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Characterization of bioenergy biochar and its utilization for metal/metalloid immobilization in contaminated soil

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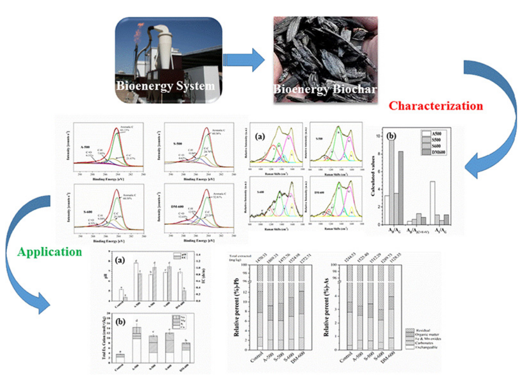
HIGHLIGHTS

- Bioenergy system biochars (BBC) can be used to mitigate the bioavailability of metal(loid) pollutants in soil.
- The use of oxidizing gas in bioenergy technology can increase the surface functionality of the carbonaceous by-product.
- BBC characteristics are closely related to the immobilization performance of Pb and As in soil.

GRAPHICAL ABSTRACT



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ABSTRACT

This study is a comparison of the effect of biochar produced by bioenergy systems, via the pyrolysis and gasification processes, on the immobilization of metals/metalloids in soil. Because the processes for these two techniques vary, the feedstocks undergo different heating regimens and, as a result, their respective char products exhibit different physico-chemical properties. Therefore, this study focuses on (1) the characterization of derivative biochar from the bioenergy system to understand their features and (2) an exploration of various biochar impacts on the mobility of As and Pb in contaminated soil. The results showed bioenergy biochars (BBCs) performed well in mitigating Pb extractability (1 M ammonium acetate) with a Pb immobilization >80%, but unfavorably mobilized the bioavailable As, likely because of electrostatic repulsion and ion exchange competition. The BBC surface functional group would chemically bond with the As and remain stable against the pH change. An increment in aromatic carbon would effectively enhance cation-π interaction for Pb immobilization. Nevertheless, an amendment with richer condensed structure and higher inorganic minerals (Ca^{2+}, K^{+}, Mg^{2+}, and Na^{+}) can lead to better performance in retaining Pb.

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1. Introduction

By exploiting a renewable fuel via an environmentally acceptable route, biofuel generated from the thermochemical processing of biomass, e.g., pyrolysis and gasification, has rightly attracted public attention (Maglinao et al., 2015; Nam et al., 2016; Titirici et al., 2015). The development of this thermochemical technique is currently quite popular because of its wide applicability in bioenergy production, generating >10% of the global supply (Sikarwar et al., 2016). More importantly, this technology is also considered an effective means to manage and recycle waste, thus mediating possible risks from improper landfills and burning (Ibarrola et al., 2012). Technically, gasification is the production of combustible gases, such as carbon monoxide, hydrogen, and methane, via thermochemical processing of solid carbonaceous materials at high temperature (>700 °C) under controlled conditions (pressure, temperature, and gasification agent) (Kwon et al., 2012, 2015), whereas pyrolysis is used to convert biomass to char and bio-oil product under a limited supply of oxygen within a lower temperature range, 300–700 °C (Lehmann, 2009). The resulting gas-phase syngas and bio-oil can be used as a source of renewable energy, or directly or indirectly as a precursor to a variety of value-added chemicals (Huber et al., 2006; Puig-Arnavat et al., 2010). With respect to energy balance, the energy consumed to run such bioenergy platforms accounts for only 10–25% of the energy generated (Lehmann, 2007).

In addition to the main energy product, a certain amount of solid-phase bio-energy biochar (BBC) along with ash content, referred to as an inevitable co-/by-product, is formed simultaneously. Considerable research has focused on the energy conversion efficiency of bioenergy systems. However, derived biochar which is among the primary by-products of the thermal processing of biomass has received limited attention. Indeed, the main focus of the bioenergy system is to maximize energy profits. To cater to the demand for sustainable chemistry, understanding the physicochemical properties of BBC and expanding its application are of vital significance in strengthening the economic feasibility of the bioenergy industry.

Currently biochar, consisting of high carbon and inorganic nutrients, has shown great potential in terms of environmental applications, such as soil remediation, wastewater treatment, and energy storage and as an environmental catalyst (Ahmad et al., 2014b; Jiang et al., 2013; Lee et al., 2017a; Xiong et al., 2017). However, if it were only possible to obtain biochar via conventional energy-intensive techniques, it would not be economically feasible to scale up to an industrial scale. Shabangu et al. (2014) reported that a process aimed primarily at producing biochar has struggled to return a profit, as no market exists to account for the value of biochar. Nevertheless, a large-scale bioenergy system is more likely to secure a consistent supply of biochar, with relatively high homogeneity, compared to other approaches. Hence, researchers need to reexamine the role allocation of biochar and place more emphasis on BBC instead of conventional pyrolyzed biochar.

BBC is a versatile functional material. For example, owing to the high treatment temperature and the use of an oxidizing agent during the gasification process, gasification biochar (GBC) contains more recalcitrant carbon and a higher ash content compared to conventional biochar, thus rendering it more stable in the environment. Nevertheless, the injection of proper gasification agents, such as air, steam, and carbon dioxide, can sharply increase the specific surface area and pore volume which are the critical indexes corresponding to adsorption capacity (Cho et al., 2017; Rajapaksha et al., 2014). In short, gasification provides the benefits of green power, while contributing to the diversity of biochar.

Over the years, metal(loid) contamination of soils has been a concern (Cho et al., 2017; Rajapaksha et al., 2014). Agricultural soils, particularly adjacent to chemical plants or military open-field soils, have been highly impacted by metal and metalloid contamination resulting from anthropogenic activities, and thus can pose a serious health risk through direct ingestion, uptake in plants, and even tracking into homes (Ahmad et al., 2012). Furthermore, these contaminants often exhibit a high bioresistance, thus making natural degradation more difficult. Among them, arsenic (As) and lead (Pb) are the most typical and representative elements that can pose serious health risks. Arsenic exists extensively in geosphere and seawater systems, where it ranks 20th and 14th in abundance, respectively (Shaheen et al., 2017). Because of the extended use of Pb-containing products, a substantial amount of Pb has leached into the environment. With the accelerated pace of urbanization and industrialization, anthropogenic activity increases Pb contamination (Antoniadis et al., 2017; Venegas et al., 2016).

Few investigations exist of BBC-induced changes in soil properties in terms of immobilization/mobilization of metals/metalloids. Hence, there is an urgent need to evaluate the feasibility of applying BBC for soil remediation. To establish a link to combine bioenergy by-products and environmental remediation, this study aimed to (1) characterize the BBC resulting from different thermal techniques, (2) survey the effects of different types of BBC on Pb and As immobilization efficiency, and (3) explore the applicability of BBC in immobilization of Pb and As from a mechanistic viewpoint.

2. Materials and methods

2.1. Soil sampling and characterization

Contaminated soil was collected from an uncultivated area adjacent to the Tancheon mine in Gongju, Chungcheongnan-do, Korea. Soil pH and electrical conductivity (EC) were measured according to Rajapaksha et al. (2014). Ammonium acetate extraction was used as a proxy for investigating metal(loid) mobility in the soil and determining soil exchangeable cations (Ca^{2+}, K^{+}, Mg^{2+}, and Na^{+}) using Brown's method and extractable As and Pb using inductively coupled plasma optical emission spectrometry (ICP-OES) (Antoniadis et al., 2017). The determination of water-soluble cation and anion contents was completed using ICP-OES and ion chromatography (IC). Organic carbon (OC) was measured by loss using the ignition method (Lichner et al., 2013).

2.2. Biochar production and characterization

Biochars were collected from two different bioenergy production platforms; the pyrolysis process, aiming for a bio-oil product, and the gasification process, aiming for a syngas product. The pyrolysis process was used to produce algal char (A-500) using a fixed bed reactor at 500 °C and sorghum biochars (S-500 and S-600) with a fluidized bed reactor at 500 and 600 °C. Dairy manure biochar (DM-600) was produced over a pilot scale fluidized bed gasifier at a temperature of 600 °C with air (Nam et al., 2015, 2017). As >30% of dairy farms in the US use sand as a dairy bedding material, the flushed dairy manure contains high ash contents (>75%). Only sand separated from the dairy manure can be used as a thermochemical conversion fuel (Nam et al., 2017). Biochar properties were characterized including proximate and ultimate analysis (Ahmad et al., 2013; Rajapaksha et al., 2014), pH & EC (Ahmad et al., 2013), N_2 adsorption and desorption isotherms, scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), and Raman and X-ray photoelectron spectroscopy (XPS). The operational steps are provided in the Supplemental Information (SI).

2.3. Incubation experiment

A month-long laboratory incubation experiment was performed. Four biochars were applied to the prepared soil in 600-mL polyethylene bottles at an application rate of 5% (85 t ha^{-1}) on a weight basis. This is based on the calculation assuming an incorporation depth of 15 cm and an average bulk density of 1.15 g cm^{-1}. Each group had four repetitions, including a set of control samples without any inputs. Before transporting to an automated incubator (MIR-554, Sanyo, Japan), deionized water was added to each unit to maintain the water level at 70%