JOURNAL OF ENVIRONMENTAL SCIENCES XX (2016) XXX–XXX

Available online at www.sciencedirect.com
ScienceDirect
www.elsevier.com/locate/jes

JES JOURNAL OF ENVIRONMENTAL SCIENCES
www.jesc.ac.cn

Selected dark sides of biomass-derived biochars as environmental amendments

Zien Chen[1], Lei Luo[1,*], Diyi Xiao[1], Jitao Lv[1], Bei Wen[1], Yibing Ma[2], Shuzhen Zhang[1]

1. *State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China. E-mail: qfchenzien@foxmail.com*
2. *Institute of Agricultural Resources and Regional Planning, Chinese Academy of Agricultural Sciences, Beijing 100081, China*

ARTICLE INFO

Article history:
Received 15 March 2016
Revised 7 June 2016
Accepted 8 June 2016
Available online xxxx

Keywords:
Biochar
Swine manure
Heavy metal
Free radical
Dissolved biochar

ABSTRACT

With the rapid increase in the application of biochars as amendments, studies are needed to clarify the possible environmental risks derived from biochars to use safely the biomass resources. This work reported selected dark sides of maize straw- and swine manure-derived biochars pyrolyzed at 300 and 500°C. During the pyrolysis processes, total heavy metals in the biochars were enriched greatly accompanying with considerable emission of the heavy metals into atmosphere and the trends became increasingly obvious with pyrolysis temperature. Meanwhile, the biochars showed distinctly decreased available heavy metals compared with raw feedstocks, which could be mainly attributed to the sorption by the inorganics in the biochars. The water- and acid-washing treatments significantly increased the releasing risks of heavy metals from biochars into the environments. Electron paramagnetic resonance analysis indicated that persistent free radicals, emerged strongly in the biochars as a function of the aromatization of biomass feedstocks, were free from the influence of water-, acid-, or organic-washing of the biochars and could remain stable even after aged in soils for 30 days. Dissolved biochars, highly produced during pyrolysis processes, showed distinct properties including lower molecular weight distribution while higher aromaticity compared with soil dissolved organic carbon. The results of this study provide important perspectives on the safe usage of biochars as agricultural/environmental amendments.

Introduction

Biochars have been receiving increasing attention in various environmental applications due to their high surface reactivity for contaminant immobilization and strong ability for carbon sequestration (Lehmann, 2007; Ghosh et al., 2011). Various agricultural wastes including swine manures and sewage sludge were used as biomass feedstocks to produce biochars (Zhao et al., 2013), and the effect of production conditions on the biochar properties relating to the contaminant immobilization and carbon sequestration has been well addressed (e.g., Uchimiya et al., 2011; Luo et al., 2015). Several previous studies also reported the presence of toxic contaminants in biochars, such as heavy metals (Meng et al., 2013; Hussain et al., 2016) and polycyclic aromatic hydrocarbons (Freddo et al., 2012). Unfortunately, the behaviors of the contaminants during the pyrolysis processes and potential risks from the biochars have not been well-documented. To avoid unintended consequences of the potential huge applications, comprehensively investigating the properties of biochars

---

* *Corresponding author*. E-mail: leiluo@rcees.ac.cn (Lei Luo).

http://dx.doi.org/10.1016/j.jes.2016.06.004

Please cite this article as: Chen, Z., et al., Selected dark sides of biomass-derived biochars as environmental amendments, J. Environ. Sci. (2016), http://dx.doi.org/10.1016/j.jes.2016.06.004

relating to environmental risks becomes important and urgent for environmental/agricultural purposes.

Our previous work confirmed the presence of heavy metals in biomass feedstocks, such as crops and swine manures (Luo et al., 2009). However, these pollutants usually exist at relatively low concentrations in the biomass feedstocks, very little is known about their behaviors relating to potential risks in the biochars derived from these biomass feedstocks. Meanwhile, it has been demonstrated that biochars show strong affinity for heavy metals while the immobilization mechanisms of heavy metals in biochars remain inconsistent. For instance, some researchers ascribed the affinity to the complexation reaction of heavy metals with organic ligands in the biochars (Uchimiya et al., 2011) while others attributed the immobilization to the inorganic fractions in biochars (Cao et al., 2009). On the other hand, recent studies indicated that free radicals were substantially generated in the biochars during the pyrolysis processes in the presence of transition metals such as Cu and Fe, which could negatively affect plant germination and growth (Fang et al., 2014; Liao et al., 2014). Although the generation mechanisms of the free radicals and the influence of the feedstock components has been well discussed (Dellinger et al., 2007; Fang et al., 2015), the information on the influencing factors associated with biochar components on the emergence of the free radicals in biochars is still limited. A thorough investigation on the behaviors of heavy metals and free radicals in the biochars is needed to understand and mitigate any undesirable effects.

To acquire amendments with desired properties, most researchers tended to treat the biochars with water or acid to remove dissolved organic carbon (DOC) or ashes from biochars (e.g., Uchimiya et al., 2010, 2011; Zhang and He, 2013; Zheng et al., 2013). Recently, our work reported that high contents of DOC or dissolved biochar (DBC) were released from the pyrolyzed biochars (Luo et al., 2015). In addition, previous work indicated that the free radicals in biochars could induce strong hydroxyl radicals in aqueous phase and thus proposed that the presence of ultrafine particles (i.e., DBCs) in the biochars might induce the reactions (Liao et al., 2014; Fu et al., 2016). The properties of DBCs related to (photo)degradation have been addressed using fluorescence analysis (Jamieson et al., 2014; Fu et al., 2016), while the properties including their molecule and structure compositions, which determine the behaviors of contaminants and nutrients as well as free radicals in the environment, still remain largely unknown. Electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS), as a very powerful tool for the characterization of DOC (Lv et al., 2016), is ideal for exploring the character of DBCs at the molecular level. Comprehensively evaluating the effect of the treatments (water- and acid-washing) on the properties and behaviors of biochars including DBCs in the environments is needed for the safe usage of the biomass resources.

The objectives of the study were therefore to (1) examine the fates and speciation of selected heavy metals in typical biomass feedstocks during pyrolysis processes, (2) elucidate the factors affecting the occurrence of free radicals in the biochars and the molecular properties of dissolved biochars, and (3) explore the effects of water- and acid-washing treatments on the properties of the biochars relating to environmental risks. To this end, two representative feedstocks, namely maize straw and swine manure, were used in the study. Based on the characterization, the potential environmental risks from the biomass-derived biochars will be elucidated to enjoy the full beneficial potentials of these materials.

1. Experiments

1.1. Biochar production

Maize (*Zea mays* L.) straw (MS) and swine manure (SM, collected from a swine farm, located in Beijing suburbs) were used as feedstocks for biochar production. All feedstocks were dried at 80°C for at least 48 hr, and then pulverized to less than 2 mm. The feedstocks were pyrolyzed at 300 and 500°C, respectively, for 1 hr under N_2 atmosphere in a muffle furnace as described by Luo et al. (2015). All the feedstocks and derived biochars were divided into three aliquots and treated as below: (1) control, i.e., directly used for the property characterization and referred to as raw MS/SM, MS300/500 and SM300/500, respectively; washed with (2) 0.005 mol/L NaCl and (3) 0.1 mol/L HCl, respectively. In order to remove all the washable components, each treatment was conducted four times by constantly stirring for 6 hr each time at a solid-to-solution ratio of 10 g biochar/L. After the washing, the treated biochars were rinsed thoroughly with Milli-Q water and referred to as water-washed and HCl-washed biochars, respectively. The supernates after being filtered at 0.45 μm and the treated solid after being dried overnight at 80°C were kept for the following characterization.

1.2. Physical and chemical analysis

Yields of the biochars were calculated based on mass balance. Biochar pH values were measured at a ratio of 1:10 (W/V) in Milli-Q water after being shaken for 24 hr. The ash content was determined by the residual weight after heating the biochar at 750°C for 6 hr in a muffle furnace. X-ray diffraction (XRD) patterns were recorded on an X-ray diffractometer (X'Pert Pro, PANalytical, the Netherlands) using Cu Kα radiation. Surface element distribution of the biochars was examined using a scanning electron microscope (SEM, SU-8020, Hitachi, Japan) at 15 keV equipped with an energy dispersive X-ray spectroscopy (EDS).

Total heavy metals including As, Cd, Cu, Pb and Zn were determined after the samples (feedstocks and the derived biochars) were digested with concentrated HNO_3 + 30% H_2O_2 in a microwave accelerated reaction system (Mars 5, CEM, USA). In addition, 5% HF was added to digest the sample completely. The available heavy metals (except As) in the samples were determined after extracted with diethylene triamine pentacetate acid (DTPA) (Meng et al., 2013) and the available As was extracted with 0.1 mol/L phosphate buffer (pH 7.2) (Gleyzes et al., 2002). The filtered supernates from the water- and HCl-washing treatments were determined directly for the water- and acid-extractable heavy metals. Concentrations of the heavy metals were analyzed using an inductively coupled plasma-mass spectrometer (ICP-MS, Agilent 8800, Agilent, USA).

Please cite this article as: Chen, Z., et al., Selected dark sides of biomass-derived biochars as environmental amendments, J. Environ. Sci. (2016), http://dx.doi.org/10.1016/j.jes.2016.06.004