlich isotherm models and with summarized in Fig. 3. The phosphate adsorption by 20MMSB was better described by the Langmuir model ($R^2=0.9976$) than the Freundlich model ($R^2=0.9011$). The maximum phosphate adsorption capacity was found to be 121.25 mg P per gram. Compared with the previous finding for other sorbents (Chen et al., 2011; Krishnanand Haridas 2008; Ren et al., 2015; Wang et al., 2015; Xie et al., 2015; Ye et al., 2015), 20MMSB showed higher phosphate adsorption capacity.

The desorption of phosphate from loaded 20MMSB particles by different solutions was also evaluated. It was found that only 1.74%, 5.55%, 9.64%, and 37.53% phosphates were released in DW, NaCl, Na₂CO₃ and HCl solution, respectively (see Fig. S5 of SI). The generally low phosphate desorption rates indicated the strong interaction between adsorbate and adsorbent (Ren et al., 2015).

3.4. Adsorption mechanisms

In order to further explore phosphate adsorption mechanisms by the MMSB, the 20MMSB samples before and after phosphate adsorption were characterized by FTIR spectroscopy and XRD analysis. The FTIR spectra of these samples can be found in the Supplemental Information (see Fig. S6 of SI). In general, the FTIR broad band centered around 3448 cm⁻¹ was associated with the -OH stretching vibrations of the hydroxyl groups in the Mg (OH)₂ or the sorbed water molecules, and peak located around 1630 cm⁻¹ was recorded as water deformation (Yan et al.,

2015). The benzene ring C=C stretching peak at 1460 cm^{-1} imply the aromatization process happened during the biochar preparation (Leng et al., 2015). The peaks around $900\text{-}1000\text{ cm}^{-1}$ were assigned to the stretching and bending vibration of Mg–O, and Mg–OH (Tongamp et al., 2007). The strong peak at 585 cm^{-1} was attributed to the Fe–O lattice vibration of Fe_3O_4 (Chen et al., 2011; Yan et al., 2015), indicating the existence of Fe_3O_4 particles. After P adsorption, the peaks at 870 and 770 cm^{-1} corresponded to the Fe–OH vibrations were nearly disappeared with appearance of the asymmetric vibration of P–O bond at around 1050 cm^{-1} , implying the interaction between Fe–OH group and P ions with possible formation of surface inner-sphere complex (Zhang et al., 2009; Lǔ et al., 2013). Compared with the peak at 585 cm^{-1} before P adsorption, the strength of Fe–O lattice vibration peak at 585 cm^{-1} decreased but still could be observed easily after phosphate adsorption, which means the Fe–O group also dedicated to the O ions adsorption. Nonetheless, the result of the appearance of P–O bond at around 1050 cm^{-1} in the 20MMSB sample after P adsorption was different from indifferent surface functionality of a tomato tissue-derived MgO-impregnated biochar observed before and after P sorption (Yao et al., 2013), suggesting the contribution of Fe–O to binding phosphate in the Mg-predominated 20MMSB (Table1). On the other hand, the little change in Mg–O and Mg–OH peaks at $900\text{-}1000\text{ cm}^{-1}$ before and after P sorption likely suggested the formation of only new outer-sphere surface complex between surface MgO and phosphate (Mg–O---P).

The XRF analysis provided additional evidence of phosphate interactions with magnetic MgO-impregnated biochar upon sorption. The P-loaded 20MMSB exhibited strong signals of not only the existence of Fe_3O_4 and MgO, but also new crystals in the forms of MgHPO_4 and $\text{Mg}(\text{H}_2\text{PO}_4)_2$, which clearly indicated the precipitations between phosphate ions and Mg oxide (see Fig. S7 of SI).

Combining all evidence, we may propose that the phosphate adsorption were controlled by the protonation, surface inner-sphere complexation, surface electrostatic attraction and precipitation combined processes (see Fig. S8 of SI). During the initial stages of the adsorption experiment with pH ranged between 4.0 to 9.6 and phosphate existed in the form of HPO_4^{2-} and H_2PO_4^- in solution, surface electrostatic attraction between phosphate ions and protonated MgOH^+ would be expected. As pH increased and reaction continued, precipitation between phosphate ions and MgO particles on carbon surfaces within the matrix would take place, which resulted in the formation of MgHPO_4 and $\text{Mg}(\text{H}_2\text{PO}_4)_2$ crystals. The fact that all final solution pH ranges were around 8.55 and 10.86 after phosphate sorption was consistent with the precipitation being the predominant mechanism. On the other hand, although phosphate also formed inner-sphere surface complex with Fe oxide in biochar, this reaction was likely less dominant compared to Mg-phosphate precipitations considering high content of impregnated MgO in the 20MMSB.

3.5. Phosphorus-loaded adsorbent on plant growth

The potential recycling and use of phosphate-loaded 20MMSB as a phosphate fertilizer for plant growth was assessed in pot experiment for ryegrass seedling growth. The phosphate-loaded 20MMSB amendment showed much greater plant growth heights than the SB and control treatment (see Fig. S9 of SI). The aboveground biomass dry weight of ryegrass seedling in the phosphate-loaded 20MMSB treatment was 1.124 g/pot, which was significantly higher than the SB added treatment (0.613 g/pot) and control (0.367 g/pot). The differences in yield of *ryegrass* clearly indicated that phosphate-loaded 20MMSB had the potential to substitute phosphate-based fertilizers.

4. Conclusions

The biochar with 20% Mg content (20MMSB) shows high phosphate recovery ability, with maximum adsorption capacity around 121.25 mg P/g at pH 4.0. The adsorption isotherm fitted the Langmuir model, and the adsorption process was controlled by surface electrostatic attraction with MgO, surface inner-sphere complex with Fe oxide and Mg-phosphate precipitation reactions. Phosphate-loaded 20MMSB exhibited excellent magnetic recovery ability and limited phosphate desorption. Application of the phosphate-loaded 20MMSB significantly ryegrass growth and could be used as phosphate-based fertilizer for agronomic production.

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Figure captions

Fig.1. Magnetic response of MSB and 20MMSB.

Fig.2. Effect of solution pH on the P adsorption.

Fig.3. P adsorption isotherm modeling.

Fig.1. Magnetic response of MSB and 20MMSB.

Fig.2. Effect of solution pH on the P adsorption.

Fig.3. P adsorption isotherm modeling.

Table 1. Physio-chemical properties of the raw material and biochar

Material	Fe (%)	Mg (%)	C (%)	H (%)	N (%)	$S_{BET}(m^2/g)$	$TPV (cm^3/g)$	$APR (nm)$
SHR	ND	ND	45.85 ± 0.22	6.16 ± 0.17	0.55 ± 0.02	ND	ND	ND
SB	0.76 ± 0.02	0.44 ± 0.02	66.28 ± 1.68	2.15 ± 0.02	0.90 ± 0.02	24.59	0.038	1.78
MSB	3.21 ± 0.06	0.43 ± 0.03	64.33 ± 1.86	1.77 ± 0.14	1.07 ± 0.02	92.54	0.101	2.07
2MMSB	3.23 ± 0.10	2.12 ± 0.10	61.52 ± 0.44	1.54 ± 0.08	1.87 ± 0.06	118.03	0.096	1.96
5MMSB	3.22 ± 0.05	5.04 ± 0.03	58.45 ± 0.83	1.51 ± 0.06	1.74 ± 0.03	73.95	0.130	2.72
8MMSB	3.22 ± 0.06	8.21 ± 0.22	46.14 ± 0.09	1.43 ± 0.08	1.92 ± 0.04	61.39	0.157	3.51
15MMSB	3.21 ± 0.04	14.97 ± 0.13	40.05 ± 0.17	2.17 ± 0.05	2.11 ± 0.01	35.66	0.282	3.74
20MMSB	3.21 ± 0.06	20.47 ± 1.66	26.23 ± 0.72	2.37 ± 0.09	1.52 ± 0.03	27.22	0.343	4.32
SHR, sugarcane harvest residue; SB, biochar made from SHR; MSB, magnetic biochar made from SHR; MMSB, magnesium magnetic biochar made from SHR with a specific Mg percentage as indicated.								

ND, means no detection.