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Polymeric Alginate Microspheres Containing Biochar to Immobilize Phosphate Ions

Murilo T. Domingues[*a], Carolina C. Bueno[a], Cláudia H. Watanabe[a], Leonardo F. Fraceto[a], Juan C. Loyola-Licea[c], David Crowley[b], André H. Rosa[a]

[a] Department of Environmental Engineering, Sao Paulo State University, Sorocaba, SP, Brazil
[b] Department of Environmental Sciences, University of California – Riverside
[c] Instituto Tecnológico de Saltillo – México
murilo.mtd@gmail.com

The use of fertilizers with slow releasing rates in agricultural practice has proven to be a viable and sustainable practice to increase the efficiency of nutrient elements assimilation by crop plants. In this context, the present study is based on the preparation, characterization, and performance evaluation of polymeric alginate microspheres, or beads, containing biochar for the immobilization and slow release of orthophosphate. To achieve this objective, biochar was prepared from the pyrolysis of sugarcane bagasse at different temperatures (300 - 700 °C) under nitrogen atmosphere. The biochar material and three kinds of microspheres (with biochar, phosphorus and alginate; alginate and phosphorus; only alginate) were analysed by FT-IR to identify the functional groups present. The results show changes in the functional groups in biochar and a difficulty to characterize the microspheres by this method. The quantification of the phosphate ions release over time, from microspheres containing biochar, was evaluated by comparing the control experiments, without biochar, using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). It was found that microspheres with biochar and phosphorus had a higher releasing rate, twice than those without biochar. Besides being a good procedure to provide nutrients to plant, the microsphere system can also be an excellent water resource to the plant and a good restorer of the soil pH when it is acid. Then, these preliminary results open a new multidisciplinary perspective for the use of biochar, and suggest opportunities for incorporation of biochar into slow releasing fertilizers, that may enable the usage of smaller amounts of fertilizers and improve the fertilizer efficiency.

1. Introduction

The human population growth continuously demands the development of new procedures to improve the agricultural productivity, with a constant concern to avoid both financial resources and nutrients waste during soil management. In 2050, it is expected that the world population reaches around 9 billion people and food production should grow about 70 % globally, to support the expected demographic increase (FAO, 2011). To maximize their production and respond to this situation, producers will need either higher quantities of fertilizers, improved fertilizers' delivery systems, or other strategies to provide the crops with the nutrients used by their metabolism. Under this scenario, not only land and water will gradually be less available, but also the global deposits of phosphate rock, which soon may represent a limiting factor for several human activities, including agriculture. Hence it is very important to develop systems to provide the crops with optimum amounts of nutrients and water. In this way, the waste of nutrients and a potential environmental pollution can both be avoided.

The essential macronutrients for the development of plants are phosphorus, nitrogen, potassium, calcium and magnesium. Currently, around 40 % of nitrogen, 80-90 % of phosphorus, and 50-70 % of potassium used as fertilizers are not assimilated by the plants but lost in the environment, causing serious environmental problems (Malavolta, 2006). Therefore, efficient nutrient release systems, aimed at

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improving the crop efficiency, can also reduce the fertilizers usage volume and the surface water contamination.

According to Zhao et al. (2010), most studies on the slow nutrients release have been performed regarding nitrogen, whereas there are few studies of modified release of other macronutrients, such as phosphorus, and micronutrients for the soil (Botero et al., 2010). While inorganic phosphorus is found in rock sediments around the Earth (Schlesinger, 1991) (Föllmi, 1996) (Smil, 2000), only three countries control more than 85% of the known global phosphorus reserves (Van Kauwenbergh, 2010 *apud* Elser and Bennett, 2011).

The poor mobility of soil inorganic P is due to the large reactivity of phosphate ions towards Ca, Fe and Al ions. The pH, the concentrations of anions that compete with P ions for ligand exchange reactions and the concentrations of metals (Ca, Fe and Al) influence the speciation of soil P by adsorption/desorption and precipitation/dissolution reactions and, thereby, its chemical mobility and bioavailability (Hinsinger, 2001).

The material studied in this investigation is a composite organic/inorganic system, prepared from sugarcane derived-biochar, encapsulated within alginate beads as the control releasing system, and orthophosphate. It is relevant to mention that a variety of materials have been employed as nutrients releasing systems, such as various polymeric materials (Bogdansky, 1990), dendrimers (Kono, 2002), microspheres formed of organic material (Soppimath et al., 2001), cyclodextrins (Matioli, 2000), hydrogels (Rui et al., 2007) (Lan & Mingzhu, 2008), clays (Mangrich, 2010), and biodegradable polymers (Zhao et al., 2010).

Biochar is produced by the process of heating biomass in the absence, or under low concentration of oxygen known as pyrolysis. Biochar has recently attracted the attention as a soil amendment material due to high soil fertility found in some organic soils in Brazil (Grossman, 2010), with explanatory hypothesis of such increase in fertility based on the cations exchange capacity of the biochar, the increase in the habitats for the soil microflora, and prolonged water retention within the micro- and mesopores of the material (Liang et al., 2006) (Lehmann, 2007). Furthermore, it has been noted that soil pH can be modified by adding biochar, as Van Zwieten et al (2010) reported, with an increase in pH when added to acidic soils.

The purpose of this paper was to evaluate the phosphate release rate from a composite system of polymeric alginate microspheres, with the addition of biochar derived from sugarcane bagasse.

2. Methodology

2.1 Biochar preparation

The biomass of sugarcane was harvested *in nature,* peeled off and its juice extracted in order to obtain the bagasse. The sugarcane bagasse was washed with deionized water and dried at 75 °C for two hours. The pyrolysis process was performed in an electrical oven (EDG F 1800, 3P), within which a reaction chamber was placed. About 400 g of dried biomass were fitted in a cylindrical stainless steel reaction chamber, with a volume of 2,016 cm^{-3}, adapted with a stainless steel “spear” through which Nitrogen gas was injected at a rate of 0.5 L min^{-1}. The heating rate of the oven was set to 25 °C min^{-1}. The pyrolysis process took place following this program: An initial ramp from room temperature to 100 °C; 100 °C for 15 min; ramp from 100 °C to target temperature (300, 450, 700 °C); target temperature for 2 hr.; ramp from target to room temperature. Nitrogen was introduced during the whole program, but for some samples the gas flow rate was reduced to 0.25 L min^{-1} during the cooling ramp, after the oven reached 100 °C or a colder temperature. The oxygen content within the reaction chamber was estimated to be very low after the initial ramp, with about 10 litres of nitrogen introduced in the first 20 minutes, into a 2 L reactor mostly containing organic matter, but with some open spaces filled with air. Sugarcane samples were processed at 300, 450 and 700 °C (B-300, B-450 and B-700, respectively). Obtained biochar was then crushed and sieved down to diameters of 0.25, 0.45, and 0.85 mm. The pH of each biochar sample was measured in $CaCl_2$ solution (0.01 mol L^{-1}) according to Forster (1995).

2.2 Microsphere preparation (Alginate-biochar-phosphate)

Polymeric microspheres containing potassium phosphate (KH_2PO_4) were prepared with 0.5 g of biochar (300, 450 and 700 °C) and 50 mL of KH_2PO_4 (50 mg L^{-1}) solution and then stirred for an hour. Preliminary assays showed that B-450 biochar particles smaller than 0.250 mm had better homogenization in alginate solution, consequently this system had a higher incorporation of phosphate ions (previous investigation, data not shown). Considering it, B-450 biochar was chosen for testing phosphorus release. Microspheres prepared for slow P-release were distributed in Treatment A (0.5 g of B-450 and 50 mL of KH_2PO_4 solution) and Treatment B or control, a solution containing only 50 mL KH_2PO_4 (Table 1). In the next preparation step, 50 mL of sodium alginate solution (2 % m V^{-1}) was added and stirred for an hour. The final suspension was added drop wise to a $CaCl_2$ solution (20 % m m^{-1}) using a peristaltic pump, which allowed the formation of polymeric microspheres.

Table 1: Biochar and phosphate content in alginate beads (microspheres)

Treatment	Biochar B-450	KH_2PO_4 solution
A	0.5 g	50 mL
B	0.0 g	50 mL

Three other kinds of microspheres were also synthesized: i) alginate-biochar-phosphorus (10 mL of alginate solution (2 % m V^{-1}), 10 mL of phosphorus solution (50 mg L^{-1}) and 0.1 g of B-450); ii) alginate-phosphorus (10 mL of alginate solution (2 % m V^{-1}) and 10 mL of phosphorus solution (50 mg L^{-1})); iii) alginate (10 mL of alginate solution (2 % m V^{-1}) and 10 mL of deionized water). The solutions (i, ii and iii) were then stirred for an hour and dropped into a $CaCl_2$ solution to form the microspheres.

2.3 FTIR characterization

Samples of biochar (B-300, B-450 and B-700) were crushed and sieved (diameter < 0.250 mm), and analysed to observe changes in chemical functional groups. The microspheres i, ii and iii (described in section 2.2) were dried overnight at 65 °C, ground and also analysed. All spectra were collected from 4,000 to 400 cm^{-1} using 8 cm^{-1} spectral resolution and 32 accumulations for each sample using a FT-IR Spectrometer (Varian 660-IR). The sample discs were prepared by mixing 3 mg of biochar into 97 mg of KBr.

2.4 Essay for the slow releasing of phosphate

For the phosphate release experiments, 1 g of microspheres were placed into 100 mL of deionized water, and 1 mL aliquots were collected at time 0, 5, 15, 30, 60, 120, 240, 480, 1,440 and 2,880 min. These samples were then used for phosphorus quantification by optical emission spectrophotometry using inductively coupled argon plasma (ICP-OES - Agilent Technologies 700 series). Measurements were carried out in duplicate and the variance between any measurements in this study was calculated to be smaller than 5 %.

3. Results

It was observed that pH increased along with the temperature used for biochar preparation (Table 2). This trend may be associated with carbonates formation during organic matter thermal decomposition (Yuan et al., 2011). The biochar yield was calculated considering the initial dry bagasse mass (100 %) and final biochar mass. As expected, B-300 had higher content of final biochar product, while B-700 shows lower yield, since at higher temperatures most of its organic content volatilizes (Table 2).

Table 2: Biochar yield under different pyrolysis temperatures

Biochar samples	Pyrolysis Temp. (°C)	Yield (%, m m^{-1})	pH
B-300	300	9.10	6.01
B-450	450	5.44	8.38
B-700	700	2.09	8.50

The biochar FT-IR spectra are dominated by three principal bands, located at 1,700, 1,597 and 1,432 cm^{-1}, as described in Chun et al. (2004). The band at 1700 cm^{-1} is assigned to the aromatic carboxyl/carbonyl (C=O) stretching, the band 1,597 cm^{-1} to the aromatic C=O ring stretching, and the band 1,432 cm^{-1} corresponds to a COOH and CHO stretching.

The FT-IR peaks at 1,700 cm^{-1} and 1,432 cm^{-1} appear with higher intensity in B-300, a medium intensity in B-450, and disappear in B-700. On the other hand, while the peak at 1,597 cm^{-1} was present in all samples of biochar, its intensity is the highest in B-450 (Figure 1). These absorbance differences prove the change in biochar chemical composition when prepared at different temperatures, indicating a decrease in acidic groups when elevated pyrolysis temperature is used (Chun et al., 2004).

In the case of alginate microspheres, FT-IR spectra observe wide plateaus and slightly different peaks to biochar, wavelengths 1,592 and 1,415 cm^{-1}, (Figure 2). This can be explained due to a masking effect because of the huge amount of alginate employed (20 g L^{-1}) as compared with biochar (0.5 g L^{-1}) and phosphorus (25 mg L^{-1}), *i.e.* the biochar peaks shown in Fig. 1 (1,597 cm^{-1} and 1,432 cm^{-1}) may be contained within the alginate peaks with wavelengths of 1,592 and 1,415 cm^{-1}, correspondingly.

It was determined that 94 % of the polymeric microspheres' weight corresponded to the water content. Microsphere mass was measured, right after preparation, at 43.21 - 46.59 g and, after overnight drying at room temperature the weight was read at 2.29 - 2.93 g. This observation shows that the alginate beads, besides being a slow releasing system of nutrients, may also have the function of releasing water to the environment and being a potential moist reservoir in agricultural soil or substrata.

All the microspheres in the releasing assay were used just after its production to avoid desiccation. The release of phosphate ions is shown in Figure 3 where it can be seen that the control (no biochar, 50 mL KH_2PO_4; Table1), release ~0.75 mg L^{-1} phosphate ions at the equilibrium time of ~120 minutes. In sharp contrast to this trend, Treatment A (0.5 g of B-450, 50 mL of KH_2PO_4) release more than twice the amount of the cation than B, and the equilibrium time is only reached at around 2,880 minutes (two days). These results indicate the contribution and importance of the biochar in the process of weakly trapping and slow releasing of phosphate ions in the studied system. It is important to state that these results depend on the kind of biomass used to produce biochar. Here, the contribution of phosphorus in Treatment A was insignificant once biochar from lignocellulosic biomass has relatively low levels of phosphorous (Yao, 2012). On the other hand, biochar made from manure has a higher content of phosphorus (Doydora, 2011), what would compromise the results in assays testing phosphorus release.

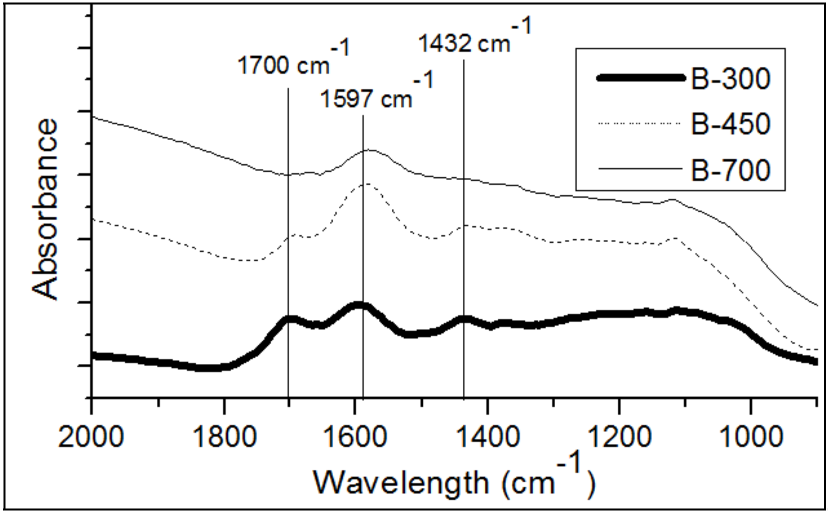

Figure 1: FT-IR spectra of biochar prepared at 300 (B-300), 450 (B-450) and 700 °C (B-700)

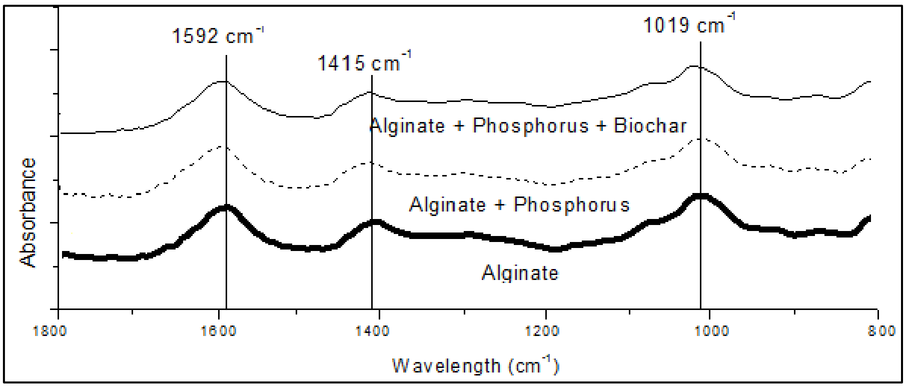

Figure 2: FT-IR spectra of microspheres made by: alginate; alginate and phosphorus; alginate, biochar and phosphorus

4. Conclusions

Biochar encapsulated within polymeric alginate beads, and managed as a slow releaser system of phosphorus, could be an innovative procedure to substitute conventional fertilizers in crops cultivation, to minimise phosphorus loses by leaching and reduce water pollution and eutrophication. Another important fact of the present work is the waste management and valorisation of sugarcane bagasse residues (Varbanov and Duić, 2013), once these abundant crop residues can be converted into biochar and returned to improve soil fertility. Moreover, this type of fertilizer may contribute to a better, more conscious use, of phosphorus, since it is an intensively extracted non-renewable resource, and very important for the maintenance of world agriculture.

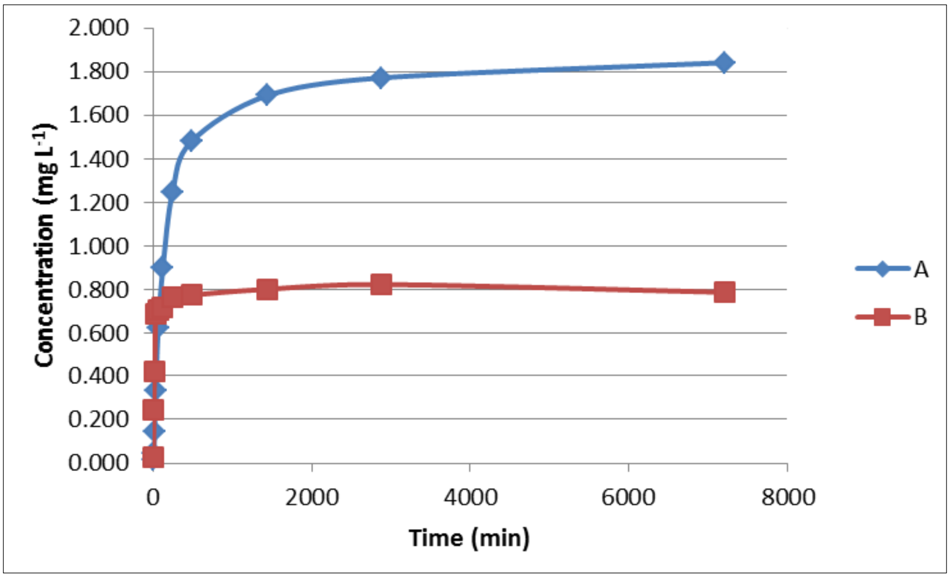

Figure 3: Phosphate ions release over time. Treatments: A) and B) (See Table 1)

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