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Toxic and nontoxic elemental enrichment in biochar at different production temperatures

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ABSTRACT

The major impediment to the use of biochar for soil amendment is the presence of toxic elements; however, it is not known how variations in production temperature affect the enrichment behaviour of toxic elements as identified by mass loss and whether the level of nontoxic elements compromises biochar quality. These goals require an understanding of the solid phase which constitutes the tar and ash fractions that harbour majority of the Cation exchange capacity (CEC) and functional groups of biochars and the possible mechanisms through which these metals interact with the solid phase. Results showed that the enrichment behaviour of individual toxic and nontoxic elements at low production temperatures of 350 and 450 °C was significantly different ($p < 0.005$) to that of high production temperature of 650 °C. The concentration of individual toxic elements revealed maximum enrichment of 193,957 ± 36,881 μg kg^{-1} and 1650 ± 203 μg kg^{-1} for Na and B respectively at the 450 °C. While the concentrations of individual nontoxic elements, exhibited maximum enrichment of 665,187 ± 119,715 μg kg^{-1}, 58,335 ± 13,985 μg kg^{-1}, 8858 ± 3574 μg kg^{-1} and 4907 ± 1174 μg kg^{-1} for K, Mg, Si and Al respectively at the 450 °C. Conversely, As was the only toxic element that exhibited maximum enrichment of 21 ± 9 μg kg^{-1}, at the 650 °C. Total toxic elemental concentrations indicated strong relationship with percentage mass loss ($r^2 = 0.998$, $p < 0.05$), which was greatest at 450 °C, but indicated strong negative relationship with percentage ash content ($r^2 = -0.946$, $p < 0.210$), which was greatest at 650 °C. Therefore, the 650 °C was effective in reducing both the toxic and nontoxic elements in biochar and thus, presented a quality biochar, due to its pi electrons which can result in dual benefits such as stronger binding of inorganic and organic elements to biochar in soils.

1. Introduction

Despite the fact that coconut shell (CS) accounts for about 1/5th of the biomass reported to be globally available for the production of low-cost sorbent (Smith et al., 2009), but studies focusing on the toxic elemental assessment in CS biochar are not available in the literature. It has also been reported that there is a lack of sufficient data with regards to non-toxic elemental content in biochar (Chan and Xu, 2009). In the past, researches were mainly focused on CS Activated Carbon (AC), which was used for the treatment of waste water (Daud and Ali, 2004; Xie et al., 2011). Similarly, the use of AC and presently carbon nanotubes of varying feedstock, in waste water treatment is on the increase (Gupta et al., 2011a, 1998, 2004, 1997, 2011b, 2012a, 2012b, 2013; Gupta and Nayak, 2012; Gupta and Ali, 2001; Jain et al., 2003; Karthikeyan et al., 2012; Khani et al., 2010; Mittal et al., 2009, 2010; Saleh et al., 2011; Saleh and Gupta, 2012a,b). However, the risks that may be posed by the presence of toxicants in the resulting sorbents were not considered prior to utilization. Presently, the International-Biochar-Initiative (2015)-(IBI) had recommended toxicant assessment in biochar.

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More importantly, the need for an immediate cause of action with respect to the production and use of cleaner technologies in areas such as energy, industry and agriculture to reduce the emission of greenhouse gases and ameliorate climate change have been highlighted (Fornes et al., 2015; Huisingh et al., 2014; Xiang et al., 2015). As a result, there is a need to understand the enrichment behaviour of toxic and nontoxic elements in CS biochar. Consequently, as biomass is combusted, a solid phase in the form of ash is generated (Boman et al., 2006; Gupta et al., 2012c). The resulting ash contains significantly enriched nontoxic elements (NTEs) such as Ca, K, Mg, and lightly enriched toxic elements (TE) such as Zn, Cu, Cd, Pb and Cr; co-existing in the resulting charcoal (Zevenhoven-Onderwater, 2001). Since the solid phase controls the enrichment behaviour of toxic and NTEs in charcoal, charcoal production should, therefore, be tailored towards production temperatures that may decrease the solid phase as this might be a good concept to overcome the problem of greater enrichment of these elements in the resulting charcoal.

A previous study reported that the concentrations of elements in charcoal were similar to those found in biochar (Freddo et al., 2012). In this study, we demonstrated that unlike charcoal and animal manure biochar, the enrichment behaviour of metals in plant derived biochar differs from those of the aforementioned substrates. In fact, charcoal is different from biochar in that biochar is applied to the soil for the purpose of remediation, and also different in that charcoal is produced by burning organic matter in fire (combustion), which generates ash (Gupta et al., 2005; Lehannes and Joseph, 2009). The solid phase in biochar is therefore, not related to the ash content alone, but also to the tar fraction. This metal-rich solid phase is identified by the fraction evidenced by the mass loss (%) as measured by thermogravimetric analysis (TGA), which corresponds to the greater degradation of inorganic substances in the region of 600–800 °C (Kucerik et al., 2004).

While regulators are concerned about the TEs only, but the dangers posed by the NTEs are also critical. Indeed, NTEs such as Al have been reported to hinder plant growth in low pH soils (Von Uexküll and Mutert, 1995), water extractable K has been suggested to be the cause of phytotoxicity in biochar bioassays (Fornes et al., 2015). While the TEs can result in cancer, neurological deterioration, muscular dystrophy and multiple sclerosis (Gupta et al., 2012a; Järup, 2003). Additionally, when biochar containing TEs is added to the soil, this may increase the TE pools in soils, which may, in turn, curtail the activity of soil microorganisms (Donkova and Kaloyanova, 2008).

Biochar is the carbon-rich product of any biological origin that results from biomass pyrolysis under anoxic conditions at temperatures <700 °C (Lehmann and Joseph, 2009). In the past, research on metal enrichment was mainly focused on metals in fuel production and incinerations systems which generate coal during combustion (Boman et al., 2006). Wang et al. (2015), had used enrichment coefficient to describe the enrichment of toxic and NTEs in biochar, but the model was not able to demonstrate whether the level of enrichment was critical or not. In this study, geochemical approach was used to describe the levels of enrichment. Likewise, production temperature was used to decrease the solid phase that eventually forms and is identified by mass loss (%) in biochar.

Although inorganic elements incorporated in wood/biochar by spiking with metal solutions are known to increase the mass loss (%) in wood biomass/biochar relative to non-spiked wood/biochar (Kim et al., 2012; Kinata et al., 2012, 2013; Mayer et al., 2012). However, metal spiked wood has been criticized since the metals do not undergo complete diffusion into the wood components that result in a mass loss (Kinata et al., 2012). Consequently, the resulting greater mass loss attributable to embedded metals in those studies may be due to a large proportion of the metals that did not penetrate the wood components. This is evidenced by the fact that metal fixation on wood by vacuum treatment exhibited greater mass loss than metal spiked wood (Kinata et al., 2012). Recently, Van Wesenbeeck et al. (2014), relied on information from the studies mentioned above to conclude that the greater metal content in two contrasting sewage sludge biochar can be attributed to greater mass loss and low ash content in one of the feedstock. Since biochar chemical properties vary according to feedstock and production temperature, the effects of the variations in biochar production temperature on inherently embedded metals on the fate of mass loss (%) in biochar are still unknown. Secondly, in this study, it is suggested that the varying production temperatures will result in varying functional group characteristics in biochar. For example, our Cation exchange capacity (CEC) data shows that the CS450 had the greatest CEC then the CS350, while the CS650 had the lowest. This implies that at CS450 and CS350, the biochar contains some metals which are held at the exchange sites in a reversible manner and these metals can be desorbed into soil solution under certain conditions of high or low pH. Therefore, greater CEC means greater mobility and availability. While amorphous aromatic C at CS450 and CS350 means weak pi conjugation and also greater tendency for the metals to become mobile. However, at CS650, lower CEC means less metals are held in a reversible manner at the exchange sites and on application to the soil these metals can be rendered immobile by pi conjugation between the metals and the condensed aromatic C at CS650.

Therefore, the objectives of this study are (i) To test the hypothesis that varying the production temperature of biochar can result in good quality biochar by presenting reduced concentration of the toxic and NTEs as identified by mass loss (%) and ash content (%) characteristics. (ii) To compare the TEs concentrations determined in this study with the International Biochar Initiative (IBI) guidelines (iii) To assess the levels of toxic and NTEs burden in biochar using geochemical approach. (iv) To recommend the biochar that will achieve greater binding of metals in soils and therefore decreased metal mobility based on functional group characteristics.

2. Materials and methods

2.1. Biomass

2.1.1. Coconut shell (CS)

The CS samples tested in this study were sourced from a public market; Pasar Awam Taman Universiti (N 01° 32′ 16″ and E 103° 37′ 44.3″); Johor Bahru Malaysia.

2.2. Preparation

The CS samples were cleaned, packed into plastic containers, sealed and then taken to the laboratory where they were washed with distilled water and air dried at 37 °C for 14 days, after which they were ground by a Hammer mill (<2 mm) mesh screen.

2.3. Biochar production system, process and characterization

Coconut shells (CS0) were pyrolyzed in triplicates at 3 dissimilar temperatures, which are henceforth termed: CS350, CS450 and CS650, but contrasted at 2 production temperatures: high production temperature (HPT); CS650 and low production temperatures (LPT); CS350 and CS450. The CS and CS Biochar (CSBs) characteristics such as pH, C, N, P, CEC were reported in a previous

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