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Phosphorus removal from eutrophic water using modified biochar

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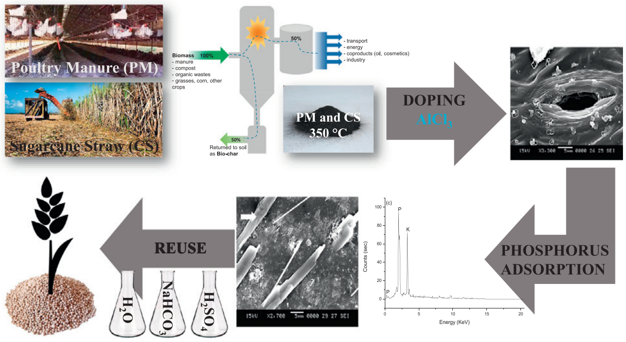
HIGHLIGHTS

- Biochars do not have P adsorption capacity without pre-treatment.
- Doping process with $AlCl^3$ conceded P adsorption ability.
- Al^{3+} binds to the carboxylic groups of the biochar.
- Doped biochars can be used in eutrophic water recovery.
- Doped biochars and in their MPAC can be used in agriculture.

GRAPHICAL ABSTRACT



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ABSTRACT

Increasing problems related to water eutrophication, commonly caused by the high concentration of phosphorus (P), are stimulating studies aimed at an environmentally safe solution. Moreover, some research has focused on the reuse of P due to concerns about the end of its natural reserves. Biochar appears to be a solution to both problems and may act as a recovery of eutrophic/residual water with the subsequent reuse of P in agriculture, the purpose of which is to test such an assertion. Samples of biochar from poultry manure (BPM) and sugarcane straw (BCS) had their maximum adsorption capacities of Al obtained by Langmuir isotherm. These values were used to conduct the so-called post-doping process, conferring P adsorption capacity to the pyrolysed materials. Langmuir and Freundlich isotherms were adjusted for the same biochar types (Al-doped) at increasing P concentrations, in order to obtain their maximum P adsorption capacities (MPAC) and their parameters. The desorption of the adsorbed P in its MPAC was tested by three extractors: H_2SO_4, $NaHCO_3$, and H_2O. Finally, these biochars were used in competitive adsorption assays of phosphate, sulfate, chloride and nitrate anions and applied in a synthetic eutrophic water. The high values of MPAC of the powder materials (701.65 and 758.96 mg g^{-1} of P for BPM and BCS, respectively) are reduced by almost half for the fragment materials (356.04 and 468.84 mg g^{-1} of P for BPM and BCS, respectively), these values being almost entirely extracted the extractors. Its application in eutrophic/residual water, in addition to presenting a good MPAC, these materials adsorbed, in equal proportions, phosphates and sulfates, as well as to a lesser extent, nitrates and chlorides. Thus, biochar from poultry manure and sugarcane straw, after post-doping with Al, have high MPAC, being excellent materials for the recovery of waters and subsequent reuse in agriculture.

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1. Introduction

Increasing concerns regarding the exhaustion of P natural reserves, after estimates for its end by 2050 (Gilbert, 2009), have caused researchers to seek the reuse or recycling of this element, reducing somewhat the apprehension generated, mainly around its use as fertilizer in tropical soils, which are so poor in P.

Adsorption techniques have been used for several years for the recovery of eutrophic water, which predispose the high growth of microorganisms and aquatic plants, causing a rapid consumption of oxygen, with the subsequent death of the aquatic fauna. Adsorbent materials such as Fe and Al oxyhydroxides are commonly used because of their low cost and easy handling in water quality recovery (Jan et al., 2015; Jones et al., 2015).

Recently, several authors have focused on biochar as a source of study for this purpose in several experiments. The biochar generated after the pyrolysis of plant or animal residues is characterized by several soil benefits, such as increased physical qualities, increased microbial biomass, and soil organic carbon, as well as xenobiotic removal, acting to recover contaminated environments (Lehmann et al., 2015). In addition to these positive aspects, the modified biochar has been shown in a number of papers as a potent adsorbent of P, which can act in the recovery of eutrophic waters (Yao et al., 2013; Jung et al., 2015a; Cui et al., 2016; Takaya et al., 2016). Thus, the P of eutrophic and residual water can be reused. The recovery of this P in solution/suspension and its subsequent application to the soil as a phosphate fertilizer is becoming an increasingly widespread idea, thus closing a cycle of P utilization, which addresses not only the problem but also ensures its reuse, thus increasing the time for the exhaustion of world reserves of phosphate rocks (Trazzi et al., 2016; Roy et al., 2016).

Nevertheless, such a scenario is not as simple, and to close this reuse/recycling cycle as desired, some biochar modification techniques are needed. The biochar, due to the large amount of phenolic and carboxylic groups and a high proportion of fulvic and humic acids, is seen as a large anion (Jing et al., 2015) which, without previous treatment, would not be able to adsorb significant amounts of phosphate. A technique called "doping," which consists of saturating the biochar with a metal cation, making it an "anionic adsorbent," ensures its electropositivity, allowing the material to adsorb anions, no longer repelling them. A number of cations are used for doping, with Mg^{2+} and Ca^{2+} being more commonly used due to their low cost and easy handling (Yao et al., 2013; Zhang et al., 2013; Jung and Hong, 2016; Jung et al., 2016).

Jung and Hong, 2016 found an adsorption of 3.7 and 8.3 mg g^{-1} of P in the source material (seaweed) and the biochar of this pyrolyzed material at 600 °C, respectively. The adsorption value rises to 16.1 mg g^{-1} of P in this material after doping with $MgCl_2$, increasing to 19.8 mg g^{-1} by subjecting the same doped biochar to an electric field. The electric field increases the surface area and amount of micropores, promoting more adsorption sites of P. Jung et al., 2016, in another work, using biochar from seaweed pyrolyzed at 600 °C and doped with Ca found a P adsorption of 63.3, 94.5 and 127.5 mg g^{-1}, after maintaining the adsorption temperature at 10 °C, 20 °C and 30 °C, respectively. In the adsorption/desorption work, Yao et al. (2013) find a maximum P adsorption capacity (MPAC) greater than 100 mg g^{-1} of P in the Mg-doped tomato leaf biochar and a desorption of 7.55 mg g^{-1} of P in the material extracted with Mehlich-3. The value recovered accounts for 19% of the total amount adsorbed, this value being higher than the concentration found in many phosphate fertilizers and sufficient to meet the demand of the plant. The authors confirmed this fact after finding a germination of 53–85% higher in seeds that received the doped biochar as a source of P. These procedures, characterized by saturating the material to be pyrolyzed with metal cations, following the pyrolysis process normally after immersion of the material in a solution of Mg or Ca in excess (pre-pyrolysis doping). Nevertheless, some authors propose that the doping process should be done after complete pyrolysis, i.e. following production of the biochar, using cations such as Al^{3+} or Fe^{3+} (post-pyrolysis doping). Such a procedure, according to Jung et al. (2015b), would lead not only to a reduction in the time of production of the modified biochar, but also to an increase in its physical and chemical qualities, such as an increase in surface area and production of AlOOH nanoparticles. These authors found a MPAC of 647 mg g^{-1} of P after 8 h of reaction with the Al-doped seaweed biochar, which is much higher than that found in other experiments using the pre-pyrolysis doping process. Contrarily, Zhang and Gao (2013) found a MPAC of 1.35 and 17.41 mg g^{-1} of P and As, respectively, with $AlCl_3$-doped biochar, conducing the pre-pyrolysis process.

Nevertheless, such situations occur in an ideal environment where there is no competition between anions for the adsorption sites, and MPAC values are usually reduced by including other anions in the solution. Dai et al. (2014) found a small reduction (3.02%) in the MPAC by adding 0.1 mol L^{-1} of Cl^-, NO_3^- and SO_4^{2-} with 100 mg L^{-1} of P, and SO_4^{2-} was the one that presented greater affinity in the exchange sites due to their greater valence and predominance of covalent bonds. Cai et al. (2017) observed a reduction in P removal of 59.9% and 72.5% after addition of 0.15 and 0.50 mmol L^{-1}, respectively, of arsenate and a reduction of 26.2% and 40.2% on the P adsorption by adding $HCO3^-$ at the same concentrations. The addition of NO_3^- and SO_4^{2-} did not significantly reduce the P adsorption. The high adsorption of As by the Fe-doped biochar leads the authors consider their removal in conjunction with P in water decontamination.

These techniques are being increasingly studied, aiming at the day when the use of these materials can become routine, not only as a means to recover eutrophic/residual water, but also to mitigate another major problem: the exhaustion of the natural reserves of P. Thus, the purpose of this paper was the production of Al-modified biochars from sugarcane straw and poultry manure doped by the post-pyrolysis process. The determination of adsorption and desorption isotherms of P in a pure solution and with competitive anions was also the subject of this paper, closing a cycle of adsorption (recovery of eutrophic and residual water) and desorption (reuse of P adsorbed as phosphate fertilizer).

2. Material and methods

2.1. Selection of raw materials for biochar production

Two raw materials were selected according to their contrasting characteristics and their large production, often being an environmental problem: poultry manure (PM), collected at a farm called Frango Feliz, located at ESALQ-USP, and sugarcane straw (CS) from a sugar/ethanol production site in Piracicaba, SP.

2.2. Biochar production

The pyrolysis process was performed by the SPPT company in a metallic reactor, in an atmosphere saturated with N_2, raising the temperature by 10 °C every minute in the first 30 min and then at 20 °C every minute until the desired temperature was reached.

Two pyrolysis temperatures – 350 °C and 650 °C – were used based on values mentioned in the literature and because they cover the main phases of transformation of the raw material, being responsible for its changes and for the characteristics of the biochar produced. Temperatures below 350 °C are considered as torrefaction rather than pyrolysis, while pyrolysis above 650 °C results in reduced biochar production (Crombie et al., 2015).

2.3. Characterization of the material

Chemical and microbiological characterizations of these materials were previously done on Novais et al., 2017.