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Research article

Poultry manure and sugarcane straw biochars modified with $MgCl_2$ for phosphorus adsorption

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ABSTRACT

Increases in agricultural productivity associated to the crescent use of finite reserves of phosphorus improved the demand for ways to recycle and reuse this nutrient. Biochars, after doping processes, seem to be an alternative to mitigate the large use of P reserves. Sugarcane straw and poultry manure were submerged in an $MgCl_2$ solution in a 1:10 solid/liquid ratio and subsequently pyrolyzed at 350 and 650 °C producing biochar. Increasing concentrations of P were agitated with biochars in order to obtain the maximum adsorption capacity of P with the aid of Langmuir and Freudelich isotherm. MPAC was extracted, successively, with H_2SO_4 (0.5 mol L^{-1}), $NaHCO_3$ (0.5 mol l^{-1} a pH 8.5) and H_2O, until no P was detected in the solution. Biochars without the addition of Mg did not have the ability to adsorb P but had this property developed after the doping process. The poultry manure biochar presented higher MPAC (250.8 and 163.6 mg g^{-1} of P at 350 and 650 °C, respectively) than that of sugarcane straw (17.7 and 17.6 mg g^{-1} of P at 350 and 650 °C, respectively). The pyrolysis temperature changed significantly the MPAC values for the poultry manure biochar, with an increase in the adsorbed P binding energy for both biochars. H_2SO_4 showed the best extraction power, desorbing, with a lower number of extractions, the greater amount of the adsorbed P. These materials doped with Mg and subjected to pyrolysis have characteristics that allow their use in P adsorption from eutrophic and wastewaters and therefore its use as a slow release phosphate fertilizer, indicating to be competitive in quality and quantity with available soluble chemical sources in the market.

1. Introduction

Increases in population associated with the consequent increase in the demand for food and reduction of the finite reserves of phosphorus (P), have generated great concern in agriculture, mainly with regard to the increasing use of phosphate fertilizers. Particularly in tropical soils, where reduced levels of available P are associated with elevated levels of Fe and Al oxyhydroxides, large doses of phosphate fertilizers are necessary for high yields, directing the main focus of this concern to agriculture-based countries such as Brazil (Roy et al., 2016).

P recycling and reusing strategies have thus become recently studied (Drenkova-Tuhtan et al., 2016; Fink et al., 2016). The reuse of P can be achieved by immobilization, from the locations where it previously caused an environmental problem, such as in eutrophic or wastewater, for later use as phosphate fertilizer in agriculture. Eutrophic waters, according to CONAMA (2005), have values equal to or greater than 0.025 mg L^{-1} of P, but in some countries this value is not permitted to exceed 0.020 mg L^{-1} (Klein and Agne, 2013).

Among several approaches aiming at P reuse, biochar can be used as a P adsorbent. Biochar is the product formed by pyrolysing vegetable or animal residues at high temperatures and under hypoxic conditions (Lehmann and Joseph, 2015). Previous studies, however, have proven that biochars without any additional treatment have very low or none P adsorption capacity (Jung et al., 2015; Cui et al., 2016), due to its behavior as a "great anion", with a high proportion of carboxylic and phenolic groups, which prevents the adsorption of anions such as phosphates (Agegnehu et al., 2016).

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Enhanced biochar P adsorption capacity can be achieved through the "doping" treatment. This procedure consists in adding metallic cations, such as Mg^{2+} and Ca^{2+}, to the raw material. These cations are precipitated onto the surface of the biochar during the pyrolysis reaction, creating cationic bridges that can adsorb anions such as phosphate (Jing et al., 2015).

Doped biochars have high capacity for P adsorption and can be efficiently used in P recovery from eutrophic or wastewater. Cui et al. (2016) observed that although untreated biochar did not adsorb P, even at high P concentrations (50 mg L^{-1} of P), the doping process with $MgCl_2$ reached 98.3% removal of P from a eutrophic water, which contained 1.82 mg L^{-1} of P. Jung and Ahn, 2016 observed an increase of almost six times in P adsorption by a biochar doped with $MgCl_2$ and Yu et al. (2016) reported a maximum P adsorption capacity (MPAC) of 129.9 mg g^{-1} with a biochar from cotton pyrolyzed at 600 °C and doped with $MgCl_2$.

Variations in MPAC depends on the pyrolysis process and the raw material characteristics. The increase in temperature leads to an increase in surface area, in C content and reduces H content, leading to an increase in P adsorption, besides increasing K_L and K_F values (Langmuir and Freudelich isothermic constants respectively), proportionally associated with adsorption energy (Fang et al., 2015). Fang et al. (2014) reported an increase in adsorption of 2.5, 5.0 and 6.2-fold after doping with Mg at pyrolysis temperatures of 300, 450 and 600 °C, respectively. Fang et al. (2015) reported MPAC of 293.2, 315.3 and 326.6 mg g^{-1}, respectively, for a biochar doped with Ca and Mg and pyrolyzed at 300, 450 and 600 °C. A 1.1-fold increase in the K_L constant and a 1.3-fold increase in the K_F constant, with the temperature increase from 300 to 600 °C were observed.

Additionally, raw material characteristics and the properties of its respective biochar after pyrolysis reaction influence MPAC. Biochar produced at lower pyrolysis temperature will have properties similar to those of their respective raw material, while higher pyrolysis temperature causes greater changes in biochar's properties, with little resemblance to its original material, but to grafite (Lehmann and Joseph, 2015). The doping treatment is affected by the stability of the original material. In this sense, unreactive materials produce biochars with lower MPAC when compared to biochars derived from reactive materials. Zhang et al. (2012), observed a high variation in MPAC when studying biochars of five raw materials doped with Mg under electric field. The highest adsorption was obtained for biochar from sugarcane beet tailings (835 mg g^{-1}), followed by those from cotton, sugarcane bagasse and pinus bark. The lowest MPAC was obtained with biochar from pinus bark (3.17 mg g^{-1}). This variation was consistent with the surface area of the biochars produced, with the lowest specific surface area observed for pinus bark (2.8 m^2 g^{-1}) and the highest (122.5 m^2 g^{-1}) for sugarcane bagasse.

There are some works that modify biochar with Mg for P adsorption with positive response (Sizmur et al., 2017), but few look after its possible reuse in agriculture or what to do with the material after de recovery of P in waste waters. Thus, the present work aimed at the production and characterization of biochars from sugarcane straw and poultry manure, doped with $MgCl_2$ and pyrolyzed at 350 and 650 °C, as well as the determination of their MPAC values and their abilities to release adsorbed P.

2. Material and methods

2.1. Raw material selection

The raw materials used were sugarcane straw, collected from a plantation in Piracicaba-SP and poultry manure collected from the University of Sao Paulo farm (ESALQ-USP). The raw materials were selected because of their contrasting physical and chemical attributes, permitting the investigation of the effects of contrasting materials on P adsorption capacity. In addition, the high production of these residues and their accumulation in the field have created a management problem for many companies.

2.2. Biochar production

The raw materials (sugarcane straw and poultry manure) were immersed in a solution of $MgCl_2$ (60 g $MgCl_2 \cdot 6H_2O$ in 90 mL of deionized water) in a proportion solid: liquid of 1:10 and incubated for 2 h, as suggested by Jung and Ahn (2016). The material was dried in an oven at 80 °C for 3 h and pyrolysis was carried out by SPPT Research Technologies, in a metallic reactor, under a N_2 atmosphere, heating rate of 10 °C/min for the first 30 min and 20 °C/min until the final temperature. The untreated raw materials were pyrolyzed under the same conditions. This process is called post-pyrolisis modification, since the doping process was carried out before the pyrolysis.

Two pyrolysis temperatures were used, 350 and 650 °C. The main physical and chemical changes of raw biomass are carried within this temperature range and largely affect the final characteristics of biochars, generating products with contrasting attributes (Novotny et al., 2015).

After processing, eight biochars were produced: sugarcane straw pyrolyzed at 350 °C (BCS 350 °C); sugarcane straw pyrolyzed at 650 °C (BCS 650 °C); sugarcane straw pyrolyzed at 350 °C and doped with $MgCl_2$ (BCS-Mg 350 °C); sugarcane straw pyrolyzed at 650 °C and doped with $MgCl_2$ (BCS-Mg 650 °C); poultry manure pyrolyzed at 350 °C (BPM 350 °C); poultry manure pyrolyzed at 650 °C (BPM 650 °C); poultry manure pyrolyzed at 350 °C and doped with $MgCl_2$ (BPM-Mg 350 °C) and poultry manure pyrolyzed at 650 °C and doped with $MgCl_2$ (BPM-Mg 650 °C).

2.3. Biochars characterization

Chemical and Physical analyses followed the methodology recommended by the International Biochar Initiative Guideline (IBI, 2015) and are thoroughly described in Conz et al. (2017) and were previously done in Novais et al. (2017). The crystallography of biochars was carried out using X-ray diffraction (LabX, XRD-6000, Shimadzu X-ray Diffractometer) with a scanning angle between 4 and 70° 2θ (λ 0.02 °s^{-1}). Biochars were investigated in infrared spectroscopy (ATR/FTIR-4100, Jasco, Fourier Transform Infrared Spectrometer). Finally, the biochars were coated with gold (SCD 050 Sputter Coater, Bal-Tec) and photographed using a scanning electron microscope-SEM (EVO 50, Carl Zeiss). Qualitative analysis of the chemical composition was performed using X-ray dispersive energy and EDS-Energy Dispersive Spectroscopy (500 Digital Processing, IXRF Systems).

2.4. Adsorption isotherms

Each point of the adsorption isotherm consisted of 0.15 g of doped or undoped biochar and 75 mL of KH_2PO_4 solution as raw of P. Increasing concentrations of P, ranging from 0 to 1500 mg L^{-1} (0; 10; 25; 50; 75; 100; 150; 200; 250; 375; 500; 560; 620; 750; 850; 1000; 1250; 1500 mg L^{-1}) for biochar from poultry manure and 0–1000 mg L^{-1} (0; 10; 25; 50; 75; 100; 150; 250; 500; 750; 1000 mg L^{-1}) for biochar from sugarcane straw. Biochar and the respective P solution were shaken in horizontal stirrer, for 24 h, at 120 rpm, and the solution was filtered through a Whatman filter paper (white band). The P in the filtrate was read in a UV/VIS spectrophotometer, λ 720 nm (600 Plus, FEMTO), allowing the adjustment of the adsorption curves, plotted from Langmuir