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Nutrient release from switchgrass-derived biochar pellets embedded with fertilizers

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ABSTRACT

Biochar pellets produced by blending switchgrass biochar, lignin and fertilizers K and P together followed by pelletization were characterized and investigated for their ability to release K and P. Pellets processed at 180 °C with increasing lignin content from 10 to 30 wt.% had higher density, thermal stability and durability, and produced lower pore volume and smaller pore size than pellets processed at 105 °C. Fertilizer-embedded biochar pellets with 10–30 wt.% lignin and processed at 180 °C had a slower K and P release than pellets dried at 105 °C, with release rates (53–62% in K and 49–62% in P) within the first 24 h followed by gradual releases (78–87% in K and 73–78% in P) for the next 18 days. Therefore, by controlling lignin content and processing temperature of the pellets, one can control the release rate of nutrients present in biochar pellets.

1. Introduction

Biochar is a carbon-rich product that is produced from biomass through thermochemical process, pyrolysis and gasification, under limited or absent oxygen (Lehmann et al., 2011). Biochar contains recalcitrant carbonaceous structures and minerals depending on biomass types and operation parameters of the process. Biochar produced from lignocellulosic feedstock has high carbon content, whereas biochar from nutrient-rich feedstock such as poultry litter has characteristics similar to a fertilizer (Cantrell et al., 2012). Biochar pH ranges from 5.2 to 10.3, ash content from 1.1% to 55.8%, carbon content from 23.6 to 87.5%, and surface areas range from 0 to 642 $m^2\ g^{-1}$ (Lehmann et al., 2011). Cation exchange capacity (CEC) of biochar ranges from 10 to 69 $cmol_c\ kg^{-1}$ (Kim et al., 2013). When applied to soil, biochar provides plant nutrients, increases CEC and water holding capacity, and improves the soil as a microbial habitat (Lehmann et al., 2011).

When lignocellulosic biomass-derived biochar produced by fast pyrolysis is incorporated into soil, organic or inorganic fertilizers are still needed to improve crop yield. Many studies that have investigated value-added biochars as a soil amendment suggested the blending of lignocellulosic biochars with nutrient-rich manures, compost or poultry litter before application (Hua et al., 2009; Ro et al., 2010). The incorporation of biochar with sludge composite into land application was found to significantly reduce nitrogen loss (Hua et al., 2009). However, the storage, transportation and soil application of biochar are challenging because biochar is brittle, or has wide particle size distribution and low density. Blue Leaf Inc. reported a loss as high as 30% by wind-blown during handing, transport to the field, and soil application of biochar. In particular, 25% of the biochar applied was lost during spreading to the field (Husk and Major, 2008). 20–53% of biochar incorporated into soil was also lost by surface runoff during intense rain events (Major et al., 2010).

Therefore, it is essential to design value-added biochar materials that can supply nutrients to soil over a long period of time with minimum loss of biochars and nutrients. Pelletization of biochar is one potential way to reduce transportation and handling costs and significantly decrease loss of biochar during soil application (Reza et al., 2012). Biochar pellet has been used as an alternative to biomass pellet mostly for heating material (Abdullah and Wu, 2009). For soil application, lignocellulosic and poultry litter feedstocks were blended, pelletized and slowly pyrolyzed to produce biochar pellets (Novak et al., 2014). However, there is little information available on fertilizer-embedded biochar pellets produced by fast pyrolysis. It is assumed that when lignocellulosic biomass-derived biochars that contain low plant nutrients are impregnated with additional nutrients and subsequently pelletized with a binder, the biochar pellets can control nutrient release rate as a slow release fertilizer. Slow release fertilizer is required to gradually release nutrients to soil throughout the growing season and to provide most of the nutrients to plant without leaching losses (Fernández-Escobar et al., 2004), which can, furthermore, reduce loss in farmer profit and minimize potential damage to the environment (Mortain et al., 2004). Therefore, the objective of this study was to develop biochar pellets embedded with plant fertilizer as an environmentally benign slow-release fertilizer. Biochar generated in the process of bio-oil production by fast pyrolysis was blended with commercial

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fertilizer and different ratios of a commercial lignin, and subsequently pelletized. The produced biochar pellets were mechanically and chemically characterized and their capacity to release nutrients was assessed.

2. Methods and materials

2.1. Production of biochar

Air-dried switchgrass (*Panicum virgatum* L.) was obtained from a local producer in eastern Tennessee. The switchgrass containing 7–8% moisture was milled to less than 4 mm particle sizes and then pyrolyzed at 525 °C with a residence time of 90 s and feeding rate of 10 kg h^{-1} in the presence of N_2 using a continuous dual auger pyrolysis process. A detailed description of the process is provided elsewhere (Kim et al., 2011).

2.2. Pelletization of nutrient-embedded biochar

The biochar produced by the auger pyrolysis process was blended with different percentages of lignin (10, 20 and 30 wt.%) as a binder using a mixer (Black lynx mixer, Monarch In.). Lignin (Indulin AT, kraft pine lignin) was obtained from MeadWestvaco Inc. Indulin AT lignin was a purified kraft lignin, where sodium and hemicellulose were removed by an acid hydrolysis process (Beis et al., 2010). During mixing biochar and lignin, liquid fertilizer (12:4:8 = N:P_2O_5:K_2O, Scotts Miracle-Gro) was added to water at 1.0 wt.% of total biochar and lignin mixture. Then, the fertilizer mixture was sprayed into the mixture of biochar and lignin (40–50 wt.% of total biochar and lignin). The moisturized biochar mixtures were pelletized using a pellet mill (model PP220, Pellet Pros) that consists of a die with cylindrical press channels (6 mm diameter) and rollers that force the biochar to be squeezed through the channels. Pressure in the die can reach up to 172 MPa and the pelletized biochars possessed a temperature around 65–85 °C (manufacturer's information). Pellets with dimensions of 6–10 mm in length and 5.9–6.0 mm in diameter were produced. The pelletized biochars were then processed at 105 or 180 °C for 24 h to dry in the oven. The heated biochars were cooled down and then stored in glass bottles. The biochar pellets produced with different lignin wt.% and drying temperature are referred as 10–105, 10–180, 20–105, 20–180, 30–105 and 30–180, where the first number refers to wt.% of lignin and the second the temperature used to process the pellets.

2.3. Characterization of biochar pellets

Raw biochar and the corresponding biochar pellets produced using different lignin contents (10, 20 and 30 wt.%) and processing temperatures (105 and 180 °C) were mechanically and chemically characterized. Proximate analysis including moisture content, volatile matter, and ash content, was measured by following ASTM D1762-84. Ultimate analysis including carbon, hydrogen, and nitrogen was measured by CHN analyzer (Perkin Elmer). Inorganic elements in biochars were analyzed by inductively coupled plasma-optical emission spectroscopy with an optima 7300 DV spectrometer (ICP-OES, Perkin Elmer) after microwave digestion (Kim et al., 2011). Surface functionality was evaluated by Fourier Transform Infrared (FTIR) spectroscopy in an attenuated total reflectance mode (Perkin Elmer Spectrum One spectrometer). FTIR spectra were analyzed using principal component analysis (PCA) to classify the samples by their spectral features (Martin et al., 2010). Thermal decomposition of biochar pellets under air atmosphere was analyzed using a thermogravimetric analyzer (Pyris 1 TGA, Perkin Elmer) (Kim et al., 2011). Adsorptive characterization of all samples was performed by stand N_2 adsorption at 77 K (Autosorb 1-c, Quantachrome Instrument) (Kim and Agnihotri, 2008). BET surface area (Brunauer, Emmett and Teller, BET), pore volumes, pore size distributions (Barrett, Joyner and Halenda, BJH method) and average pore sizes were extracted from the N_2 isotherm data by applying respective numerical models built into the Autosorb 1 operating software.

Density of biochar pellets was calculated by measuring diameter, length and mass of 10 cylindrical biochar pellets. Compressive mechanical strength of the biochar pellets was obtained by compression testing and determined as the force at break (Instron model 5567). Compression tests were performed using a disk shaped metal probe that was attached to a 100 kN load cell. The test was run at a compression rate of 1.0 mm min^{-1} and stopped after the pellet fell apart. The average force at break and its standard deviation were calculated based on 10 replications per test. Durability of biochar pellets was tested by abrasion index using the MICUM test (Reza et al., 2012). The rotating drum featured an inner diameter of 100 mm and a depth of 95 mm with three baffles of 25 × 50. Sixty pellets were loaded into the rotating drum and rotated with 50 rotations per minute for 60 min. After rotation, the pellets were screened using a 2 mm sieve. Particles that fall through screen were weighed and abrasion index (%) was calculated. Durability was calculated by difference between initial weight (100%) and abrasion index %. Water uptake of biochar pellets was measured by the capillary rise method (Zhang et al., 2011). Cylindrical pellet (3–4 g) hung to the microbalance (dynamic contact analyzer, DCA-32, Thermo Cahn Ins.) was immersed into distilled water and held below the water surface (1.0 mm) for a total of 8 h. The amount of adsorbed water as a function of time was recorded every 3 s. This test was performed at room temperature and in triplicates.

2.4. K and P release from biochar pellets

K and P release from biochars and biochar pellets embedded with fertilizer was assessed by batch extraction experiment using a vacuum extractor (Sampletek) equipped with 24 cylinders. The vacuum extraction was performed by drawing the extractant into receiving syringes through mechanical force controlled by a programmable micro-processor. Filter pulp (1 g) was put into the bottom of the cylinder (60 mL) and thereafter biochar pellets (approximately 5 g) were added. Successive batch extraction was performed with removal and replacement of water (50 mL, deionized water, Milli-Q, Millipore) for desired time until 432 h (18 days). The collected water was filtered using 0.45 mm filter, adjusted to less than pH2 by concentrated HNO_3 solution and stored in a refrigerator until analysis by ICP-OES.

2.5. Kinetics study

The data generated from K and P release from biochars and biochar pellets embedded with fertilizer were fitted into the first order kinetics model (Jardine and Sparks, 1984):

$$\ln(a_o - a) = \ln a_o - kt \quad (1)$$

where a_o is amount (mg kg^{-1}) of K or P present initially, a is amount (mg kg^{-1}) of P or K released at time t (h), and k is rate constant (h^{-1}).

3. Results and discussion

3.1. Characterization of biochar pellets

3.1.1. Chemical composition

The chemical characteristics of the biochar pellets are presented in Table 1. Switchgrass biochar contained 5.6 wt.% of ash, 41.6 wt.% of volatile matter and high amounts of inorganic compounds such as K (3622 mg kg^{-1}), Ca (4055 mg kg^{-1}), Mg (2504 mg kg^{-1}) and other compounds. Lignin, used in this study as a binder, contained 2.5 wt.% of ash, 58.1 wt.% of volatile matter and high amount of Na (6397 mg kg^{-1}) and S (1038 mg kg^{-1}), which derived from the Kraft process, although Indulin AT lignin was purified by acid hydrolysis. As lignin was blended with biochar with increasing amount from 10 to 30 wt.%, volatile matter gradually increased from 43.9 to 47.4% in biochar pellets processed at 105 °C and from 43.0 to 45.6% in biochar