



# Phosphoric acid pretreatment enhances the specific surface areas of biochars by generation of micropores<sup>☆</sup>

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## ABSTRACT

Biochars are being increasingly applied in soil for carbon sequestration, fertility improvement, as well as contamination remediation. Phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) pretreatment is a method for biochar modification, but the mechanism is not yet fully understood. In this work, biochars and the raw biomass were treated by H<sub>3</sub>PO<sub>4</sub> prior to pyrolysis. Due to an acid catalysis and crosslink, the micropores of the pretreated particles were much more than those without H<sub>3</sub>PO<sub>4</sub> pretreatment, resulting in the dramatical enhancement of specific surface areas of the pretreated particles. Crystalline cellulose (CL) exhibited a greater advantage in the formation of micropores than of amorphous lignin (LG) with H<sub>3</sub>PO<sub>4</sub> modification. The formation mechanisms of micropores were: (a) H<sup>+</sup> from H<sub>3</sub>PO<sub>4</sub> contributes to micropores generation via H<sup>+</sup> catalysis process; (b) the organic phosphate bridge protected the carbon skeleton from micropore collapse via the crosslinking of phosphate radical. The sorption capacities to carbamazepine (CBZ) and bisphenol A (BPA) increased after H<sub>3</sub>PO<sub>4</sub> modification, which is ascribed to the large hydrophobic surface areas and more abundant micropores. Overall, H<sub>3</sub>PO<sub>4</sub> pretreatment produced biochars with large surface area and high abundance of porous structures. Furthermore, the H<sub>3</sub>PO<sub>4</sub> modified biochars can be applied as high adsorbing material as well as P-rich fertilizer.

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## 1. Introduction

Biochars are carbon-rich materials prepared by pyrolysis under limited oxygen condition, and have attracted increased attention for potential application in carbon sequestration and soil quality improvement (Wu et al., 2013; Xiao et al., 2014). Although biochars are proposed as pollution remediation materials to adsorb various contaminants (Chu et al., 2017; Uchimiya et al., 2010), they generally have low surface area in the range of pyrolytic temperatures below 500 °C (Lian and Xing, 2017), which limited their sorption of contaminants as an adsorbent (Gomez-Eyles et al., 2013). In addition to surface area, other factors, such as pore structure, contribute to the sorptive properties (Li et al., 2017b). It is therefore useful to explore effective techniques to further optimize biochar properties

to facilitate their applications.

Various chemical treatment techniques, such as H<sub>2</sub>SO<sub>4</sub>, KOH and ZnCl<sub>2</sub> methods, have been proposed and tested to modify biochars with improved sorption capacity (Aghababaei et al., 2017; Lau et al., 2017; Xia et al., 2016). Compared to these methods, phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) treatment exhibits several advantages: relatively low pyrolysis temperature, low corrosivity to the equipment, minor pollution, and low costs (Girgis and El-Hendawy, 2002; Li et al., 2010). Previous studies have investigated the impact of H<sub>3</sub>PO<sub>4</sub> treatment on biochar characteristics, mostly on the application as adsorbent for contaminants. For instance, Fernandez et al. (2015) characterized activated hydrochars (char substrates prepared by hydrothermal carbonization) from orange peels after H<sub>3</sub>PO<sub>4</sub> modification at 600 °C. They observed better developed porosity and investigated sorption of emerging organic contaminants on hydrochars after H<sub>3</sub>PO<sub>4</sub> modification. Wu et al. (2017) studied the sorption of Cr(VI) on modified biochar from pomelo peel, and also pointed out that modified biochar possessed the developed porous

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structure after  $\text{H}_3\text{PO}_4$  treatment at 450 °C. Taha et al. (2014) studied the removal of a mixture of 15 different pesticides from water using biochars treated with  $\text{H}_3\text{PO}_4$  at 80 °C. The surface functional groups and aromatization of treated biochars was increased and pesticides could be easily removed from contaminated water using biochars treated by  $\text{H}_3\text{PO}_4$ .

These papers, however, did neither discuss possible modifying mechanisms of  $\text{H}_3\text{PO}_4$  treatment, nor the effect of precursor structural characteristics on the produced biochars. A lot of papers reported that pore structure of  $\text{H}_3\text{PO}_4$ -treated biochars was dominantly mesoporous (Guo and Rockstraw, 2006; Jagtoyen and Derbyshire, 1998). But, Zhao et al. (2017) recently reported that micropores were largely generated on modified biochars through the interaction between  $\text{H}_3\text{PO}_4$  and carbon structure. It was generally agreed that the type of pore structure depended on the nature of feedstock and pyrolysis temperature (Lian and Xing, 2017). The observation was the generation of pore structure, the decrease of pore size and the increase of porosity as a result of the escape volatile matter during carbonization (Tan et al., 2015). These pore structure in biochars plays an important role in sorption process (Chu et al., 2017). However, the discussion of which kind of pores (macro-, meso-, or micro) are central in the general sorption properties of biochars is under debate. For instance, Phueng et al. (2015) reported that the macropores ( $\geq 50$  nm) apparently have a significant effect on the water sorption capacity of the biochar. Contrarily, Li et al. (2017b) attributed the sorption capacity of biochars to mesopores (2–50 nm), rather than micropores. A third group of researchers claim that micropores ( $< 2$  nm) are central in the sorption process of inorganic and organic pollutants as reported by Pituello et al. (2015) and Liu et al. (2012).

A great deal of researches has demonstrated that sorption is an effective treatment for organic contamination in soils (Ghaffar et al., 2015; Jin et al., 2016). Carbamazepine (CBZ), an antiepileptic drug, can be frequently detected at notable concentrations in environment (Wang et al., 2013). Bisphenol A (BPA) is widely applied for plastic production and is well known for its endocrine disrupting potential (Pan et al., 2008). Both chemicals have been paid wide attention due to their health risk to humans (Gomez et al., 2007; Wanda et al., 2017). They can be discharged into the agricultural soils in different ways, including fertilization and irrigation (Knight et al., 2017; Novo et al., 2018). Therefore, CBZ and BPA were selected as representatives of organic compounds. Both chemicals were selected as the adsorbates also owing to their comparable hydrophobicity and molecular masses, but different molecular structures and functional groups (Table S1).

The main objective of this study was to illustrate the development of porous structure of the biochars as affected by  $\text{H}_3\text{PO}_4$  treatment. Specifically, different precursors of different structural characteristics will be modified and thus the mechanisms of  $\text{H}_3\text{PO}_4$  treatment will be discussed, with a major focus on the formation of porous structure of treated biochars. We hypothesize that particularly micropores are beneficial for the sorption of CBZ and BPA.

## 2. Materials and methods

### 2.1. Materials

Pine sawdust (PS), obtained from the local wood processing mill (Kunming, Yunnan, China), were used to produce biochars. The collected PS were air-dried for 3 days, oven-dried overnight at 60 °C, and then ground to pass through a 60 mesh sieve. The representative compositions of biomass, cellulose (CL) and lignin (LG), were purchased from Sigma-Aldrich Chemical Co. for biochar preparation. CBZ and BPA were purchased from Beijing Chemicals Reagent Company (Analytical grade reagents). Selected physico-

chemical properties of CBZ and BPA are given in the Supporting Information (SI, Table S1).

### 2.2. Preparation of different biochar samples

Firstly, biochar was produced at various temperatures (200, 350, 500 and 650 °C) in oxygen-limited condition. In specific, the raw materials (PS, CL and LG) were contained in a ceramic crucible and pyrolyzed in a muffle furnace for 2 h with continuous purge of  $\text{N}_2$ . The produced biochars were noted as  $\text{BC}_{\text{PS}}$ ,  $\text{BC}_{\text{CL}}$ , or  $\text{BC}_{\text{LG}}$  and the pyrolytic temperature was noted as a single number. For instance, 350 °C CL-derived biochar was noted as  $\text{BC}_{\text{CL}3}$ . The raw materials (PS, CL and LG) or the produced biochars were used as precursors for  $\text{H}_3\text{PO}_4$  treatments. The particles were immersed in 42.5 wt.%  $\text{H}_3\text{PO}_4$  solution at a ratio of 1 : 2 (g precursor/g  $\text{H}_3\text{PO}_4$ ) for 12 h (Peng et al., 2017). The mixtures of these precursors and  $\text{H}_3\text{PO}_4$  were dried and pyrolyzed at 200, 350, 500 and 650 °C for 2 h, respectively. All the pyrolysis processes were carried out under continuous  $\text{N}_2$  flow until the temperature decreased to room temperature. The charred particles were repeatedly washed with warm distilled water until constant pH values. These  $\text{H}_3\text{PO}_4$ -involved samples were noted with a suffix of “-H”, and the temperature was noted as a single number. For example,  $\text{BC}_{\text{PS}3}$ -H3 is pine sawdust-derived biochar treated with acid and then pyrolyzed at 350 °C. PS-H3 is pine sawdust treated with acid and then pyrolyzed at 350 °C. All the samples were dried in an oven at 105 °C overnight and stored in brown-colored bottles for subsequent use.

### 2.3. Characterization of the investigated biochar samples

Low-temperature  $\text{N}_2$  physical adsorption measurement is a common method for the characterization of porous structures. All the solid particles were determined by  $\text{N}_2$  adsorption at  $-196$  °C using a volumetric gas adsorption instrument (Autosorb-1C, Quantachrome, USA). Briefly, each sample was outgassed for 3 h before  $\text{N}_2$  adsorption experiment. The specific surface area (SSA) was calculated by the Brunauer, Emmett and Teller (BET) equation. The total pore volume was calculated from the amount of  $\text{N}_2$  adsorbed at a relative pressure of 0.993. The micropore volume was determined with the HK equation and the mesopore volume was calculated by subtracting the micropore volume from the total pore volume. The elemental compositions were determined using an elemental analyzer (Vario MicroCube, Elementar Company, Germany). All measurements were done in duplicate. The surface elemental compositions (specifically focused on C, O and P) were quantified by an X-ray photoelectron spectroscopy (XPS) (PHI 5000 Versaprobe-II). The functional groups were analyzed with Fourier Transformed Infrared spectroscopy (FTIR - Varian 640-IR, USA). Ash contents (ash%) of the particles were measured by heating samples at 850 °C for 4 h in air (Qian and Chen, 2013). Their total phosphorus (P) contents were extracted by 1M HCl for 16 h (Holliday and Gartner, 2007), and then measured with ICP-MS (NexION 350x, PerkinElmer, USA).

### 2.4. Batch sorption experiment

CBZ (50 mg/L) and BPA (50 mg/L) were separately dissolved in background solution as stock solutions. The stock solutions of CBZ or BPA were diluted to 9 concentrations solutions in the range of 1–50 mg/L (namely, 1.00, 1.63, 2.66, 4.34, 7.07, 11.53, 18.80, 30.66, and 50.00 mg/L). Aliquots of 4–80 mg adsorbents were mixed with the adsorbate solutions. According to our preliminary experiments, the sorption experiments were conducted in 40 mL glass vials and the solid:aqueous ratios (w:w) were in the range of 1:500–1:10000 to ensure 10–90% sorption. All the vials were kept in the dark and

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