Adsorption and desorption of phosphate on biochars

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ABSTRACT

Biochar (BC) is regarded as a potential carbon sequesterer, a soil fertility enhancer, and a preventer of nutrient leaching. Phosphorus amended biochar could enhance soil fertility. This work investigated the adsorption and desorption of phosphate from aqueous solution on two different carbonized materials. Sugar cane bagasse (SC) and *Miscanthus × giganteus*(M) samples were carbonized at various temperatures (between 300 °C and 700 °C) for residence times of 20 or 60 min. The largest surface area and the highest P adsorption at 20 °C and pH 7 was obtained for M BC prepared at 700 °C and at the longer residence time, compared to the SC BC made under the same conditions (approximately 15.5 mg g^{-1} and 12.8 mg g^{-1} for 400 mg dm^{-3} phosphate in solution, respectively). Adsorption of P on BCs was endothermic and increased with process temperature. The amount of desorbed P was proportional to its adsorption capacity. Two isotherm models (Freundlich and Langmuir) fitted the experimental results of phosphate adsorption onto the BC, and the Langmuir adsorption model described it better. Thermodynamic parameters are compared in the text with phosphate adsorption on other BCs reported in the literature. Our data suggest that adding phosphate to BC could provide a better way to apply P to soil in order to obetain better agronomic performances.

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1. Introduction

Phosphorus deficiency is a major factor restricting crop yields. This deficiency especially applies for tropical weathered soils, where the bioavailability of phosphorus (P) has a major impact on of crop production [1]. Under natural conditions, the weathering of rocks and the release of elements essential for crop growth is a slow process, and much of the P applied as fertilizer becomes fixed in forms such as calcium iron, and aluminium phosphates that are relatively insoluble and unavailable for plant growth needs. In these situations non-amended soils are capable of supporting only slow-growing vegetation and crops adapted to low soil phosphate availability.

Biochar (BC), produced by pyrolysis under limited air supply and temperatures greater than 300 °C, is applied to soil to facilitate carbon storage, the filtration of percolating soil water, and the enhancement of crop productivity. Variabilities in the properties and performances of BC are attributable to various process parameters related to its formation, such as: temperature, the residence time and the heating rate during pyrolysis [2], the feedstock [3], the particle size [4], and the method of pyrolysis [5]. The degree of alteration of the original structures of the biomass,

through microstructural rearrangement, attrition during processing, and the formation of cracks all depend upon the processing conditions to which they are exposed [6].

Piterina and Hayes [7] have shown that arbuscular mycorrhizal fungi in associations with BC can dissolve tricalcium phosphate and would make the locked P available for the plant having a symbiotic relationship with the fungus. Recognition of the properties and mechanisms of BC adsorption and desorption of phosphate applications to soil is very important for its potential uses in soil fertilizer applications. Xu et al. [8] concluded that BC application to soil altered P availability by changing the P sorption and desorption processes. These effects were dependent on soil acidity, and have important implications for improving soil productivity. The phosphorus concentration in carbonized materials vary depending on crops and growing conditions; e.g. the BC content of rice husk is 4.7 mg P g^{-1} [9], that of *Miscanthus × giganteus* (M) is 2.5 mg P g^{-1} [10], and of sugar cane bagasse (SC) is 6.1 mg P g^{-1} [11]. Residue P in BC form is readily available for plants [12].

The conditions under which BC is produced can influence its effects on P availability. As the temperature of pyrolysis increases, the specific surface area increases, and the volatile matter and surface functional groups decrease [13–15]. All those changes can influence P bioavailability. There is evidence to indicate that BC can decrease P-fixation in soil resulting in greater bioavailability of added inorganic phosphate [5,16,17]. Cui et al. [16] observed that

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the presence of BC decreased P adsorption on the Fe-oxides and thereby enhance P bioavailability. Parvage et al. [17] concluded that BC from wheat straw can act as a source of soluble P, and low and high additions of BC can have different effects on soil solution P concentration. Morales et al. [5] found that BCs, depending on how produced, can have very different P sorption and desorption properties: a BC produced by fast pyrolysis decreased the P-fixing capacity of a degraded tropical soil, whereas that formed in slow pyrolysis had the opposite effect. Xu et al. [8] found that the BC application altered the availability of P by changing the capacities of the soils to sorb and desorb P, and these effects were influenced by the soil acidity which has important implications for soil productivity. Some studies presented cation modified BCs, such as Fe [16,18], Mg [19] or La [20] which influence sorption as well as desorption properties. These cation-modified BCs enhance the sorption of P but might negatively influence the desorption of P and its plant availability.

Research on the sorption and desorption properties of BCs is still in the early stages and number of observations need to be confirmed. Most studies have worked with the capacities of BCs or of BC-complexes to adsorb. An understanding of the properties of BCs and of their influences on the mechanisms of the sorption and desorption of P is very important for a better management of soil P applications. The objective of this study was to investigate the influences on the adsorption and desorption of phosphate of the temperature and of the residence time on the carbonization process of two feedstock bio-materials.

2. Material and methods

BCs were produced by the pyrolysis of sugar cane bagasse (SC) and of *Miscanthus × giganteus* (M). The materials were air-dried and shredded into pieces ca. 2–3 cm in length. These pieces were pyrolyzed at 300, 500 and 700 °C for residence times of 20 and 60 min, and are referred to as 300/20; 300/60; 500/20; 500/60; 700/20; and 700/60 BCs, respectively. BCs were produced by slow pyrolysis in a fixed-bed reactor. The pyrolysis apparatus consisted of a temperature controller cabinet, a quartz tube reactor, and an electric furnace heater. The BCs obtained were ground, washed with deionized water, dried in a furnace at 105 °C for 24 h, and then stored in plastic containers.

The surface area was measured by N_2 adsorption using the BET surface area analyser. Ultimate analyses of BC samples were carried out with a CHNS/O analyzer (Elementar Vario LE Cube). Moisture contents of the BC samples were determined according to the standard: ICS 75.160.10, DD CEN/TS 14774-3:2004. Ash contents and volatile matter contents were determined according to ICS 75.160.10, DD CEN/TS 14775:2004 and ICS 75.160.10, DD CEN/TS 15148:2005, respectively. A Fourier transform infrared spectrometer (FTIR) (Cary 630 FTIR spectrometer, Agilent Technologies Inc.) with the resolution of $4\,cm^{-1}$ and 64 scans per sample was used to collect spectra in the range of $600-4000\,cm^{-1}$. Samples of 300/60, 500/60 and 700/60 SC BCs were selected before and after adsorption (BCs residual solids from $100\,mg\,P\,dm^{-3}$ at pH 7). A preliminary study showed that SC and MC BCs were similar in their peaks and absorbance, and no differences were found between residence times of 20 and 60 min for the same pyrolysis temperature.

Determination of zeta potential was carried out for all BCs. To each sample (0.2 g) 100 ml of de-ionized water at pH 6.5 was added. The change in the zeta potential from P adsorption was tested by adding also 0.2 g of 500/60 M BC, with or without the addition of P solution ($100\,mg\,P\,dm^{-3}$) to each flask, when the pH of suspensions had been adjusted to within 3.0 to 8.0 with NaOH or HCl. Then the analysed solutions were shaken at 250 rpm for 30 min using a mechanical shaker. The suspensions were dispersed ultrasonically for 1 h at 30 ± 1 °C in a bath-type sonicator at a frequency of 40 kHz and a power of 300 W. After that the solution was filtered using a filter paper (Whatman 42 filter paper). The zeta potential of each supernatant solution obtained was determined using a Malvern Zetasizer Nano (Malvern Instruments).

To study the effects of pH, 0.2 g of 500/20 SC and of M BC was mixed with $100\,cm^3$ of solution containing $100\,mg\,KH_2PO_4$. The pH of the solutions were adjusted to values of 3–10, before adding the biochar, using a PHM 84 pH meter (Radiometer, Denmark) with glass REF 451 and calomel pHG 201-8 electrodes. A separate set of experiments was set up for each pH measurement. The suspensions were agitated on a shaker at 250 rpm and 25 °C for 24 h. Each sample was filtered through a 0.5-μm syringe filter and the pH of the filtrate was measured.

For the different phosphate adsorption experiments, to BC (0.2 g in a conical flask) was added $100\,cm^3$ of phosphate solution each containing: 25, 50, 100, 200 and $400\,mg\,P\,dm^{-3}$ at pH 7 (the pH values were adjusted by adding HCl or NaOH ($0.1\,mol\,dm^{-3}$)). An initial study indicated that equilibrium for the adsorption of inorganic P was attained in a matter of minutes. Nevertheless the suspensions were agitated on a shaker at 200 rpm and 25 °C for 24 h. The suspensions were filtered through a 0.5-μm paper filter. The phosphate contents of the filtrates were meansured, and the solids were collected for measurements of phosphate desorption. The experiments were carried out in triplicates and the BCs from each sample were combined for the desorption experiments.

For desorption, to BCs residual solids (0.2 g) from each phosphate concentration applied were added to $100\,cm^3$ of $0.01\,mol\,dm^{-3}$ of citric acid in a conical flask, and the suspensions were agitated for 24 h on a shaker at 200 rpm and 25 °C. Samples were filtered as described for the adsorption experiments and the phosphate concentrations in solution were determined.

The equilibrium adsorption capacity was calculated using Eq. (1)

$$q_e = \frac{V(C_e - C_0)}{m} \qquad (1)$$

where: q_e is the adsorption capacity at equilibrium ($mg\,g^{-1}$), V the volume of solution (dm^3), C_0 and C_e are the initial and equilibrium concentrations of phosphate ($mg\,dm^{-3}$), and m is the weight of adsorbent (g).

Phosphate concentrations were determined using a UV–vis-4000, Varian Spectrophotometer, using the stannous chloride method [21]. Each experiment was carried out three times, and mean values are presented. Differences between sorption for BCs in each treatment were tested for significance using a factorial analysis of variance and Duncan's multiple range tests. Differences are reported as significant at $p < 0.05$.

The adsorption data of the phosphate on the BCs were analyzed using the Langmuir and Freundlich isotherm models. The Langmuir model, described Eq. (2) [22] is.

$$q_e = \frac{(k_L \times C_e)}{(1 + q_m \times C_e)} \qquad (2)$$

where: C_e is the equilibrium concentration of phosphate (mg dm^{-3}), the constant q_m ($mg\,g^{-1}$) and K_L are the characteristics of the Langmuir equation ($dm^3\,mg^{-1}$) and can be determined from the linearized form (plots of C_e/q_e vs. C_e). The Freundlich model is expressed by Eq. (3) [23]:

$$q_e = K_F \times C_e{}^n \qquad (3)$$

where: K_F is the Freundlich adsorption capacity ($mg\,g^{-1}$), n is the Freundlich constant. The above equation can be linearized to calculate the parameters K_F and n (plots of $\log q_e$ vs. $\log C_e$).