



Research article

Novel biochar-impregnated calcium alginate beads with improved water holding and nutrient retention properties

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ABSTRACT

Drought conditions and nutrients loss have serious impacts on soil quality as well as crop yields in agroecosystems. New techniques are needed to carry out effective soil water and nutrient conservation and fertilizer application tools. Here, calcium alginate (CA) beads impregnated with ball-milled biochar (BMB) were investigated as a new type of water/nutrients retention agent. Both CA and Ca-alginate/ball milled biochar composite (CA-BMB) beads showed high kinetic swelling ratios in KNO_3 solution and low kinetic swelling ratios in water, indicating that CA-BMB beads have the potential to retain mineral nitrogen and nutrients by ion exchange. Pseudo-second-order kinetic model well-described the swelling kinetics of both beads in KNO_3 solution. Over a range of temperatures, the characteristics of dehydration suggested that impregnation with BMB improved the water holding capacity and postponed the dehydration time of Ca-alginate. The cumulative swelling and release characteristics of water, K^+ , and NO_3^- indicated that CA-BMB beads have great potential as a soil amendment to improve its nutrient retention and water holding capacity.

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1. Introduction

Chemical fertilizers are widely applied in most modern mainstream agricultural settings. For example, fertilizer addition is estimated to be responsible for about 40–60% of the global grain yield (Roberts, 2009). Nitrogen (N), phosphorus (P) and potassium (K) are the most common nutrients limiting plant growth (Dai et al., 2013; Zörb et al., 2014). While fertilizer application rates are high, nutrient use efficiency is very low. For example, it is estimated that only about 33 percent of the applied N is utilized by various crops and the remaining nutrients are lost via leaching, run-off, gaseous emission and fixation by soil microbes (Baligar et al., 2001). The low use efficiency of fertilizer is a problem that has plagued the world's agriculture, both reducing food supply and farmers' profits (Shaviv and Mikkelsen, 1993b).

The main pathways of soil N and P loss are surface runoff, leaching, soil erosion, ammonia volatilization, nitrification, and

denitrification. Because fertilizer-supplied N and P are mainly in the form of NO_3^- and PO_4^- , respectively, they are poorly sorbed by the mainly negatively charged soil particles and easily lost following rainfall or irrigation. Runoff and leaching of N and P are also a non-point source of pollution that can lead to aquatic eutrophication (Huang et al., 2017; Wang et al., 2014). Potassium (K), another key nutrient, plays a particularly crucial role in a number of physiological processes vital to growth, yield, quality, and stress resistance of all crops (Zörb et al., 2014). In natural systems, soil K becomes available to plants mainly by water-solubilization of minerals (Jaiswal et al., 2016). However, exchangeable K is often sorbed by soil colloids which are then carried off and lost from the soil.

Besides nutrients, water is of course essential for plant growth and it is the biggest limiting factor in the world's ability to feed a growing population. Therefore, it would be of great benefit to agricultural and society to find a practical soil conditioner that can minimize losses of water and nutrient elements from the soil. Such a conditioner would sorb and then slowly release water and nutrients so that they can be taken up and used by plants efficiently (Shaviv and Mikkelsen, 1993a).

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In recent years, biochar began to attract attention as a soil amendment with the potential to increase plant productivity while sequestering atmospheric CO₂ (Lehmann, 2007; Lehmann and Joseph, 2009). Biochar is made by high-temperature pyrolysis of crop biomass such as crop stalks, livestock and poultry manure and other agricultural wastes, and then applied to farmland soil using appropriate methods and standards (Lehmann and Joseph, 2015). Previous studies have found that biochar might increase soil water-holding capacity and have the ability to sorb soil macronutrients such as N and P (Basso et al., 2013; DeLuca et al., 2009; Karhu et al., 2011; Lehmann et al., 2003; Yu et al., 2013). When applied to the soil, biochar can also be a source of soil nutrients and can increase the activity of soil microorganisms (Biederman and Harpole, 2013; Prendergast-Miller et al., 2014). After a great deal of recent research, studies still disagree as to whether the productivity enhancement effect of biochar is primarily through stimulation of the native microbial community, the release of new nutrients, or through its regulation of native nutrients (Biederman and Harpole, 2013).

The ability of biochar to improve the retention of some soil nutrients can be attributed to its large specific surface area, porosity and many negative surface functional groups, all of which produce its enhanced soil cation exchange capacity (Mukherjee et al., 2011). Biochar addition may also improve nutrient retention by increasing soil pH and soil organic matter mineralization rate (Laird et al., 2010; Liang et al., 2006; Méndez et al., 2012). While studies have shown that biochar can hold nutrient elements and reduce their release (Mukherjee and Zimmerman, 2013), because of its negative charge, the attraction of N (and P) to biochar is relatively weak. Compared with other sorbents, freshly made biochar usually has low anion adsorption capacity (Yao et al., 2012). Ball milling has been shown to significantly increase the surface area, porosity, and surface functional group contents of biochar (Lyu et al., 2018a, 2018b). Ball-milled biochars are likely to have improved water holding and nutrient retention characteristics.

An issue with ball-milled biochar, however, is that its small particle size may make it difficult to apply to soils in an agricultural setting and more easily lost from soil via runoff and infiltration. Previous studies have shown that transport of biochar increased with decreasing particle size (Wang et al., 2013; Zhang et al., 2010) and a significant fraction of biochar particles move to lower soil layers in saturated sandy soil, especially biochar particles of nanometer scale (Wang et al., 2013). Particles of biochars in soils, being relatively lighter than other soil solids, are also prone to preferential erosion and off-site transport in surface runoff. The consequences of the movement of biochar colloids is the off-site migration of sorbed pesticides and other contaminants which leads to a potential risk to ground and surface water (Chen et al., 2017; Kookana, 2010). Thus, this work also explores the stabilization of ball-milled biochar (BMB) by its immobilization onto gel beads.

Alginate beads have been widely used for the delivery of bioactive materials and for entrapment of contaminants or nutrients in the environmental settings including agricultural soils (Escudero et al., 2009; Luo and Zhang, 2009; Pasparakis and Bouropoulos, 2006; Thakur et al., 2016; Wang et al., 2017). Alginate can form a gel and separate from water in a process called ionotropic gelation (Patil et al., 2012). Much research has been carried out to study the factors influencing the gelation process (Bajpai and Sharma, 2004; Rassis et al., 2002; Roy et al., 2009; Smrdel et al., 2008; Sriamornsak, 1999) and has been reviewed (Bajpai and Sharma, 2004). However, few studies have examined potential uses of these gels in agriculture (Karadağ et al., 2000), and none in combination with biochar. Thus, it was hypothesized that addition of BMB to Ca-alginate will improve its ability to retain water and nutrients. This work was aimed at determining the suitability of calcium alginate/ball-milled biochar composites as a

soil amendment to improve water and nutrient management and enhance agricultural sustainability.

2. Materials and methods

2.1. Chemicals and reagents

High viscosity sodium alginate from *macrocytica pyrifera* (MP Biomedicals, Inc. Co., USA), calcium chloride (CaCl₂) and potassium nitrate (KNO₃) were purchased from Fisher Scientific. All the chemicals and reagents were of reagent grade and used without any further purification.

2.2. Preparation of BMB

Bamboo biomass was oven dried (80 °C) and then converted into biochar through slow pyrolysis using a furnace (Olympic 1823HE) in an N₂ environment at peak temperatures of 450 °C. The biochar was mechanically activated in a planetary ball mill (Across International, PQ-N₂) under air atmosphere at room temperature in lidded 500 mL capacity agate milling jars. The milling ball-to-biochar weight ratio was 10:1 and the rotational speed of the main disk was 300 rpm. Each biochar was milled for a total of 12 h, reversing milling direction every 3 h.

2.3. Preparation of beads

To achieve a uniform dispersion, sodium alginate (1% w/v) mixed with BMB was sonicated using a Model B3510-MT Ultrasonic Cleaner (Branson Ultrasonics Co., USA) which has a nominal frequency of 40 kHz, for 2 h at 25 °C. While stirring at 400 rpm the BMB dispersion was thoroughly mixed with a suspension of sodium alginate (1% w/v) at the mass ratio of 0.25 (BMB/alginate). While stirring, 100 mL of this colloidal solution was added dropwise into 500 mL of 0.1 M CaCl₂ solution and then were left overnight to stabilize. The beads were then rinsed several times with deionized water to remove residual BMB particles and non-cross-linked Ca ions from the surface of the beads. Finally, the beads were dried in an oven at 50 °C for 24 h. Pure Ca-alginate beads were prepared separately for use as controls.

2.4. Material characterization

A number of methods were used to characterize the BMB, CA and CA-BMB. Thermogravimetric analysis of the samples was performed in a stream of N₂ (50 mL min⁻¹) at a heating rate of 10 °C min⁻¹ from 30 °C to 700 °C using a Mettler TGA analyzer (Columbus, OH). The structure and surface morphology of bamboo biochar and ball-milled biochar, CA and CA-BMB (pristine and loaded with KNO₃) were examined using scanning electron microscopy/energy-dispersive X-ray spectroscopy (SEM/EDX) using a JSM-6460LV Scanning Microscope (JEOL, Tokyo, Japan). The size of alginate and Ca-alginate-BMB gel particles were measured using calipers.

2.5. Swelling capacity, kinetics and dehydration

The ability of the dried CA and CA-BMB beads to sorb water, i.e. the swelling capacity, was evaluated using gravimetric analysis. Swelling capacity was quantified as the swelling ratio (D_s):

$$D_s = \frac{W_t - W_0}{W_0} \quad (1)$$

where W₀ and W_t are the weights of the samples in the dry and saturated states, respectively.

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