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journal homepage: [www.elsevier.com/locate/jiec](http://www.elsevier.com/locate/jiec)1 Functionalizing biochar with Mg–Al and Mg–Fe layered double  
2 hydroxides for removal of phosphate from aqueous solutions3 Q1 Stefan Wan<sup>a</sup>, Shengsen Wang<sup>b</sup>, Yuncong Li<sup>c</sup>, Bin Gao<sup>b,\*</sup>4 <sup>a</sup>A.W. Dreyfoos School of the Arts, 501 S. Sapodilla Avenue, West Palm Beach, FL 33401, United States5 <sup>b</sup>Department of Agricultural and Biological Engineering, University of Florida, Gainesville, FL 32611, United States6 <sup>c</sup>Soil and Water Science Department, Tropical Research & Education Center, University of Florida, 18905 SW 280th Street, Homestead, FL 33031, United States

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## ABSTRACT

This study examined phosphate adsorption of bamboo biochar functionalized with varying amount of Mg–Al and Mg–Fe (3:1) layered double hydroxides (LDH). Results indicated that the composite containing 40% Mg–Al LDH exhibited the highest phosphate adsorption with >95% phosphate saturation achieved within 1 h, following the pseudo-second-order kinetics model. Characterization and adsorption isotherm of this composite revealed interlayer anion exchange and surface adsorption as the predominant adsorption mechanism at low phosphate concentrations and phosphate precipitation at high concentrations. A lettuce seedling bioassay further demonstrated that the spent LDH/biochar composite can be recycled as a slow-release fertilizer to enhance food production.

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## 7 Introduction

8 Q2 Discharging water and wastewater with elevated phosphorus  
9 (P) concentrations into natural environments continues to be a  
10 global issue, posing serious threats to aquatic ecosystems and  
11 environmental quality. Sustainable environmental management  
12 requires cost-effective engineering technologies that not only  
13 remove excess P from water and wastewater but also recycle it  
14 back to the land to boost food production. Adsorption is generally  
15 considered an effective treatment technique for removal of  
16 pollutants such as P from water and wastewaters [1]. Both biochar,  
17 a pyrolytic black carbon, and layered double hydroxides (LDH), a  
18 multi-functional anionic clay, have received substantial attention  
19 in the scientific community for their abilities to adsorb chemical  
20 contaminants such as heavy metals and organic compounds [2,3].  
21 Biochar is derived from thermal conversion of woody biomass in an  
22 oxygen-limited environment. Because of its large surface area,  
23 porous structure, large cation exchange capacity, and abundant  
24 functional groups [4], biochar has been studied as both a stable  
25 sorbent matrix for environmental remediation and a soil  
26 amendment for nutrient retention and carbon sequestration  
27 [5–7]. However, biochar derived from most feedstock materials

has limited adsorption capacity to anionic nutrients including  
phosphate, partly due to its lack of positively charged metal ions on  
the surface. This has greatly hindered the use of biochar to remove  
phosphate from aqueous solutions. Thus, functionalization (engi-  
neering) of pristine biochar has become an important practice for  
expanding the environmental applications of biochar technology  
[8,9].

LDH have received considerable attention due to their  
technological importance in catalysis, separation technology,  
optics, medical science, and nanocomposite materials engineering  
[2,10,11]. LDH consist of positively charged metal hydroxide layers,  
in which the anions (along with water) are stabilized in order to  
compensate the positive layer charges. The composition can be  
generally represented as  $[M^{2+}_{1-x}M^{3+}_x(OH)_2][A^{n-}]_{x/n} \cdot mH_2O$ , where  
 $M^{2+}$  is a divalent cation ( $Mg^{2+}$ ,  $Ni^{2+}$ ,  $Cu^{2+}$ , and  $Zn^{2+}$ ),  $M^{3+}$  is a  
trivalent cation ( $Al^{3+}$ ,  $Cr^{3+}$ , and  $Fe^{3+}$ ), and  $A_{x/n}^{n-}$  is an anion with  
charge  $n$ . In general, the value of  $x$  ranges between 0.17 and 0.33.  
Because of their positively charged brucite-like sheets and  
relatively weak interlayer bonding, LDH typically exhibit excellent  
affinity to various anions such as non-metal oxyanions, anionic  
metal complexes, organic anions and anionic polymers [11–14].  
Mostafa et al. [14] recently reported that a  $Co^{+2}Mo^{+6}$  LDH exhibited  
highly energetic surface due to the formation of +4 surface charges  
in the brucite layer, thereby enhancing adsorption of lead ions.  
Many workers have studied the adsorption of phosphate onto LDH.  
To name a few, Ookubo et al. [15] were among the first to examine

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the influence of aging time of Mg–Al LDH and pH on phosphate adsorption. They indicated that the adsorption mechanism was mainly due to the displacement of intercalation anion (chloride in this case) by phosphate. Seida and Nakano [16] examined the removal of phosphate by Mg–Fe LDH in relation to the buffering pH that controlled the release of metal ions ( $Mg^{2+}$  and  $Fe^{3+}$ ). Xu et al. [17] compared adsorption behaviors of arsenate and phosphate over Mg-based and Ca-based LDHs and concluded that adsorption of the Mg-based LDH adsorbent occurred by intercalation into the interlayer spacing while that of the Ca-based adsorbent occurred through precipitation of dissolved  $Ca^{2+}$  with the anion. In general, LDH exhibit high phosphate adsorption capacities; yet the very tight layer stacking, granular or bulk forms of LDH are not suitable in filtration systems for wastewater treatment because of their low hydraulic conductivity [18].

A new area of research has recently emerged, aiming to functionalize biochar with LDH for enhanced removal of pollutants from aqueous solutions with Zhang et al. [19] and Li et al. [20] introducing liquid phase co-precipitation of Mg–Al LDH on a biochar matrix for enhanced phosphate adsorption; Xue et al. [21] examining selective adsorption of nitrate by Mg–Fe LDH modified biochar; and Wang et al. [22] reporting high arsenic adsorption onto Ni–Fe LDH–biochar composite. In spite of different biochars used, these studies, in general, suggest that selective adsorption of anionic pollutants depends on the type of LDHs used, and the adsorption mechanisms are linked to interlayer spacing and electrical properties of LDHs [20,21]. Li et al. [20] further demonstrated that the Mg/Al ratio is an important factor determining phosphate adsorption capacity of Mg–Al LDH–biochar composites. A remaining research gap along this line is how the LDH/biochar ratio would influence phosphate adsorption. In addition, the potential for P-laden LDH–biochar composites to be recycled for food production and carbon sequestration deserves further study. Therefore, the objectives of this study are to (1) synthesize Mg–Al (3:1) and Mg–Fe (3:1) LDHs onto varying amounts of biochar and compare phosphate adsorption among these LDH/biochar composites and with their unmodified counterparts; (2) examine the phosphate adsorption kinetics and isotherm of the most effective LDH/biochar composite; (3) characterize selected LDH/biochar composites with X-ray diffraction (XRD), scanning electron microscopy (SEM), and X-ray photoelectron spectroscopy (XPS) to explore the adsorption mechanisms; and finally, (4) determine if the spent, P-laden LDH/biochar composite can be used as a slow-release fertilizer to enhance plant growth. The hypothesis is that if biochar can serve as a matrix for colloidal and nanosized LDH to deposit on, then there will be a synergistic effect between LDH and biochar for enhanced phosphate adsorption and the spent LDH/biochar composites can, in turn, be reutilized as a slow-release fertilizer to increase food production, reduce soluble phosphate loss from land, and sequester carbon.

## Experimental

### Materials

Analytical grade magnesium chloride hexahydrate ( $MgCl_2 \cdot 6H_2O$ ), iron(III) chloride hexahydrate ( $FeCl_3 \cdot 6H_2O$ ), aluminum chloride hexahydrate ( $AlCl_3 \cdot 6H_2O$ ), sodium hydroxide (NaOH), and potassium dihydrogen phosphate ( $KH_2PO_4$ ) were purchased from Fisher scientific and used as received. All experimental solutions were prepared using deionized (DI) water (18.2 M $\Omega$ ) (Nanopure water, Barnstead), which was also used to rinse and clean the samples. Phosphate standard solutions were prepared by dissolving  $KH_2PO_4$  in DI water. Bamboo biomass was obtained locally as the feedstock for biochar.

### Preparation of samples

Biochar was produced from bamboo feedstock through slow pyrolysis at 600 °C for 2 h under  $N_2$  flow conditions following the procedures described by Zhang et al. [9]. Biochar was dried and milled into small pieces (2 mm) before use. The Mg-based LDH/biochar composites were synthesized by a spontaneous self-assembly method through co-precipitating mixed metal solutions of Mg and Al or Fe chloride according to the literature [19,20,23]. A 3:1  $M^{2+}/M^{3+}$  ratio was selected to avoid a massive number of LDHs in this study [20]. The pH value of 100 mL aqueous solution containing  $MgCl_2$  (0.03 mol),  $AlCl_3$  or  $FeCl_3$  (0.01 mol), and varying amount of biochar (0, 5, and 10 g) was adjusted to about 10 with 1 M NaOH aqueous solution. The obtained slurry was aged for 3 d at 80 °C, followed by separation using a Whatman Filter Paper Grade 42 (pore size = 2.5  $\mu m$ ). The solid was thoroughly washed with deionized water. The LDH/biochar sample was obtained by drying the filtrate at 80 °C in an oven. The mass of the composites was determined with an analytical balance to obtain the weight percentage of LDH in the composites. Synthesis of LDH/biochar composites was replicated twice.

### Phosphate adsorption screening test

This experiment compared phosphate adsorption among different Mg–Al and Mg–Fe LDH/biochar composites and with their parent biochar and LDH. The sorption experiment was carried out in 68 mL digestion vessels (Environmental Express) at room temperature with 50 mL solutions of 50 mg P/L and 0.1 g of each adsorbent (LDH/biochar composites with raw biochar and LDH as the control). After being shaken in a mechanical shaker at 80 rpm for 24 h, the vessel was withdrawn and the mixtures were filtered through 0.22  $\mu m$  pore size nylon membrane filters (GE cellulose nylon membrane). Phosphate concentrations of the liquid phase samples were then determined. The LDH/biochar composite with the highest phosphate adsorption from the screening test was subjected to the following adsorption batch experiments.

### Adsorption kinetics and isotherm

Adsorption kinetics of the selected LDH/biochar composite was examined by mixing 0.1 g of the sorbent with 50 mL of 10 and 50 mg P/L phosphate solutions in 68 mL digestion vessels at room temperature. The vessels were then shaken at 80 rpm in a mechanical shaker. At appropriate time intervals (5, 10, 20, 40, 60, 120, 240, 360 min), the vessels were withdrawn and the mixtures were immediately filtered through 0.22  $\mu m$  pore size nylon membrane filters for phosphate measurements. In addition, pH values of solutions were measured with a pH meter (Fisher Scientific Accumet Basic AB15).

Adsorption isotherm was determined by mixing 0.1 g of the LDH/biochar composite with 50 mL of phosphate solutions of different concentrations ranging from 5 to 600 mg P/L in the digestion vessels. The vessels were shaken in the mechanical shaker at 80 rpm for 24 h at room temperature (sufficient to reach adsorption equilibrium). The samples were then withdrawn and filtered to determine phosphate concentrations.

### Liquid to solid ratio

This experiment was carried out to examine the influence of liquid to solid ratio, an important design parameter in water quality treatment, on phosphate adsorptions by mixing 0.1 g of LDH/biochar composite with 100, 150, 300, 400 mL 2 mg P/L phosphate solutions in 600 mL vessels, shaking for 24 h in the mechanical shaker (80 rpm) at room temperature. The samples

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