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Enhancing phosphate adsorption by Mg/Al layered double hydroxide functionalized biochar with different Mg/Al ratios

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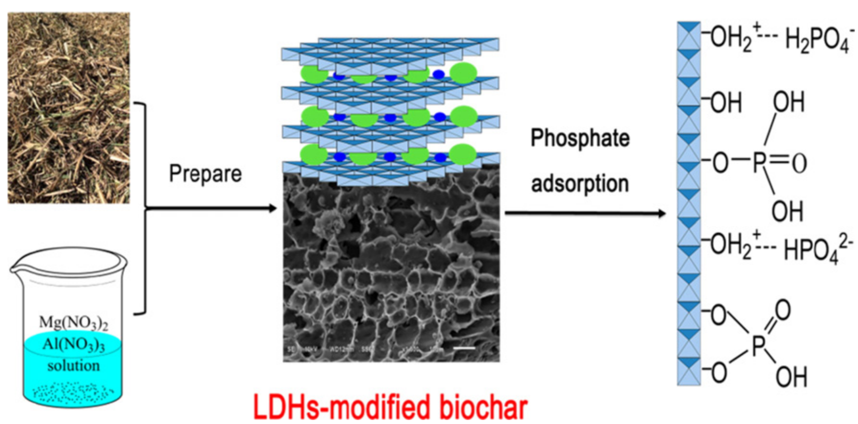
HIGHLIGHTS

- Mg/Al-LDHs modified biochar with Mg/Al ratio 2, 3 and 4 were prepared.
- Modification significantly improved biochar's phosphate adsorption performance.
- Higher Mg/Al ratio increased LDHs interlayer space and biochar phosphate adsorption.
- Adsorption maximum of 4:1 Mg/Al-LDHs biochar was 81.83 mg P/g at pH 3.
- Inorganic anions decreased phosphate adsorption in order of $F^- > SO_4^{2-} > NO_2^- > Cl^-$.

GRAPHICAL ABSTRACT



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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, 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.

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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 O_2 conditions (Ahmad et al., 2014; Xiao et al., 2015). Biochar is considered as an important carbon-rich solid biomass for bioenergy, 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 $[M^{2+}{}_{(1-\alpha)} N^{3+}(OH)_2]^{\alpha+}[A^{n-}]_{\alpha/n} \cdot mH_2O$, 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 $N^{3+}/(M^{2+} + N^{3+})$ 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 officers 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, 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 MΩ) 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 $Al(NO_3)_3$, $Mg(NO_3)_2$, KH_2PO_4, $NaNO_2$, NaF, Na_2SO_4, NaCl, NaOH, H_2SO_4, HNO_3 and H_2O_2 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 N_2 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 $Mg(NO_3)_2$ and $Al(NO_3)_3$, respectively, under stirring. The Mg/Al atomic ratio (*x*) in the solution was selected as 2, 3 and 4 based on the common $N^{3+}/(M^{2+}+N^{3+})$ 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