



# Effect of feed source and pyrolysis conditions on properties and metal sorption by sugarcane biochar

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## HIGHLIGHTS

- Aged sugarcane bagasse produces biochar of high metal sorption capacity.
- Biochar ash content play a significant role in metal sorption by sugarcane bagasse.
- Acid-washing drastically decreased activated biochar Cu sorption capacity.
- Copper sorption was inversely related to biochar oxygen content and O/C molar ratio.

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## ABSTRACT

Sugarcane biomass from different feed sources of sugar mill operation were used in producing biochar at different temperatures (350, 500, 650, and 800 °C) with/out steam activation at 800 °C. Feed sources included fresh cane-trash, fresh bagasse, and old bagasse collected from a pile left outside the plant for several years. Biochar yield and composition were determined and metal sorption capacity evaluated. Pyrolysis more than doubled biochar ash content which was 2 to 3 times higher for fresh cane trash and old bagasse than for fresh bagasse biochars. On the other hand, surface area of fresh bagasse activated biochars (493 m<sup>2</sup> g<sup>-1</sup>) nearly doubled that of the old bagasse (262 m<sup>2</sup> g<sup>-1</sup>), or fresh cane trash (204 m<sup>2</sup> g<sup>-1</sup>) biochars. Cadmium sorption capacity increased upon activation and was an order of magnitude higher for old bagasse biochars than for fresh bagasse or fresh cane trash biochars across production temperatures (ranging from 43.4 mg g<sup>-1</sup> to 63.8 mg g<sup>-1</sup> compared to 0.35 mg g<sup>-1</sup> to 0.47 mg g<sup>-1</sup>, or 4.35 mg g<sup>-1</sup> to 6.29 mg g<sup>-1</sup>, respectively). Maximum sorption capacity for Cd and Cu was highly correlated with biochar ash content, while that of Pb correlated with biochar surface area and total sulfur content. Cu sorption capacity inversely correlated with O/C ratio and reduced significantly upon acid washing of activated 500 °C old bagasse biochar (from 32.2 mg g<sup>-1</sup> to 14.3 mg g<sup>-1</sup>). Ash content seemed to play a decisive role in metal sorption capacity of sugarcane bagasse biochars. Overall, old sugarcane bagasse feedstock demonstrated best performance in producing biochars of higher metal sorption capacity compared to fresh cane-trash or fresh bagasse.

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## 1. Introduction

Intensive agronomic production systems and expansion of urban landscapes, both ubiquitous to population and economic growth, adversely affects landscape hydrology and natural system filtration capacity and ability to sustain ecosystem services, such as clean water. Engineered runoff management practices can alleviate such impact by removing pollutants from runoff water. Yet, inasmuch as such systems performing well as physical filtration systems, a more specific and selective composition is required for more efficient and effective removal of dissolved components (Davis et al., 2009, 2012; Smith and Livingston, 2013). Use of selective sorbents in the engineered soil media of runoff management practices will improve the system efficiency.

Biochar, a carbon-rich solid produced via pyrolysis of biomass showed to remove excess nutrients, heavy metals, pesticides, and other synthetic organics from water, with feedstock and pyrolysis conditions to significantly affect biochar pollutants removal efficiency (Ahmad et al., 2014; Lima and Marshall, 2005, 2007; Trakal et al., 2011; Uchimiya et al., 2010). Produced from agronomic waste streams, biochar is proposed as a cost-effective source for bulk sorbent material for such non-point-source large-scale systems. Biomass residue from sugarcane operations can serve as a low-cost feedstock for such applications (Ding et al., 2014; Mohan et al., 2014). Biochar efficacy as metal sorbent depends on biochar feedstock and pyrolysis conditions (Lima et al., 2009; Asuquo et al., 2017; Li et al., 2017). Hence, proper selection of feedstock and pyrolysis conditions is important in order to maximize sugarcane biochar performance. The objective of this study was to investigate different available feed sources along sugarcane harvesting and milling operations for their potential conversion into biochars and activated biochars. Furthermore, different pyrolysis conditions were applied in order to investigate their role in conjunction with the different properties of the original feedstock in the final physico-chemical and sorption properties of the biochars. Their composition and metal sorption characteristics were analyzed and compared in order to determine role of feedstock and pyrolysis conditions and activation step in the overall biochar performance as metal sorbent.

## 2. Materials and methods

### 2.1. Sample collection and preparation

Two types of sugarcane bagasse material, old and fresh were collected from Cora Texas Sugar Mill (White Castle, LA). The fresh bagasse was collected the same day it was generated and the old bagasse was collected from a bagasse pile left outside for several years. Additionally, a sample of fresh cane trash material was collected from a mechanical de-trasher system installed to separate and remove incoming trash (mostly leafy material) from the billeted sugarcane prior to sugar extraction. All three materials were air dried in a greenhouse prior to grinding to pass 2-mm sieve using a Retsch 2000 cutting mill. Select properties of the different feed sources are provided in Table S1.

The different feed sources were pyrolyzed in a Lindberg bench furnace equipped with a retort (Lindberg/Blue M, Type 51662-HR, Watertown, WI, USA). Samples were placed in a ceramic evaporating dish in the furnace chamber and pyrolyzed at the peak temperature for one hour under a flow of nitrogen gas set at a flow rate of  $1.6 \text{ L min}^{-1}$ . Four pyrolysis temperatures were studied from  $350^\circ\text{C}$  to  $800^\circ\text{C}$  with  $150^\circ\text{C}$  increments and a  $6^\circ\text{C min}^{-1}$  ramp rate up to the final temperature. A sample of old bagasse was also pyrolyzed at  $300^\circ\text{C}$ . Biochars were allowed to cool down to room temperature overnight in the retort under a flow of nitrogen gas.

Half of the biochar samples were further activated by steam upon completion of the 60-min pyrolysis, by continued heating to  $800^\circ\text{C}$  at the same temperature ramping rate, and after reaching  $800^\circ\text{C}$  injecting distilled water into the nitrogen gas flow at a rate of  $3 \text{ ml min}^{-1}$  for 45 min using a peristaltic pump. As before, samples were allowed to cool down overnight under a flow of nitrogen. Samples of the activated and non-activated old bagasse that were pyrolyzed at  $500^\circ\text{C}$  were either (a) used as is (unwashed) or, (b) acid-washed with  $0.1 \text{ N HCl}$  (2% w/v ratio) for 1 h with two subsequent water rinses (2% w/v ratio), and dried overnight at  $90^\circ\text{C}$ . One mL aliquot of the acid-washed suspensions were drawn using a disposable syringe and filtered through a  $0.22 \mu\text{m}$  Millipore filter (Millipore Corp., Bedford, MA) prior to dilution and analysis. Leachate elemental composition was analyzed using inductively coupled plasma, atomic emission spectroscopy (ICP-AES; Leeman Labs, Hudson, NH, USA).

### 2.2. Physical and chemical measurements, yield, and surface area

Biochars and feedstocks were evaluated for select properties including biochar yield, surface area (data reported as average of duplicate samples), and elemental and proximate analyses. Elemental analysis was conducted on a single composite sample. Prior to all measurements, biochar and activated biochar samples were ground to particle size  $<100 \mu\text{m}$ . Surface area measurements were obtained from duplicate analysis of nitrogen adsorption isotherms at  $77^\circ\text{K}$  using Nova 2200e Surface Area Analyzer (Quantachrome Corp., Boynton Beach, FL). Specific surface areas (BET, Brunauer–Emmett–Teller) were calculated from adsorption isotherms using the BET equation. The micropore size distributions were calculated using t-plots derived from the Nova 2200e software. Micropores are those having less than 2 nm in diameter and referred herein as inner surface area, while remaining surface area is herein referred to as outer surface area.

Ultimate analysis (CHNSO) was determined by dry combustion/TCD (CHN); percent sulfur content was determined by  $\text{O}_2$  flask combustion/titration and percent oxygen content was determined by pyrolysis/gravimetric determination (Micro-Analysis, Inc., Wilmington, DE). Proximate analysis (ASTM method D5142-09) was performed using Thermo-Gravimetric Analyzer (TGA701, LECO, St. Joseph, MI) to determine moisture, ash, volatile matter, and fixed carbon (results reported as average of triplicate samples).

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