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biochar with different Mg/Al ratios**

Ronghua Li ^{a, b}, Jim J. Wang ^{b*}, Baoyue Zhou ^b, Mukesh Kumar Awasthi ^{a, c}, Amjad Ali ^a,
Zengqiang Zhang^a, Lewis A. Gaston^b, Altaf Hussain Lahori^a, Amanullah Mahar^{a, d}

^a College of Natural Resources and Environment, Northwest A&F University, Yangling 712100,
China

^b School of Plant, Environmental and Soil Sciences, Louisiana State University Agricultural
Center, Baton Rouge, LA 70803, USA

^c Department of Biotechnology, Amicable Knowledge Solution University, Satna, India

^d Centre for Environmental Sciences, University of Sindh, Jamshoro, 76080 Pakistan

***Correspondence author:**

Prof. Jim J Wang

School of Plant, Environmental and Soil Sciences,

Louisiana State University Agricultural Center,

Baton Rouge, LA 70803, USA

Tel: (225) 578-1360;

E-mail: JJWang@agcenter.lsu.edu

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Abstract

Mg/Al ratio plays a significant role for anion adsorption by Mg/Al-layered double hydroxides (Mg/Al-LDHs) modified biochar. In this study, Mg/Al-LDHs biochar with different Mg/Al ratios (2, 3 and 4) were prepared by co-precipitation for phosphate removal from aqueous solution. Factors on phosphate adsorption including Mg/Al ratio, pH, and the presence of other inorganic anions were investigated through batch experiments. Increasing Mg/Al ratio in the Mg/Al-LDHs biochar composites generally enhanced phosphate adsorption with Langmuir adsorption maximum calculated at 81.83 mg phosphorous (P) per gram of 4:1 Mg/Al-LDHs biochar at pH 3.0. The adsorption process was best described by the *pseudo-second-order* kinetic model. Solution pH had greater effects on the phosphate adsorption by Mg/Al LDHs biochar composites with lower Mg/Al ratios. The presence of other inorganic anions decreased the phosphate adsorption efficiency in the order of $F^- > SO_4^{2-} > NO_2^- > Cl^-$. Phosphate adsorption mechanism involves ion exchange, electrostatic attraction and surface inner-sphere complex formation. Overall, Mg/Al-LDHs biochar composites offer a potential alternative of carbon-based adsorbent for phosphate removal from aqueous solution.

Keywords: Phosphate; adsorption; layered double hydroxides; biochar; Mg/Al ratio

1. Introduction

Biochar is a carbon-rich porous solid material, which has extensive properties such as high surface area, degree of porosity and stable carbon matrix. It is normally prepared by a pyrolysis process through thermochemical conversion of plant and animal-based waste biomass under limited O₂ conditions (Ahmad et al., 2014; Xiao et al., 2015). Biochar is considered as an important carbon-rich solid biomass for bio-energy, waste management, site remediation, climate change mitigation and soil fertility (Jeong et al., 2012; 2016; Ahmad et al., 2014; Li et al., 2015; Zhang et al., 2016). Moreover, biomass-derived biochar could adsorb heavy metal ions and organic pollutants due to the presence of many functional groups including phenolic, carboxyl, and hydroxyl groups in its carbon-based structure (Bogusz et al., 2015; Han et al., 2016; Jeong et al., 2012). Biochar is environmentally friendly, has excellent stability, and is easily prepared; it is also highly available as a raw material. Thus, based on these aspects, biochar is believed to have great potential for agricultural and environmental applications (Ahmad et al., 2014; Han et al., 2016; Mohan et al., 2014). Biochar has, however, predominantly net negatively charged surface, only offering a limited ability to adsorb anionic pollutants which are very common in wastewater (Han et al., 2016; Mohan et al., 2014; Mukherjee et al., 2015). Thus, the modification or functionalization of raw biochar for improving the affinity towards anionic pollutants has become an important practice for expanding the application of biochar technology (Chen et al., 2011; Han et al., 2016; Jung et al., 2016; Wang et al., 2015).

Layered double hydroxides (LDHs) are a kind of anionic clay with large anion sorption capacities. The general chemical composition of LDHs can be described as in the formula $[M^{2+}_{(1-\alpha)}N^{3+}(OH)_2]^{a+}[A^{n-}]_{a/n} \cdot mH_2O$, where M^{2+} is the divalent cation (Mg^{2+} , Zn^{2+} , Mn^{2+} , Co^{2+} , Ni^{2+} , Cd^{2+} , etc.), N^{3+} is the trivalent cation (Al^{3+} , Fe^{3+} , Cr^{3+} , Ga^{3+} , etc.), A^{n-} is the interlayer anion

(CO_3^{2-} , SO_4^{2-} , NO_3^- , Cl^- , OH^- , etc.) and α is the $\text{N}^{3+}/(\text{M}^{2+} + \text{N}^{3+})$ ratio. LDHs are a host-guest material consisting of positively charged metal hydroxide sheets with intercalated anions and water molecules. With easily exchangeable interlayer ions and large surface area, LDHs exhibit acceptable anionic pollutants adsorption abilities (Goh et al., 2008). LDHs can be prepared easily in the laboratory although their reserve is very limited in natural environments (Zhang et al., 2009).

Phosphate (PO_4^{3-}) is an essential nutrient that is known to be responsible for the eutrophication acceleration in many aquatic environments. Phosphate pollution leads to an increase in costs associated with water treatment, decreases recreational value of the waterway, and results in the formation of harmful algal blooms that may pose a risk to human health from the production of cyanotoxins (Lalley, et al., 2016). Therefore, the remediation of phosphates from aquatic ecosystems is a growing environmental concern. Recently, Fang et al. (2015) used binary cations (Mg^{2+} and Ca^{2+}) solution to soak raw corncob powder and made the Ca-Mg loaded biochar at 350 °C, 450 °C and 600 °C, respectively. Jung et al. (2015) prepared the Mg/Al assembled biochar by treating brown marine macroalgae in acidic MgCl_2 solution (pH 3.0) with the assistance of an electric field. Their characterizations clarified that the metals in Ca-Mg loaded biochar were in form of separated MgO and CaO nanoparticles, and those in Mg/Al assembled biochar were mainly composed with mineral mixtures including MgO, Al_2O_3 and MgAlO_2 spinel crystals. None of these metal-loaded biochar products showed the structure of LDHs. While these biochars especially the Ca-Mg loaded biochar showed the excellent phosphate recovery from biogas fermentation liquid (Fang et al. 2015), it was likely added by the significant presence of Cu in the biochar which is known to have high affinity for phosphate (Song et al. 2016). High Cu presence, if not carefully managed, can have well-known toxicity

effects on aqueous systems. On the other hand, grafting LDHs to biochar surface offers a secondary management of biochar for environmental use since it is produced after the initial biochar is made. Zhang et al. (2013) developed Mg/Al-LDHs grafted biochar composites with Mg/Al ratio in 2:1 as adsorbent for phosphate ion removal successfully. However, the information about the adsorptive properties of LDHs-biochar composites with different Mg/Al ratios as well as the influence of pH and competitive anions is very limited, since both the interlayer spacing and electrical properties of LDHs compounds are affected by the M^{2+}/N^{3+} ratio (Wan et al., 2012; Wan et al., 2009). As interlayer spacing and electrical properties of LDHs compounds are crucial characteristics for anion adsorption (Goh et al., 2008; Zhang et al., 2009), the systematic study of Mg/Al ratio impacts on phosphate adsorption by Mg/Al-LDHs grafted biochar composites needs to be further explored. In addition, clarifying the effect of Mg/Al ratio on phosphate adsorption by Mg/Al-LDHs grafted biochar composites could provide valuable information for the engineered Mg/Al-LDHs biochar preparation and expanding of biochar technology.

Therefore, the objectives of this work were to (1) use co-precipitation method to synthesize Mg/Al-LDHs biochar composites of different Mg/Al ratio and (2) investigate the phosphate adsorption behavior of the prepared biochar composites under batch conditions. Additionally, the relationship between adsorption behavior and Mg/Al ratio of Mg/Al-LDHs biochar composites and desorption by competitive anions will be characterized.

2. Materials and methods

2.1. Materials collection and preparation

Sugarcane leaves (SL) were collected from Louisiana State University AgCenter Sugar Research Station at St. Gabriel, Louisiana, and cut into < 5 cm small pieces by hand, while subsequently washed by deionized water (DW) (18.2 M Ω) to remove dust particles followed by oven drying at 55°C overnight. The dry biomass was crushed by a high-speed rotary cutting mill, and passed through a screen < 0.12 mm before being used for biochar conversion. Analytical grade Al(NO₃)₃, Mg(NO₃)₂, KH₂PO₄, NaNO₂, NaF, Na₂SO₄, NaCl, NaOH, H₂SO₄, HNO₃ and H₂O₂ used for adsorbent synthesis and analysis were purchased from Fisher Scientific (Pittsburgh, PA, USA). All the chemical solutions were prepared using DW throughout the experiment.

2.2. Biochar production and Mg/Al-LDHs biochar composites preparation

The biochars used in the present study were prepared by pyrolysis of sugarcane harvest trash leaves biomass in a Thermolyne FA1730 muffle furnace at 550°C with retention time of 1 h under N₂ flow condition as previous described by Jeong et al. (2016). The resulting biochar samples were gently crushed and passed through < 0.12 mm nylon sieve, and then washed with DW and oven-dried at 105°C for 24 h. Mg/Al-LDHs biochar composites of different Mg/Al ratios were synthesized by a modified method of Zhang et al. (2013). In brief, 10 g biochar was mixed into 300 mL of aqueous solution containing 0.3 and 0.3/ x mol/L of Mg(NO₃)₂ and Al(NO₃)₃, respectively, under stirring. The Mg/Al atomic ratio (x) in the solution was selected as 2, 3 and 4 based on the common N³⁺/(M²⁺+N³⁺) ratio range found in LDHs. The pH of the mixtures was adjusted to 10 using 1.0 mol/L NaOH aqueous solution. The prepared black slurry (biochar with aqueous solution) was sealed in a bottle and incubated 3 days at 80°C, then filtered and washed with DW for 6 times. The obtained x :1 Mg/Al-biochar composites were then dried at

105°C for 24 h, followed by gentle crushing to make uniform size < 0.12 mm and stored in desiccators before use.

2.3. Biochar and Mg/Al-LDHs biochar composites characterization

The biochars were analyzed for their total C, H and N contents using an elemental analyzer (Elementar Analysen systeme GmbH, Germany). Infrared spectra of biochars were obtained using a Nicolet iS50 Fourier transform infrared spectrometer (FTIR) (USA), while Mg and Al content in biochars were analyzed by inductively coupled plasma-atomic emission spectrometry (ICP-AES, SPECTRO Plasma 3200, Germany) after digestion (Xiao et al., 2015). The point of zero charge (pH_{zpc}) of the samples were determined using the method described by Li et al. (2013). BET surface area (S_{BET}) and total pore volume (V_{TOT}) of samples were measured by N₂ adsorption at 77 K using a V-Sorb 2800P analyzer (App-one, China). X-ray diffraction (XRD) analysis was also carried out to identify any crystallographic structure in the biochar samples using a computer-controlled X-ray diffractometer (Philips Electronic Instruments, Mahwah, NJ, USA). The morphological properties of the biochar were characterized using a field emission gun scanning electron microscope (FEG-SEM, JEOL 6335F, Japan) equipped with an energy-dispersive X-ray (EDX) spectroscopy.

2.4. Batch adsorption

Batch adsorption experiments were carried out to examine the performance of Mg/Al-biochar composites as phosphate adsorbents. The role of aqueous pH and co-existing anions, along with adsorption kinetics and adsorption isotherms were investigated. All the experiments were conducted in triplicates.

The effect of aqueous solution pH on phosphate adsorption was studied by mixing 0.05 g of Mg/Al-biochar composites with 20 mL of phosphate solution (50 mg/L Phosphorus) diluted from a 1000 mg/L phosphate stock solution in a polyethylene centrifuge. The pH of the solution was then adjusted to 3.0 and 11.0 using 1.0 mol/L HNO₃ and NaOH solutions, respectively. The centrifuge tubes containing the mixtures were fixed on a shaking table (operating at 120 rpm) at 23±0.2 °C. After overnight mixing, the biochar sample mixtures were filtrated through a 0.22 µm GE cellulose nylon membrane filter and the filtrate were analyzed for phosphate by molybdenum blue method with a Thermo Scientific EVO 60 spectrophotometer (USA) at wavelength of 880 nm, as recommended by the EPA. The blue complex is very stable and obeys Beer's law with the phosphate concentration in range of 0.025-2 mg P/L. The adsorption capacity (q_e , mg/g) of the sorbent material for phosphate was calculated by the mass balance as expressed in equation (1).

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

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

Adsorption kinetics of phosphate on the Mg/Al-biochar composites were evaluated by mixing a series of 1.0 g Mg/Al-biochar composites with 400 mL phosphate solutions (pH 3.0, 50 mg/L Phosphorus) in plastic bottles. The mixtures in bottles were then magnetically stirred at 120 rpm at 23±0.2 °C. At selected time intervals (5, 10, 15, 20, 30, 45, 60, 90 and 120 min), the mixtures were immediately filtered through 0.22 µm GE cellulose nylon membrane filters. The concentration of phosphate in the filtrates was analyzed. *Pseudo-first-order* and *pseudo-second-order* kinetic models (Li et al., 2013) as expressed in equation (2) and (3) were used to fit the adsorption experiment data, respectively.

1 *pseudo-first-order* kinetic model, $\ln(q_e - q_t) = \ln q_e - k_1 t$ (2)

2 *pseudo-second-order* kinetic model, $t/q_t = 1/(k_2 q_e^2) + t/q_e$ (3)

3 where k_1 and k_2 are the first-order and second-order apparent adsorption rate constants (1/h and
4 g/mg/h), respectively; q_t and q_e are the amount of phosphate sorbed (mg/g) at time t and at
5 equilibrium, respectively.

6 Phosphate sorption isotherms on the Mg/Al-biochar composites were determined by mixing
7 0.05 g Mg/Al-biochar composites with 20 mL of a series of phosphate solutions (pH 3.0, 5 to
8 500 mg/L Phosphorus) in a polyethylene centrifuge tube. After overnight mixing, samples were
9 filtrated through a 0.22 μ m GE cellulose nylon membrane filter. The concentration of phosphate
10 in the filtrate was analyzed. Langmuir and Freundlich isotherm models (Li et al., 2013)
11 represented in equation (4) and (5) were used for phosphate adsorption isotherms, respectively.

12 Langmuir isotherm model, $q_e = K_L Q C_e / (1 + K_L C_e)$ (4)

13 Freundlich isotherm model, $q_e = K_f C_e^n$ (5)

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

18 The effects of co-existing anions on phosphate adsorption was evaluated by the mixing 0.05
19 g Mg/Al-biochar composites with 20 mL of phosphate solution (pH 3.0, 50 mg/L Phosphorus)
20 containing equal concentrations of co-existing anions (such as Cl^- , NO_2^- , F^- and SO_4^{2-}) in a
21 polyethylene centrifuge tube. Solution without co-existing anions was used as blank test. After
22 overnight equilibration, the mixture was filtrated through a 0.22 μ m GE cellulose nylon
23 membrane filter, and then analyzed for phosphate concentration.

3. Results and discussion

3.1. Characterization of adsorbents

The physicochemical properties of the prepared biochar samples are presented in Table 1. Compared with raw biochar, the C content in the Mg/Al-LDHs biochar samples decreased after Mg/Al-LDHs introduction, and the S_{BET} and V_{tot} of the biochar composites decreased as well. The Mg/Al-LDHs was expected to incorporate into porous surface of carbon matrix of such biochar which was known to be dominated by pores of 20 nm and greater (Jeong et al., 2016). It should be pointed out that the actual loading ratio for 2:1, 3:1 and 4:1 Mg/Al-LDHs biochar composites was 1.78, 2.68 and 3.62, respectively. This was likely due to the influence of lower Mg/Al ratio presence already in the raw biochar (Jeong et al., 2016) than the prepared solution Ma/Al ratio. The morphology of biochar, 2:1Mg/Al-LDHs biochar, 3:1Mg/Al-LDHs biochar and 4:1Mg/Al-LDHs biochar composites characterized by SEM-EDX, are shown in Fig. 1. It can be seen clearly that the particles of biochar exhibited sharp edges and corners, while the surfaces of Mg/Al-LDHs biochar composite particles were covered by new smooth metal oxides homogeneously. The EDX data showed extremely high peaks for C and O in raw biochar; while Mg/Al-LDHs biochar composite showed additional peaks for Mg and Al, all of which are typical elemental composition of the salts used in the biochar composites preparation. In addition, Si, Na and Ca, some common elements within sugarcane leaves, were also found in EDX spectra of all samples. To determine whether there is any dissolution of Mg or Al from the Mg/Al-LDHs biochar composite during the utilization process, 0.05g 2:1Mg/Al-LDHs biochar, 3:1Mg/Al-LDHs biochar and 4:1Mg/Al-LDHs biochar composites were immersed in 20 mL DW at pH 3.0 and 11.0 for 24 h, respectively. Analysis of the supernatant by ICP-AES showed that Mg and Al were strongly bound in the biochar matrix with undetectable dissolution of Mg or Al in the

supernatant, indicating excellent stability of Mg/Al-LDHs biochar composite in acidic and basic solution.

The XRD patterns of the Mg/Al-LDHs biochar composites, in the range of 7-70°, are presented in Fig. 2. The XRD analysis revealed that raw biochar without Mg addition is dominated with a broad diffraction peak at 2 theta around 21.0°, which is attributed to the cellulose (002) crystal plane. Compared with that of raw biochar, the prepared Mg/Al-LDHs biochar composites showed typical hydrotalcite compound structure with sharp reflection peaks including (003), (006), (012) and (015), as well as (018), (110), (113) and (116). These peaks implicated the *R3m rhombohedral* symmetry of the Mg/Al-LDHs (Wang et al., 2009), and the results proved that Mg/Al-LDHs were successfully grafted in the matrix of biochar (Zhang et al., 2013). For LDHs material, the cell parameter a can be calculated by the equation $a = 2 d_{110}$ and c can be obtained by the equation $c = 3 d_{003}$ of the diffraction peaks (Vaccari, 1998; Wan et al., 2012). As the position of peak (110) was not changed, indicating the parameter a was kept constant in about 0.48 nm for all the prepared Mg/Al-biochar composites, therefore the interlayer space could be calculated by subtracting the width of the brucite-like layer from the basal spacing d_{003} . The calculated cell parameters are listed in Table 2. It can be seen in Table 2, that interlayer spaces are 0.280, 0.294 and 0.310 nm for the Mg/Al-biochar composite with Mg/Al ratio increasing from 2 to 4, respectively. The findings of our study were in accordance with the previous studies (Grover et al., 2009; Wan et al., 2012; Wan et al., 2009). This phenomenon could be explained by the fact that as Mg/Al ratio increases from 2 to 4, the electric charge density between the layers becomes weaker, resulting an increase in the interlayer spaces (Wan et al., 2012).

3.2. Effect of pH on the phosphate adsorption

The pH is one of the important parameters to control the surface charge of the adsorbent and species of adsorbate in an aqueous medium. The effect of solution pH on sorption of phosphate to Mg/Al-LDHs biochar composite is showed in Fig.3a. It can be seen that adsorption of P on Mg/Al-LDHs biochar composite was highly pH dependent and the adsorption amount steadily decreased with increasing pH from 3 to 11. Therefore, pH value 3 is an ideal parameter in this study. Similar trends were also observed for phosphate and chromate adsorption on other metal oxides (Liu, et al., 2010; Lu et al., 2014; Lü et al., 2013; Yuan et al., 2013). The results were related to the acid-base properties of adsorbent and phosphate species in solution at different pH values. In the pH range 3-11, H_2PO_4^- and HPO_4^{2-} were the dominant species. The adsorption free energy of H_2PO_4^- was lower than that of HPO_4^{2-} , therefore H_2PO_4^- was more easily adsorbed on adsorbent surface than HPO_4^{2-} (Chowdhury and Yanful, 2010; Chubar et al., 2005). Meanwhile, when the solution pH was lower than pH_{zpc} , the surface of the adsorbent became protonated and more positively charged with the decrease of pH (Li et al., 2013), which leads to more favorable adsorption of phosphate anions. At pH above pH_{zpc} , an increasing electrostatic repulsion between more negatively charged surface sites and phosphate ions resulted in lower phosphate adsorption. On the other hand, at higher pH, the competitions between hydroxyl ions and phosphate species on the adsorbent surface would also reduce the phosphate adsorption (Jung et al., 2015; Lalley et al., 2016; Lü et al., 2013). From Fig. 3a, it can be seen that 2:1 Mg/Al-LDHs biochar composite was more affected by solution pH than 4:1 Mg/Al-LDHs biochar composite. This could be explained by the fact that the stronger buffering capacity of the 4:1 Mg/Al LDHs biochar for phosphate adsorption against pH change than the 2:1 Mg/Al LDHs biochar was due to the general difference between PZC values of Mg oxides (~12) and Al oxides (8.3-9.2). For the 4:1

Mg/Al LDHs biochar, the greater protonation of dominant Mg-oxide surface would adsorb more phosphate than the less protonated Al oxide surface in the 2:1 Mg/Al LDHs biochar, leading to stronger phosphate adsorption buffering ability against the pH change since the solution pH was generally less than 12. The greater impact of pH on phosphate adsorption by the 2:1 Mg/Al LDHs biochar composite than by the other two composites was indeed observed at the solution pH greater than the PZC (8.3-9.2) of Al oxides (Fig. 3a).

The change in equilibrium solution pH as a function of initial pH is depicted in Fig.3b. It was found that, for three different Mg/Al-LDHs biochar composites, the equilibrium pH of each composite-related filtrate was higher than the initial pH from 3 to 9, and lower than the pH from 9 to 11. This can be attributed to the acid-base properties of hydroxyl groups on adsorbent surface, which resulted in the protonation or deprotonation of its structure (Lǔ et al., 2013; Yang et al., 2007). The positively protonated Mg/Al-LDHs surface was favored for phosphate adsorption. When the equilibrium (final) pH of the filtrate was higher than that before adsorption, it indicated the release of the adsorbent surface-protonated hydroxyl groups into the solution which resulted in a rise in the equilibrium solution pH (Lǔ et al., 2013). The equilibrium (final) pH of the filtrate was lower than the pH of solution before adsorption (pH 9-11) could be explained by the fact that this pH was higher than the overall Mg/AlLDHs PZC of 9.3 (Fig. 3b). Therefore the surface became negative, releasing H^+ and causing the lower final pH than initial solution pH along with decreased phosphate adsorption (Liu et al., 2008).

3.3. Phosphate adsorption isotherm

The adsorption isotherms of phosphate on Mg/Al-LDHs biochar composites are demonstrated in Fig. 4a. It is evident, that with the increasing initial phosphate concentration, the

phosphate adsorption amount was increased dramatically and then reached equilibrium gradually. These isotherms were best fitted by the Langmuir model with higher R^2 values than the Freundlich model (Table 3). The calculated Langmuir maximum adsorption capacity (Q) for phosphorous were 53.39, 72.05 and 81.83 mg P/g for the 2:1 Mg/Al-LDHs, 3:1 Mg/Al-LDHs and 4:1 Mg/Al-LDHs biochar, respectively, which was much greater than 3 mg P/g for raw biochar (data not shown) as well as equivalent 8.67 mg P/g for pure Mg/Al-LDHs mineral reported by Halajnia et al (2013). These results clearly indicated that phosphate adsorption was favorable by Mg/Al-LDHs biochar composite and was enhanced with increasing Mg/Al ratio in the Mg/Al-LDHs biochar composite. The much increased phosphate adsorption with grafting LDHs into biochar than pure Mg/Al LDHs mineral suggested the strong enhancing effect of combining porous biochar matrix and positively charged Mg/AL-LDHs for anion adsorption. In addition, the fact that phosphate adsorption capacity increased with the increasing Mg/Al ratio in Mg/Al-LDHs biochar composites might be explained by the increasing interlayer space and S_{BET} of the Mg/Al-LDHs in the corresponding biochar composites (Table 2). Thus, phosphate ions would more easily access the larger interlayer space of 4:1Mg/Al-LDHs over 3:1 and 2:1 ones. The phosphate adsorption capacities found in these Mg/Al-LDHs biochar composites in this study are higher than many of the other adsorbents reported in literatures (Table 4), such as magnetite particles functionalized orange peel biochar (1.24 mg/g) (Chen et al., 2011), ferric oxides loaded cotton stalks biochar (0.963 mg/g) (Ren et al., 2015), Fe-Cu binary oxides (39.8 mg /g) (Li et al., 2014), mesoporous ZrO_2 (29.7 mg/g) (Liu et al., 2008) and Al oxide hydroxide (35 mg/g) (Tanada et al., 2003) etc. Clearly, Mg/Al-LDHs biochar composite could serve as a potential adsorbent for phosphate removal.

3.4. Phosphate adsorption kinetics

Adsorption kinetics is one of the most important factors in evaluating the efficiency of an adsorbent. The phosphate adsorption by the Mg/Al-LDHs biochar composite as a function of time is presented in Fig.4b. It is clear that initially phosphate adsorption was fast followed by a relatively slow adsorption, which is similar to other studies (Lalley et al., 2016; Lü et al., 2013; Zhang et al., 2009). The phosphate adsorption increased with extended contact time, and more than 99% phosphate was removed within 60 min. The initial rapid adsorption might be due to the electrostatic attraction between the positive charged metal oxide surfaces and the negative charged phosphate ions. The later slow adsorption indicated that intraparticle diffusion may be involved (Lalley et al., 2016; Lü et al., 2013; Zhang et al., 2009). The kinetic data of phosphate adsorption was also fitted with *pseudo-first-order* and *pseudo-second-order* kinetic model. The obtained kinetic models parameters are listed in Table 5. It was found that the phosphate adsorption could be better described by the *pseudo-second-order* kinetic model since the correlation coefficient (R^2) was higher than that of *pseudo-first-order* kinetic model. These results were consistent with chemical behaviors of phosphate adsorption exhibited by other metal oxides and LDHs-based adsorbents (Tanada et al., 2003; Chubar et al., 2005; Yang et al., 2007; Zhang et al., 2009; Chen et al., 2011; Lü et al., 2013; Li et al., 2014; Jung et al., 2015; Lalley et al., 2016).

3.5. Effects of competitive anions on phosphate adsorption and phosphate desorption performance

The coexistence of other anions typically occurs in the real contaminated water. Therefore, in order to investigate the effect of co-existing anions on the phosphate adsorption, the

1 adsorption experiments were further carried out by taking equal concentrations of competing
2 anions as that of phosphate solution (50 mg/L) (Fig. 5a). It can be seen from Fig. 5a, in the
3 presence of Cl^- , no obvious decrease in phosphate adsorption by the three adsorbents was
4 observed, for NO_2^- , only a slight decrease was observed especially by 2:1 Mg/Al-LDHs biochar
5 composite. This result was consistent with other studies in some extents (Chubar et al., 2005; Lu
6 et al., 2014; Lů et al., 2013). Chloride ion from the soluble salt had negligible effect on the
7 adsorption process indicating the strong interaction between phosphate and adsorbent surface.
8 Generally, phosphate has also been considered to form inner-sphere complexes with metal
9 hydroxides, whereas chloride often was weakly bound with surface sites of metal hydroxides
10 forming outer-sphere complexes, which led to ineffective competition (Lu et al., 2014). The
11 coexistence of SO_4^{2-} or F^- exhibited significant negative influence on phosphate adsorption. The
12 reduction in amounts of phosphate adsorption by 2:1 Mg/Al-LDHs, 3:1 Mg/Al-LDHs and 4:1
13 Mg/Al-LDHs biochar composites was 19.8%, 16.0% and 7.8% in the presence of SO_4^{2-} and
14 29.7%, 27.1% and 18.0% with F^- , respectively. Overall, the results showed that in the presence
15 of Cl^- , F^- , NO_2^- and SO_4^{2-} , the phosphate adsorption decreased in the order of $\text{F}^- > \text{SO}_4^{2-} > \text{NO}_2^-$
16 $> \text{Cl}^-$. The obvious inhibition of phosphate adsorption by sulfate and fluoride ions were likely due
17 to the strong competition of these ions for the binding sites on the adsorbent surface. In view of
18 chemistry, the ionic radius of SO_4^{2-} is larger than that of Cl^- , NO_2^- and NO_3^- (all smaller than
19 0.200 nm). Thus the anions with similar ionic radius such as H_2PO_4^- (0.238 nm) and SO_4^{2-}
20 (0.230 nm) are strongly associated with the positively charged Mg/Al-LDHs interlayer space
21 (Goh et al., 2008). On the other hand, F^- has a strong electro-negativity and it is easily combined
22 with the protonated adsorbent surface (Li et al., 2014). Therefore, the adsorption of phosphate
23 was significantly decreased at the coexistence of F^- . Similar results were also previously

observed for other adsorbents. For example, the presence of SiO_3^{2-} , HCO_3^- , and SO_4^{2-} would lead to the reduction of phosphate adsorption by Fe-Al-Mn tri-metal oxide adsorbent by as much as 41-66% (Lü et al., 2013). The phosphate adsorption was reduced from 84.4% to 48.5 % when calcined Mg-Al LDHs was employed as adsorbent (Das et al., 2006). Finally, the introduction of F^- in the aqueous solution reduced the phosphate removal rate of Fe(III)-Cu(II) binary oxide adsorbent by as much as 70% (Li et al., 2014). Clearly, the presence of different anions affects the performance of metal oxide or LDHs biochar composite adsorbents. Our results showed that Mg/Al-LDHs biochar composites had less impact of the co-existence of SO_4^{2-} or F^- on phosphate adsorption, especially at the Mg/Al ratio of 4:1. Hence, 4:1 Mg/Al-LDHs biochar composite might has great utilization potential as the impact of coexisting species was less noticeable and the phosphate adsorption capacity was higher than others.

The desorption study provides valuable information about the reversibility of phosphate adsorption and the potential reusability of the adsorbent (Novillo et al., 2014). For this evaluation, the Mg/Al-LDHs biochar composites were first subjected to adsorption, prior to the desorption, by treating the materials with phosphate solution (200 mg/L Phosphorus) at pH 3.0 for 24 h. The phosphate uptake was 40 mg P/g. After that, the phosphate loaded materials were treated with DW at different pH values 1.05, 7.04 and 10.91, respectively. The results of the phosphate desorption are presented in Fig. 5b. Phosphate can be desorbed at acid and alkali pH, with the highest removal rate of 70% at pH 10.91; while at neutral pH only 3.38% of phosphate ions were desorbed. The results were similar with Lalley's (2016) findings. Alkali desorption reagent enhanced the competition between hydroxyl ion and phosphate ion, resulting in more phosphate desorbed from the adsorbent. On the other hand, the strong acidic desorption reagent could destroy the structure of metal oxides, leading to the release of sorbed phosphate. The results of

1 this study indicated that the Mg/Al-LDHs functionalized biochar composites could be
2 regenerated, and the biochar composites have the features of facilitating the recycling of the
3 Mg/Al-LDHs biochar composites for later use as phosphate fertilizer or adsorbent.

4 *3.6. FTIR analysis of the adsorbent before and after phosphate adsorption*

5 The FTIR analysis was conducted on the 4:1 Mg/Al-LDHs biochar composite before and
6 after phosphate adsorption (Fig. 6). For the Mg/Al-LDHs biochar composite sample before
7 phosphate adsorption, the FTIR low frequency peaks within 500–800 cm^{-1} including 557, 630,
8 and 683 cm^{-1} were assigned to the Al–O or Mg–O band stretching vibrations (Frost et al., 1999;
9 Frost and Kloprogge, 1999; Richardson and Braterman, 2007 Lǔ et al., 2013; Zhang et al., 2013),
10 whereas the 903 cm^{-1} peak was associated with stretching and bending modes of Al–O (Frost et
11 al., 1999; Lǔ et al., 2013). The absorption bands at 973, 1060 and 1120 cm^{-1} were attributed to
12 the stretching modes of Al–OH (Frost et al., 1999), whereas the peak at 717 cm^{-1} was to the
13 translational mode of both Al–OH and Mg–OH (Richardson and Braterman, 2007; Lǔ et al.,
14 2013). The benzene ring C=C stretching peaks at 1459 and 1553 cm^{-1} indicated aromatization
15 occurred during the biochar preparation (Li et al., 2016). The broad bands located at 1631 and
16 3368 cm^{-1} were associated with the O–H stretching vibrations and H–O–H stretching and
17 bending vibrations of the hydroxyl groups in the Mg/Al-LDHs biochar composite or the sorbed
18 water molecules (Zhang et al., 2013).

19 After Mg/Al-LDHs biochar composites were reacted with phosphate, the strength of Al–
20 O stretching vibration at 557, 630 and 683 cm^{-1} decreased but still could be observed, which
21 confirmed the involvement of Al–O or Mg–O bonds in phosphate adsorption. Moreover, the shift
22 of 717 cm^{-1} band to 730 cm^{-1} and the reduction of the peak strength at 903 cm^{-1} along with the
23 complete disappearance of 973 cm^{-1} and emergence of a strong asymmetry vibration peak of P–

O bond at 1053 cm^{-1} indicated that phosphate was strongly adsorbed by metal oxide surface (Mg–O and Al–O) through the formation of potentially monodentate and bidentate inner-sphere surface complexes (Del Nero et al., 2010; Li et al., 2013; Lř et al., 2013; Novillo et al., 2014; Zhang et al., 2009). The observed corresponding increase in solution pH with phosphate adsorption is consistent with ligand exchange with surface hydroxyls (Sparks, 2003), supporting the formation of inner-sphere surface complex. On the other hand, the relatively broad nature of peak 1053 cm^{-1} with clearly seen shoulder around 1130 cm^{-1} could suggest the presence of some out-sphere surface complexes such as of H_2PO_4^- (Del Nero et al., 2010; Li et al., 2013), which would be favored with electron attraction due to positively charged Mg/Al LDHs surfaces at pH < the Mg/Al LDHs overall PZC of ~ 9.3 (Chubar et al., 2005; Lu et al., 2014). The peaks located at 1277 cm^{-1} and 1384 cm^{-1} for N–O stretching bond disappeared, indicating the release of NO_3^- from the Mg/Al-LDHs biochar composite interlayer (Novillo et al., 2014; Wan et al., 2012; Zhang et al., 2013). This result was consistent with the character of LDHs which had some easily exchangeable interlayer anions (Goh et al., 2008). Based on these results mentioned above, several phosphate adsorption mechanisms may be hypothesized (Fig. 7). The phosphate adsorption onto the Mg/Al-LDHs biochar composite was controlled by the exchange of phosphate with the interlayer NO_3^- , the electrostatic attraction between the positively charged metal oxides surface and the negative phosphate ions, as well as the inner-sphere surface complex formation process through ligand exchange.

4. Conclusions

Mg/Al-LDHs biochar composites with Mg/Al ratios in 2, 3 and 4 were successfully prepared. With the increasing Mg/Al ratio, the interlayer space of the LDHs of the biochar composites

increased, resulting in greater phosphate adsorption capacities. The Langmuir maximum adsorption capacity of the 4:1 Mg/Al-LDHs biochar composite for phosphate for was 81.83 mg P/g at pH 3. The phosphate adsorption process was best described by the *pseudo-second-order* kinetic model. The presence of inorganic anions decreased phosphate adsorption efficiency in the order of $F^- > SO_4^{2-} > NO_2^- > Cl^-$ with that of the 2:1 Mg/Al LDHs biochar composite affected the most and the 4:1 Mg/Al LDHs biochar composite the least. Phosphate adsorption was controlled by ion exchange, electrostatic attraction and surface complex formation process. The results demonstrated that modification of the biochar with higher Mg/Al ratio LDHs could provide a potential carbon-based adsorbent for phosphate removal and expand the application of biochar technology.

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Table legends

- Table 1 Elemental composition and textural properties of the Mg/Al-LDHs biochar samples
- Table 2 The cell parameters of the prepared Mg/Al-biochar composite
- Table 3 Langmuir and Freundlich model parameters obtained during phosphate adsorption
- Table 4 Comparison of phosphate adsorption with other reported adsorbents
- Table 5 The kinetics model parameters for phosphate adsorption

Table 1 Elemental composition and textural properties of the Mg/Al-LDHs biochar samples

Sample	S_{BET} (m ² /g)	V_{tot} (cm ³ /g)	Mg (%)	Al (%)	C (%)	H (%)	N (%)
biochar	31.21	0.038	ND	ND	66.28 ± 1.68	2.15 ± 0.02	0.90 ± 0.02
2:1 Mg/Al-LDHs biochar	10.17	0.008	13.34 ± 0.14	7.48 ± 0.08	39.68 ± 1.58	1.96 ± 0.06	0.72 ± 0.09
3:1 Mg/Al-LDHs biochar	11.41	0.013	14.05 ± 0.13	5.24 ± 0.10	43.63 ± 0.22	2.10 ± 0.05	0.75 ± 0.01
4:1 Mg/Al-LDHs biochar	12.25	0.016	14.55 ± 0.08	4.02 ± 0.11	44.47 ± 0.36	2.24 ± 0.02	0.76 ± 0.09

Note: ND means no detection.

Table 2. The cell parameters of the prepared Mg/Al-biochar composite

	$d110$ (nm)	a (nm)	$d003$ (nm)	c (nm)	Interlayer space (nm)
2:1 Mg/Al-LDHs biochar	0.152	0.304	0.760	2.280	0.280
3:1 Mg/Al-LDHs biochar	0.152	0.304	0.774	2.322	0.294
4:1 Mg/Al-LDHs biochar	0.153	0.306	0.790	2.370	0.310

Table 3 Langmuir and Freundlich model parameters obtained during phosphate adsorption

Adsorbent	Langmuir			Freundlich		
	Q (mg/g)	K_L (L/mg)	R^2	K_f (mg ⁽¹⁻ⁿ⁾ L ⁿ /g)	n	R^2
2:1 Mg/Al-LDHs biochar	53.39	11.51	0.9992	10.12	2.83	0.9036
3:1 Mg/Al-LDHs biochar	72.05	20.01	0.9967	16.30	3.02	0.8813
4:1 Mg/Al-LDHs biochar	81.83	22.45	0.9988	24.17	3.52	0.8529

Table 4 Comparison of phosphate adsorption with other reported adsorbents

Adsorbents	Temperature (K)	pH	Dosage (g/L)	Isotherm	Kinetics	Q_m (mg/g)	Ref.
magnetite particles grafted orange peel biochar	298	—	6.25	Langmuir	—	1.24	Chen et al., 2011
ferric oxides loaded cotton stalks biochar	298	—	20	—	pseudo-first-order	0.963	Ren et al., 2015
Fe-Cu binary oxides	298	5.0	0.2	Langmuir	pseudo-second-order	39.8	Li et al., 2014
mesoporous ZrO ₂	293	6.7-6.9		Langmuir	—	29.7	Liu et al., 2008
Al oxide hydroxide	298	4.0	—	Langmuir	Freundlich	35	Tanada et al., 2003
ZrO ₂ ·xH ₂ O	295	3.0	2.0	Langmuir	pseudo-second-order	47.62	Chubar et al., 2005
Ag nanoparticles grafted Bayoxide® E33	294	7.0	5.0	Langmuir	pseudo-second-order	38.8	Lalley et al., 2016
nanostructured Fe-Al-Mn oxide	298	6.8	0.2	Langmuir	pseudo-second-order	48.3	Lǔ et al., 2013
La ₂ O ₃ grafted oak biochar	298	—	2.0	Langmuir	pseudo-first-order	142.7	Wang et al., 2015
2:1 Mg/Al-LDHs biochar	298	3.0	2.5	Langmuir	pseudo-second-order	53.39	This study
3:1 Mg/Al-LDHs biochar	298	3.0	2.5	Langmuir	pseudo-second-order	72.05	This study
4:1 Mg/Al-LDHs biochar	298	3.0	2.5	Langmuir	pseudo-second-order	81.83	This study

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Table 5 The kinetics model parameters for phosphate adsorption

Adsorbent	<i>Pseudo-first-order</i>			<i>Pseudo-second-order</i>		
	q_e (mg/g)	k_1 (1/h)	R^2	q_e (mg/g)	K_2 (g /(mg h))	R^2
2:1 Mg/Al-LDHs biochar	16.83	1.17×10^{-2}	0.7748	20.09	0.313	0.9989
3:1 Mg/Al-LDHs biochar	18.60	5.30×10^{-3}	0.8783	20.03	0.551	0.9993
4:1 Mg/Al-LDHs biochar	19.18	4.61×10^{-3}	0.8969	20.07	0.776	0.9991

Figure captions

Fig.1. SEM images and EDX spectrum of the samples.

(a), (b), (c) and (d) are SEM images of the raw biochar, 2:1, 3:1 and 4:1 Mg/Al-LDHs biochar composites, respectively; (e), (f), (g) and (h) are EDX spectrum of the raw biochar, 2:1, 3:1 and 4:1 Mg/Al-LDHs biochar composites, respectively.

Fig.2. XRD patterns of the different biochar samples.

Fig.3. Effect of solution pH on (a) phosphate adsorption and (b) equilibrium solution pH.

Fig. 4. Phosphate adsorption by different Mg/Al-LHDs biochars composites: (a) isotherms and (b) kinetics.

Fig.5. Effects of competitive anions on phosphate adsorption (a) and phosphate desorption (b).

Fig.6. FTIR spectroscopy of the 4:1 Mg/Al-LDHs biochar before and after phosphate adsorption.

Fig. 7. Schematic illustration of the phosphate adsorption process.

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