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Physical and chemical properties of pyrolyzed biosolids for utilization in sand-based turfgrass rootzones ☆

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ABSTRACT

Biosolids are several forms of treated sewage sludge that are intended for use as soil conditioners for horticultural, agricultural and industrial crops. The objectives of this research were to determine the chemical and physical properties of biosolids pyrolyzed at several different temperatures, and their effect on perennial ryegrass seed germination and growth. Biosolids were thermally treated in an oxygen-free (nitrogen atmosphere) retort oven at 300, 400, 500, 700 and 900 °C. As pyrolysis temperatures increased, bulk densities, total surface areas, micropore surface areas, % minerals and pH values of the pyrolyzed biosolids increased, while carbon percentage decreased compared to untreated biosolids. Fourier-transform infrared spectroscopy analysis showed decreased surface functionality as pyrolysis temperature increased. Perennial ryegrass (*Lolium perenne* L. 'Nui') plants were grown in mixtures of 10% (v/v) biosolids or 10% (v/v) of the various pyrolyzed biosolids and 90% coarse sand. Ryegrass plants grown in the biosolids and the 300 °C pyrolyzed biosolids mixture had the greatest shoot heights of any of the treatments after 4 weeks of growth. These results indicate that pyrolyzing biosolids at 300 °C would produce material with excellent potential as a long-term peat replacement for water and nutrient retention in sand-based rootzones.

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1. Introduction

Biosolids is the term created by the Water Environment Federation in 1991 to describe several types of stabilized sewage sludge used for supplying nutrients and replenishing organic matter in agricultural lands, forests, rangelands and disturbed sites (USEPA, 2000). Because biosolids have a high content of essential plant nutrients, their land application versus being landfilled or incinerated is an appealing management option. The use of biosolids is regulated in the U.S. under the Title 40 Code of Federal Regulations, Part 503, which defines biosolids into several categories primarily based on pathogen load, with the safest category (lowest pathogen load) termed Class A biosolids, which meet USEPA guidelines for land application with no restrictions (USEPA, 2000). Biosolids generated by the Metropolitan Water Reclamation District of Greater Chicago (MWRD) are Class A biosolids and have been used for land restoration and remediation at several different sites in Illinois, and have generally performed superior to composts traditionally used to promote plant growth and improve soil quality parameters (Tian et al., 2016). A recent study using MWRD biosolids to reclaim a former industrial brownfield site near Chicago found that the biosolids outperformed organic compost in regards to soil quality, vegetation establishment, and earthworm populations (Basta et al., 2016). When mixed with dredged sediments from local waterways, MWRD biosolids had little or no effect on surface/groundwater quality and heavy metal levels while improving turfgrass growth (Brose et al., 2016). However, concerns about both nutrient runoff into waterways and presence of pathogens and chemical pollutants such as heavy metals, pharmaceuticals and personal care products have driven public opposition against the use of even Class A biosolids (USEPA, 2000; Yager et al., 2014). Indeed, biosolids were found to be highly enriched in organic contaminants when compared to effluents or effluent-impacted water (Kinney et al., 2006). Additionally, biosolids of any category are

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currently not allowed in certified organic production practices in the U.S. (Organic Materials Research Institute, 2016).

Pyrolysis is the thermochemical decomposition of organic material at elevated temperatures in the absence of oxygen. Pyrolysis of biosolids has been proposed as a sustainable treatment option for biosolids, producing biochar (agricultural charcoal), bio-oil and syngas (International Biochar Initiative, 2013; Kah et al., 2016; Roberts et al., 2017). The bio-oil and syngas can be used to produce energy, consequently making the process energy neutral (Laird et al., 2009; McNamara et al., 2016). Pyrolysis of biosolids at or above 300 °C should also eliminate offensive odors and potential pathogens, while substantially decreasing levels of organic chemical contaminants (Bulmău et al., 2014; Buss et al., 2015; Hoffmann et al., 2016).

We have been studying the use of biochars derived from a variety of woody feedstocks for replacing peat in the construction of new sand-based turfgrass rootzones such as golf greens, golf tees, and athletic fields to increase water and nutrient retention (Vaughn et al., 2015a). In addition, since biochar decomposes extremely slowly, its lifespan in the rootzones should be much longer than peat, which is generally only several years (Kussow, 1987; Bigelow et al., 2004). However, biochars produced from traditional sources such as wood wastes have low bulk densities (~0.2–0.3 g cm^{-3}) compared to sand (~1.9 g cm^{-3}). In our research we have found upward migration of the biochar in the turf rootzones, diminishing its water and nutrient retention in the deeper, desired areas of the rootzones. However, MWRD biosolids have a bulk density similar to sand (~1.9–2.0), indicating that pyrolyzed biosolids would also have high bulk densities, preventing the material from migrating upward in rootzones. Unpyrolyzed MWRD biosolids were previously found to be superior to peat and yard-waste compost in the enhancement of nitrogen mineralization and soil microbial populations in golf course putting greens, increasing the desirability of using them in this application (Tian et al., 2008).

The objectives of the current research were to determine the chemical and physical properties of MWRD biosolids pyrolyzed at several different temperatures, and their effect on perennial ryegrass seed germination and initial plant growth.

2. Materials and methods

2.1. Production of pyrolyzed biosolids

Class A biosolids (from here on abbreviated as MWRDB) were obtained from the Metropolitan Water Reclamation District of Greater Chicago. Pyrolyzed biosolids were produced by inserting approximately 1000 g of MWRDB into ceramic jars which were placed in an Across GCF Series 1100 Controlled Atmosphere Muffle Furnace (Across International, Berkeley Heights, NJ). The oven was sealed and evacuated to 10 psig and purged with nitrogen to 3 psig, and this step was repeated 5 times consecutively to ensure an oxygen free environment. The samples were then heated at 5 °C/min to maximum temperatures of 300, 400, 500, 700, or 900 °C, respectively, and held at that temperature for 1 h, and then were cooled back down to room temperature at a rate of 1 °C/min. During each pyrolysis run, the retort chamber pressure was maintained between 1 and 3 psig with a nitrogen flow rate ranging from 300 to 600 mL/min. Pyrolyzed biosolids will referred henceforward as 300PB, 400PB, 500PB, 700PB and 900PB based on maximum pyrolysis temperature.

2.2. Physico-chemical properties of the materials

Elemental composition data of the samples (using approximately 2 mg of material per measurement) for percent carbon, hydrogen, nitrogen and oxygen were obtained using a Perkin Elmer 2400 CHNO series II Analyzer (Norwalk, CT), utilizing cysteine as the standard. Ash content was determined using a Q2950 (TA Instruments, New Castle, DE) thermogravimetric analyzer by heating samples to 1000 °C at 10 °C min^{-1} under an air atmosphere. Density measurements were determined in triplicate and averaged using helium pycnometry on a Micromeritics Accupyc II 1340 using a 10 mL sample cup (Norcross, GA). Extractable chemicals present in the materials, including elements monitored in biosolids by the USEPA, were performed by Midwest Labs., Inc., Omaha NE, USA following EPA 503 protocols.

2.3. Surface area properties

Surface textures were determined using a Quantachrome ASiQ (Quantachrome Instruments, Boynton Beach, FL, USA) gas sorption analyzer. Samples were outgassed at 210 °C for 10 h prior to analysis. Analyses were performed at 77 K using N_2 as the adsorptive gas. Surface areas were determined using the BET equation within the reduced pressure ranges of: $0.05 < P/P_o < 0.30$, where P_o = the saturation pressure. Energy Dispersive Spectroscopy (EDS) measurements were made on a JOEL JSM-6010LA SEM with an integrated EDS attachment operating at 10 keV. Powder X-ray diffractograms were recorded on a Bruker D2 Phaser (Bruker AXS Inc., Billerica, MA) using θ/θ geometry and Cu-Kα radiation generated at a current of 10 mA and 30 kV. Scans were run over a 2θ range of 10–90 degrees with a step size of 0.02 degrees and a time per step of 0.2 s. The sample stage was rotated at 10 rpm during the scan. Initial divergence slit size was 0.6 mm and a 1 mm air scatter screen was used above the sample. A Lynxeye™ detector was used in conjunction with a 2.5 degree Soller slit and a Ni Kα filter. Weight percentages of the phase composition of the components of the MWRDB and pyrolyzed biosolids were calculated using Match! software (Putz and Brandenburg, 2016).

2.4. Temperature programmed oxidation/mass spectrometry (TPO/MS)

For TPO analyses, approximately 10 mg of the samples were placed in sample tubes sandwiched between packings of quartz wool and dried and degassed at 120 °C under vacuum for 20 min. Gas flow was then started using a mixture of 5% O_2 in helium (ILMO gas, Jacksonville, IL) set at a flow rate of 40 mL/min and the cell purged for 20 min prior to the start of the measurement. Under this gas flow and at this starting temperature, the sample was heated at 10 °C/min to 700 °C. The mass spectrometer outputs representing the following m/e were recorded: 18 (H_2O), 28 (CO), 32 (O_2), and 44 (CO_2).

2.5. Fourier transform infrared spectroscopy (FT-IR)

Sample functionality was examined by FT-IR and the spectra were recorded using a Nicolet iS10 (Thermo Fisher Scientific Inc., Waltham, MA) 370 spectrometer equipped with a dATR SensIR DuraScope, with a single-bounce diamond stage using a scanning range of 550–4000 cm^{-1} for 128 scans averaged at a spectral resolution of 4 cm^{-1}. Spectra were acquired and analyzed with Nicolet Omnic software by subtracting the background air spectrum.

2.6. Perennial ryegrass germination and growth

Perennial ryegrass (*Lolium perenne* L. 'Nui') seed was obtained from Kelly Seed, Peoria, IL, USA. Calcareous sand with a pH of 7.7 meeting United States Golf Association standards (United States Golf Association, 2004) was purchased (Markham Peat, Inc., Le Claire, IA) and used in treatment mixtures. Standard golf green construction utilizes organic materials (10–20% v/v%) combined