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Research article

Pyrolysis of wetland biomass waste: Potential for carbon sequestration and water remediation

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ABSTRACT

Management of biomass waste is crucial to the efficiency and sustainable operation of constructed wetlands. In this study, biochars were prepared using the biomass of 22 plant species from constructed wetlands and characterized by BET-N_2 surface area analysis, FTIR, TGA, SEM, EDS, and elemental compositions analysis. Biochar yields ranged from 32.78 to 49.02%, with mesopores dominating the pore structure of most biochars. The biochars had a R_{50} recalcitrance index of class C and the carbon sequestration potential of 19.4–28%. The aquatic plant biomass from all the Chinese constructed wetlands if made into biochars has the potential to sequester 11.48 Mt carbon yr^{-1} in soils over long time periods, which could offset 0.4% of annual CO_2 emissions from fossil fuel combustion in China. In terms of adsorption capacity for selected pollutants, biochar derived from *Canna indica* plant had the greatest adsorption capacity for Cd^{2+} (98.55 mg g^{-1}) and NH_4^+ (7.71 mg g^{-1}). Whereas for PO_4^{3-}, *Hydrocotyle verticillata* derived biochar showed the greatest adsorption capacities (2.91 mg g^{-1}). The results from this present study demonstrated that wetland plants are valuable feedstocks for producing biochars with potential application for carbon sequestration and contaminant removal in water remediation.

1. Introduction

In recent years, water eutrophication worldwide has been accelerated due to excessive release of nitrogen (N) and phosphorous (P) (Conley et al., 2009). Several technologies have been developed for removal of N and P in eutrophic water, and phytoremediation using enhanced constructed wetlands has emerged as a cost-effective and environment-friendly approach (Cheesman et al., 2010; Huett et al., 2005). However, the plant biomass must be properly harvested to enhance the removal of nutrients from the wetland (Zhao et al., 2012). Therefore, rational disposal of a large quantity of harvested plant biomass is the urgent need of practical application. At present, the proposed utilization mode for the harvested plant biomass is the development of energy and fertilizers such as biogas, biofuel, biofertilizer, and biochars (Bird et al., 2011; Brentner et al., 2011).

Biochar, created by pyrolysis of plant biomass, is stable carbon-enriched solid materials, which has been increasingly used in agriculture for improving soil productivity (Cao and Harris, 2010; Lehmann, 2007). In addition, biochar is widely considered a carbon sink due to its high recalcitrance to biotic and abiotic degradation, thus facilitating carbon sequestration (Harvey et al., 2012). Recently, biochars have also been reported to have sorption capacity for organic contaminants, heavy metals and nutrient ions, such as ammonium (NH_4^+), nitrate (NO_3^-) and phosphate (PO_4^{3-}). This has been considered a cost-effective approach for remediation of contaminated water and soil (Cao et al., 2011; Hollister et al., 2013; Sarkhot et al., 2013; Xu et al., 2013; Zeng et al., 2013). The production and use of biochar may offer an opportunity to tackle a number of environment issues (Windeatt et al., 2014), and therefore, research interest into the characteristics and performance of biochars has been intensified in recent years.

The performance of biochars varied greatly and is affected by both feedstock property and pyrolysis conditions (Ahmad et al., 2014). While studies have been conducted to evaluate the effect of pyrolysis temperature on characteristics of biochars derived from agricultural residues, forestry residues, livestock manures, and municipal wastes (Ahmad et al., 2014; Hale et al., 2013; Wang et al.,

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2015; Xu et al., 2013), few reports are related to aquatic plant biomass derived biochar, especially the effect of different plant species on biochar characteristics. There are a wide variety of aquatic plants growing in constructed and natural wetlands. Considering the large quantity of aquatic plants at the global level, converting the biomass into biochar will significantly mitigate climate change by sequestering carbon, while providing energy, filtering contaminant and increasing crop yields (Woolf et al., 2010). However, the properties of biochars derived from the aquatic plant biomass and their potential for carbon sequestration and soil/water remediation remain largely unknown. The objectives of this study were to analyze the differences in physicochemical properties of biochars obtained from 22 wetland plant species using a uniform pyrolysis process to understand how feedstocks affect biochar characteristics, and to evaluate the potential of biochars in sequestering carbon and removing ammonium, phosphate and cadmium from contaminated water.

2. Materials and methods

2.1. Raw materials and pyrolysis procedure

Twenty-two species of aquatic plant were collected from four constructed wetlands in Zhejiang province, China for this study. They included *Nymphaea tetragona*, *Phragmites*, *Acorus calamus*, *Eichhornia crassipes*, *Ludwigia peploides* and *Myriophyllum spicatum* from Ningbo (29°51′36″ N 121°33′36″ E), *Colocasia esculenta*, *Pontederia cordata*, *Typha orientalis Presl*, *Myriophyllum verticillatum* and *Sagittaria sagittifolia* from Yongkang (28°55′12″ N 120°01′12″ E), *Monochoria korsakowii*, *Miscanthus*, *Scirpus tabernaemontani*, *Hydrocotyle verticillata* and *Cyperus alternifolius* from Shaoxing (30°00′36″ N 120°34′48″ E), and *Canna indica*, *Vetiveria zizanioides*, *Zizania caduciflora*, *Pennisetum purpureum Schum*, *Thalia dealbata* and *Phragmites australis* from Lin'an (30°13′48″ N 119°43′12″ E). After harvest, the biomass was rinsed with tap water and sun-dried for one week before it was ground to <2-mm prior to pyrolysis.

The powdered biomass was dried in an oven at 105 °C overnight and pyrolyzed in a modified muffle furnace system under N_2 atmosphere with the temperature being raised to 500 °C at a rate of 5 °C/min and maintained at the peak temperature for 2 h (Fig. S1). The pyrolysis temperature of 500 °C was considered as an optimized temperature that balances the yield and quality of char well (Ahmad et al., 2014; Lehmann, 2007). The biochars (i.e. the solid residues from the pyrolysis) were referred to as CI, MV, PP, NT, AC, CE, PC, TD, EC, SR, MK, MI, CA, LP, ZC, HV, VZ, PA, ST, PM, TO, and MS in accordance with the name of plant species used for the feedstock. Subsamples of the biochars were passed through a 0.25-mm sieve prior to use.

2.2. Physicochemical characterization

Elemental (C, H, N) analysis was performed using a CHN Elemental Analyzer (Flash-EA112, Thermo Finnigan, USA). The oxygen content was calculated by mass balance. The H/C and (O + N)/C atomic ratios were calculated to evaluate the aromaticity and polarity of the biochar, respectively. Fourier transform infrared analysis (Nicolet 6700) was applied to identify the surface functional groups by scanning the 400 and 4000 cm^{-1} region at 2 cm^{-1} resolution. The biochar was also analyzed using thermogravimetric analyzer (TGA) (SDT Q600, US) from 25 °C to 900 °C under air atmosphere at a rate of 10 °C min^{-1}. Scanning electron microscope imaging analysis was conducted using a Scanning Microscope (Quanta FEG 650, FEI, NLD) to compare the structure and surface characteristics of biochars. Surface elemental analysis was conducted simultaneously with the SEM at the same sites using energy dispersive X-ray spectroscopy (EDAX Inc. Genesis XM). The specific surface area of biochar was measured by N_2 adsorption isotherms at 77 K using a surface area analyzer (Quadrasorb Si, QUANTACHROME, USA) and by the Brunauer–Emmett–Teller method. Total pore volume of biochars was estimated from a single N_2 adsorption point at a N_2 relative pressure of 0.99, and the pore size distribution was obtained by analyzing the N_2 desorption data according to the Barrett–Joyner–Halenda method (Chen et al., 2012). Ash content was measured by combusting the samples at 750 °C for 5 h. The cation exchange capacity was measured with the ammonium acetate and potassium chloride replacing method (Mukherjee et al., 2011). The pH of biochars was measured by adding biochar sample to deionized water at a mass/water ratio of 1:20 (Inyang et al., 2012).

2.3. Carbon sequestration potential

Weight loss and heat flow characteristics associated with the thermal oxidation of biochars were examined using thermal gravimetric analysis (TGA). Biochar samples (6 mg each) were heated from 25 °C to 900 °C at an increment of 10 °C min^{-1} in air using a thermogravimetric analyzer. The index R_{50}, for assessing the thermal recalcitrance potential of biochar, was calculated by the TGA data using the method proposed by Harvey et al. (2012):

$$R_{50,x} = T_{50,x} \Big/ T_{50,\mathrm{graphite}} \tag{1}$$

where $T_{50,x}$ and $T_{50,\mathrm{graphite}}$ are the temperature corresponding to 50% oxidation/volatilization of biochar and graphite, respectively. Values are obtained directly from TGA thermograms that have been corrected for water and ash content following the method described by Harvey et al. (2012).

The carbon sequestration potential (CS), proposed to measure the final amount of biochar retained after adding to soil, was calculated by the following equation recommended by Zhao et al. (2013):

$$CS(\%) = (M{*}Y{*}C_b{*}R_{50})/(M{*}C_r) \tag{2}$$

where M is the mass of raw materials (g), Y is the yield of biochar (%), C_b is the carbon content of the biochar (%), R_{50} is the recalcitrance index and C_r is the carbon content of raw materials (%).

There is a difference in biomass yield among the different aquatic plant species. When we evaluated the carbon sequestration capacity of biochars derived from different species of wetland plants, the biomass difference should also be taken into consideration.

$$CS_a(\mathrm{kg/ha}) = CS{*}C_r{*}Y_b \tag{3}$$

where, CS is the carbon sequestration potential of biochar calculated in Eq. (2), C_r is the carbon content of raw materials (%) and Y_b is the above-ground biomass of the corresponding aquatic plant (kg/ha).

2.4. Sorption experiments

Ammonium and phosphate solutions were prepared by dissolving ammonium chloride (NH_4Cl, certified A.C.S, Fisher Scientific) and potassium phosphate dibasic anhydrous (K_2HPO_4, certified A.C.S, Fisher Scientific) in DI water, respectively. The pH for each sorption solution was adjusted to 7 ± 0.1. The adsorbent (0.2 g) was added to 50 mL solutions with concentrations (mg L^{-1}) of 20, 50 and 100 for N, and 4, 10 and 20 for P in a conical flask. Cadmium solutions were prepared by dissolving nitrate cadmium (Cd