



Research article

Enhanced removal of phosphate from aqueous solutions using a modified sludge derived biochar: Comparative study of various modifying cations and RSM based optimization of pyrolysis parameters



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ABSTRACT

Different biochars produced by the impregnation of Mg, Ca, Al, Cu, and Fe were compared for the phosphate (P) uptake capacity and the effect on solution pH. Among them, Ca- and Mg-rich biochars demonstrate better sorption ability to P and have less effect on pH change. The optimum conditions of the pyrolysis processes were determined using response surface methodology. Comparison of the P removal efficiency of these two biochars under optimum conditions imply the superior adsorption capability of Ca-rich biochar. According to XRD analysis, calcite is the dominant mineral on the biochar surface, indicating the potential of Ca-rich biochar for P removal by adsorption and precipitation. Predictive second-order kinetic and linear Langmuir isotherm models could adequately interpret the P sorption process for optimized Ca-rich biochar. The maximum P sorption capacity of Ca-rich biochar of 153.85 mg/g is superior to other adsorbents reported in literature.

1. Introduction

Phosphorus (P) is one of the most critical elements in biological building blocks and is essential for plant growth; P also causes eutrophication in aquatic environments in excessive amounts (Hosni et al., 2008). Of all the P fertilizer applied to agricultural soil, the crop takes only a small amount, resulting in the remaining being lost to the environment via runoff and subsurface drainage (Saadat et al., 2018; Zhang et al., 2016). Growing concerns about P future availability, as well as its detrimental environmental impacts (water eutrophication), have made its capture and recovery crucial.

Various technologies have been developed for P removal, among which adsorption is believed to be the most applicable owing to its material availability and/or cost efficiency, easy operation, and eco-friendliness (Feng et al., 2017; Li et al., 2016; Shen et al., 2018). Among the various adsorbents studied for P removal, biochar, the solid product derived by pyrolysis of organic matter, has recently attracted increasing attention due to its high sorption capacity and great application benefits in many environmental fields (Cui et al., 2016; Kuppusamy et al., 2016). Ideally, the raw or phosphate-laden biochar (after heavy metal content control) can be directly applied to agricultural fields to improve soil fertility and crop productivity, therefore requiring no need for its regeneration (Yao et al., 2011).

The source of feedstock plays a significant role in the biochars'

pollutant sorption properties (Song and Guo, 2012). In recent years, sewage sludge has received considerable attention in the biochar production field. The application of sewage sludge-derived biochar apart from its main purpose, i.e. the adsorption and release of pollutants such as P, is also a potential sludge management strategy, particularly compared to current methods of landfilling and direct agricultural utilization (Hossain et al., 2011; Kuppusamy et al., 2016). Sewage sludge-derived biochar is also proposed as a valuable soil amendment due to its significant amounts of micro- and macro-nutrients, how it enhances soil water retention, soil aggregation, and aeration, and its affinity to polycyclic aromatic hydrocarbons (PAHs) (Song and Guo, 2012). However, the P removal capacity of almost all kinds of raw biochar including sludge-derived biochar is limited due to their predominantly negatively charged surface (Cui et al., 2016; Li et al., 2016).

Extensive attention has recently focused on the modification or functionalization of raw biochar to enhance its affinity towards anionic pollutants such as P and, consequently, its environmental benefits (Fang et al., 2015; Jung et al., 2015). Research has proven that impregnating or coating cationic minerals such as Mg, Fe, Al, Cu, Ca/Mg, and Mg/Al on the biochar surface either prior to or after pyrolysis could develop effective functional adsorbents and subsequently enhance the biochar's adsorption capacity for anionic pollutants (Cui et al., 2016; Jung and Ahn, 2016; Jung et al., 2016; Li et al., 2016a; Rajapaksha et al., 2016; Ren et al., 2015). However, previous studies attest the differences in the

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biochars' adsorption capacity according to the application of various feedstock types, metallic cations, and modification processes. Even when applying similar modifying agents, these variances appear. For instance, while Li et al. (2016) report that MgO-impregnated magnetic biochar removed up to 121.25 mg/g P from an aqueous solution, Cui et al. (2016) found that the maximum P sorption capacity of MgCl₂-alginate modified biochar was only 46.56 mg/g. Conversely, a porosity-enhanced biochar containing MgO nanoparticles showed a P sorption capacity as high as 620 mg/g (Jung and Ahn, 2016). Similarly, completely different P sorption capacities of 81.83 mg/g (Li et al., 2016a) and 887 mg/g (Jung et al., 2015) were observed for Mg/Al modified biochars prepared from two kinds of feedstock. Therefore, in spite of researchers' efforts to enhance the sorption capacity of biochars and despite the clear relevance of the modifying agent and the pollutant uptake capacity of biochars and their contaminant recoverability, as well as the important role of impregnated cations on the pH of modified biochar (as an important biochar property as a fertilizer), the information about the effect of modifying cations on biochars' P sorption capability is limited. In other words, no publication could be located regarding the comparison of pollutant removal ability of a biochar modified with different cationic metals to select the suitable cationic mineral for impregnation.

Available literature in this field has focused primarily on P uptake using Mg-modified biochars, although from an industrial point of view, recovery of P as calcium phosphate is more favorable than other forms (Hosni et al., 2008). A recent study by Marshall et al. (2017) applied unmodified biochar for P removal from an aqueous solution containing calcium ions. In their study, biochar successfully acted as a seed for the precipitation of calcium phosphate, yielding the maximum adsorption capacity of 37.5 mg/g. However, from the practical point of view, co-application of unmodified biochar and Ca-containing solution to farmland to recover P may be impossible. Impregnating Ca onto the biochar surface can solve the application bottleneck. Therefore, this study investigates impregnation with Ca to enhance the sorption capacity of sludge-derived biochar for P, as well as compare conventional cationic minerals studied previously.

Previous research describes the synthesis of biochar by pyrolysis and the effects of heating temperature, holding time, heating rate, type of gas and gas flow rate on pollutant. Of these factors, heating temperature and holding time significantly influence biochar quality based on scientific reports (Song and Guo, 2012; Xu et al., 2016). However, little attention is given to the optimization of important biochar pyrolysis parameters using Response Surface Methodology (RSM). RSM is a multivariate technique used for the statistical and mathematical optimization of process parameters by carrying out the minimum number of experimental trials. Therefore, more than selection of an appropriate modifying agent, optimization of pyrolysis conditions to prepare suitable biochar-based adsorbents should be considered.

With the above issues in mind, the objectives of the present study were therefore to (1) compare the P removal capability of the sludge-derived biochars modified with different types of modifying agents (Mg, Ca, Cu, Al, Fe) and investigate their effect on solution pH, (2) investigate the effects of heating temperature and holding time on the P removal ability of selected modified biochars and optimize these two important pyrolysis parameters with RSM, and (3) apply biochar impregnated with the most suitable cationic mineral and prepared under optimized pyrolysis conditions for P adsorption.

2. Materials and methods

2.1. Preparation of different modified biochars

The sewage sludge feed stock used in this study was collected from the anaerobic digester of a local municipal wastewater treatment plant. The sludge was washed several times to remove impurities, then dried at room temperature (~20 °C), crushed and passed through a 0.3 mm

sieve. To prepare modified biochar, the solutions of magnesium chloride (MgCl₂), calcium chloride (CaCl₂), copper sulfate (CuSO₄), aluminum chloride (AlCl₃), and ferric and ferrous chloride (FeCl₃ and FeCl₂) were prepared by dissolving a predetermined amount of each compound in distilled water. Subsequently, a certain amount of the dried sewage sludge sample was immersed in one of the mentioned solutions and applied for 2 h under a constant stirring condition at 60 rpm. The mixed samples were filtered and dried at room temperature to remove water content. Pyrolysis of such prepared sample occurred in a furnace at 600 °C for 3 h under an oxygen-limited condition. The obtained modified biochar samples were washed with distilled water, dried at 105 °C for 24 h, and stored in sealed containers before use. In addition, raw biochar (only pyrolyzed at 600 °C for 3 h) was also prepared to compare the modified biochar capacity.

2.2. Phosphate adsorption experiments

Batch adsorption experiments examined the adsorption efficiency of different modified biochars for recovering phosphate from aqueous solutions. The effect of modifying agents, pyrolysis time and temperature, and co-existing anions, along with adsorption kinetics and adsorption isotherms were investigated. A stock phosphate solution was prepared by dissolving K₂HPO₄ in distilled water. Initially, to compare the phosphate sorption capability of the raw and five different modified biochars, all samples were prepared at 600 °C and 0.04 g of each sorbent was added into 1 L solutions containing 40 mgL⁻¹ phosphate. The initial pH for each solution was adjusted to 7.0 before adsorbents addition and the samples were placed in a shaker operating at 60 ± 1 rpm and 25 ± 3 °C. After 24 h mixing, the biochar sample mixtures were filtered through a 0.45 μm filter and the concentration of phosphate in the filtrate was analyzed using a Hach DR/5000 spectrophotometer (USA) at 880 nm wave length. Subsequently, adsorbed phosphate amounts were calculated based on the concentration differences between the initial and equilibrium solution. The percentage of P removal from aqueous solution (%R) was calculated by using the following equation:

$$\%R = \left(\frac{C_i - C_f}{C_i} \right) \times 100. \quad (1)$$

where C_i and C_f are the initial and final concentrations of P in solution, respectively.

Based on the previous batch sorption experiment results, the biochar with higher phosphate sorption capacity (Ca-rich biochar) was selected to investigate sorption kinetics and isotherms. Adsorption kinetics of phosphate on modified biochar were evaluated by mixing a series of 0.1 g Ca-rich biochars with 50 mL phosphate solutions (pH 7, 100 mg/L phosphate). The mixtures were then shaken in the shaking incubator at 60 ± 1 rpm at 25 ± 3 °C. At appropriate time intervals, the mixtures were immediately filtered and the concentration of phosphate in the filtrates was analyzed. Phosphate sorption isotherms on Ca-rich biochar samples were examined at pH 7 with phosphate concentration varying from 30 mg/L to 600 mg/L at 25 ± 3 °C. At the end of each experiment, the suspensions were filtered, and the filtrate solution was separated for phosphate analysis. The effects of co-existing anions on phosphate removal were evaluated by mixing 0.1 g Ca-rich biochar with 50 mL of phosphate solution (pH 7, 100 mg/L phosphate) containing 0.01 M concentrations of co-existing anions (such as NO₃⁻, Cl⁻, SO₄²⁻, and HCO₃⁻). A solution without co-existing anions was prepared as blank. All samples were shaken homogeneously at 60 ± 1 rpm at 25 ± 3 °C. After 24 h mixing, the samples were filtered and analyzed for phosphate concentration. In all experiments the average value of three replicates was calculated and indicated.

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