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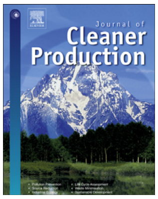

Operational control on environmental safety of potentially toxic elements during thermal conversion of metal-accumulator invasive ragweed to biochar

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ABSTRACT

Ragweed (Ambrosia artemisiifolia L.), a metal-accumulator invasive species, was pyrolyzed under a range of pyrolytic conditions to investigate their influence on immobilization and environmental safety of potentially toxic elements (PTEs) in the produced biochar. Conditions tested included temperature, retention time, heating rate, gas flow rate and particle size. Temperature and particle size had pronounced effects on product yields and physico-chemical characteristics of the produced biochar. All PTEs were enriched in the biochar, and the effect was more pronounced with higher temperature over 500 °C. However, fractionation of PTEs in biochar by following the sequential extraction process indicates that the mobile (bioavailable) fraction of most of the PTEs was transformed into more stabilized (residual) form ($P < 0.01$) after thermal conversion. Conclusively, biochar from metal-accumulating invasive ragweed with sustainable disposal and desired characteristics (with an optimal temperature range of a 500–600 °C and heating rate of 10 min^{-1} using smaller-size particle) can be produced by an appropriate combination of different pyrolytic condition with low environmental and ecological risk.

1. Introduction

Potentially toxic elements (PTEs) occur naturally in the soil-water environment, but their levels increase in the soil due to lithogenic and anthropogenic activities, threatening both environmental health (Yousaf et al., 2017a) and living things such as microbes, plants and animal in ecosystems (Chibuike and Obiora, 2014). The trace elements like Co, Cu, V, Ni, Zn, Fe, and Mn are known to be essential for the growth of at least one biological species in small concentrations, but the increased amount of these elements can have harmful and chronic health impacts (Yousaf et al., 2018). On another hand, some metallic elements, i.e., Pb, Cd, Hg and As are considered systematic toxicants (potentially toxic elements) (Bandiera et al., 2016), that can pose a severe threat to environmental and human health (Yousaf et al., 2016b). In recent days, phytoextraction by invasive plants is getting more and more attention due to its environmentally friendly and cost-effectiveness for removal of these PTEs from soil system. Although, invasive plants are regarded as one of the greatest threats to the biodiversity, natural ecosystem, human health and economy with the ability to destroy native species-rich ecosystem (Weber and Li, 2008). However, some of these invasive species have been reported to restore abounded and contaminated sites due to their extraordinary metal-accumulative nature and ability to extract higher concentrations of PTEs from metal-contaminated soils (Pandey, 2012).

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The main features of these plants are their unpalatable nature, high biomass production, rapid propagation and its growing ability in extremely contaminated sites. Many reports have shown that the invasive species are good accumulators of PTEs and they have natural ability to uptake and store these PTEs in their tissues (Zayed et al., 1998). Safe disposal of these invasive plants after phytoremediation of PTEs-contaminated soil is another issue (Liao et al., 2013). However, with the advancement in biomass pyrolysis technology, it can be easy to overcome the disposal problem and proliferation of metal-accumulating invasive species by converting them to a value-added product like biochar (Xu et al., 2017). Another benefit is the transforming the stored PTEs into more stabilized form (Yousaf et al., 2017b).

Biochar is a carbon-rich material produced by thermal conversion of biomass in little or the absence of oxygen. Due to its aromatic structure, biochars have been reported to be a highly stable, and chemically and biologically inert. Biochar can persist in soils for an extended period (Yousaf et al., 2016a), resulting in the environmental and agronomic management (Usman et al., 2015). This technology is receiving attention worldwide due to its ability to sequester greenhouse gas (Matovic, 2011) providing an ultimate solution to mitigate global warming (Spokas and Reicosky, 2009). Biochar technology has the capacity to fix atmospheric carbon into soil carbon sink for a long-term (Lehmann, 2007), other than that it also enhances the fertility of soil to sustain plant growth (Stefaniuk et al., 2016). Biochar can act as a sorbent for different organic and inorganic contaminants (Zama et al., 2017) as well as it can sustain soil nutrients reducing the fertilizer application by this means playing a role in the reduction of environmental pollution (Yao et al., 2012). The properties of biochar like carbon sequestration, environmental remediation and fertility mainly depend upon its physiochemical properties (Jin et al., 2016). The physical and chemical characteristics of biochar primarily depend upon the feedstock, production process (thermal conversion) (Chang et al., 2016) and operational conditions (Al-Wabel et al., 2013).

Two of the most important factors that can affect the quality and controls the properties of biochar are pyrolysis temperature (Chen et al., 2016) and type of feedstock used (Park et al., 2014). Temperature has a direct effect on elements by potential lost or fixed into a stable state, and it tends to increase the pH value of the biochar (Devi and Saroha, 2014). Previous research showed that metals in feedstock can be transformed into more stable form during pyrolysis. The temperature is considered to be a most influential factor affecting biochar characteristics (Luo et al., 2015) and it is important to study the changes within the biochar to find out the relation with pyrolysis temperature (Mukherjee et al., 2011). Also, PTEs can get enrich in biochar after pyrolysis (Anyika et al., 2016), their availability and eco-toxicity can be decreased significantly as the unstable and bioavailable PTEs converted into stable forms (Sun et al., 2010). Previously, efforts to investigate the PTEs enrichment in plants has been focused extensively, however, the transformation mechanism, fractionations of PTEs and environmental/ecological issues related to pyrolysis conditions during thermal conversion of metal-accumulating invasive species to biochar remain unclear.

Keeping in view the importance of research required on the transformation behavior of PTEs in metal-accumulating invasive species-produced biochars under various pyrolysis conditions to control the release of PTEs in environment, the current study was conducted with following objectives: (1) to investigate the operational controls on properties and product yield of pyrolysis of metal-accumulating invasive (*Ambrosia artemisiifolia* L.) species; (2) to study the migration behavior and fractionation of PTEs in biochars in order to explore the effect of operating conditions on immobilization of these PTEs; (3) to access the potential ecological risk of PTEs released from biochars produced under various operating conditions.

2. Methods and materials

2.1. Materials

Ambrosia artemisiifolia L., an invasive plant species that is native to North America and has been identified to be an efficient accumulator of PTEs (Tang et al., 2015), was used as feedstock for biochar production. The plant sample was collected from an industrial area of Hefei, Anhui province of China (by cutting from ~2 cm above the ground) and primarily dried at 70 °C for 48 h. After oven-drying, the sample was crushed into small particles using Thomas-Wiley mill (Model 4 Wiley® Thomas Scientific, USA). The samples were kept safe in airtight bags until to be used for biochar production.

2.2. Pyrolysis experiments

The fixed bed pyrolysis reactor (model BTF-1,200C, AnHui BEQ equipment, technology Co., Ltd, China) integrated with digital PID controller (proportional-integral-derivative) to achieve a maximum working temperature of 1200 ± 1 °C with wide-ranging heating rates and retention times was used for pyrolysis purpose. Approximately 300 g of dried and ground biomass (*Ambrosia artemisiifolia* L) was taken in ultra-high purity quartz boat (150 mm L x 70 mm W x 50 mm H) and housed inside the reactor. A residual air was purged by using a constant supply of nitrogen to provide the inert reaction medium and the carrier gas (N_2) flow rate (mL min^{-1}) was adjusted according to the experimental conditions by a mass flow controller (MFC). There were a total of twenty-one experimental runs (with three replications each) by conducting a series of experiments including temperatures (300, 400, 500, 600 and 700 °C), retention time (15, 30, 60 and 90 min), heating rates (1, 2, 5 and 10 °C min^{-1}), gas flow rates (20, 50, 100 and 200 mL min^{-1}) and particle size (<200, 200–100, 100–50 and 50-10 mesh) keeping other parameters constant (temperature: 500 °C, retention time: 60 min, heating rate: 10 °C mint^{-1}, gas flow rate 200 mL min^{-1} and particle size 10 mesh). The biochar produced after complete pyrolysis was left to cool down overnight in an anaerobic environment in a glass vacuum desiccator (hold vacuum up to 740 mm Hg) contained silica gel.

2.3. Physico-chemical characterization of biochar

To find out the biochar yield (recovery rate), mass balance technique was employed. Elemental composition of biochar (carbon (C), Nitrogen (N), Hydrogen (H) and Sulphur (S)) was determined by using CHN elemental analyzer (Varian EL 111). Oxygen concentration was found using weight difference method. In order to determine pH values of biochar, KCl solution (1.0 mol/L) was used with a ratio of 1:10 (W/V). ASTM 3174 (2011) and ASTM (2007) techniques were employed for proximate analysis including Ash content, FC, and VOC (volatile organic carbon) on a dry weight basis, with an experimental error less than ≤ 0.5%. Surface area and interstitial pores of biochar were analyzed using N_2 adsorption in samples using BET (Brunauer, Emmett, and Teller) (Quantachrome Autosorb-1C, USA). The electrical conductivity (EC) of the biochar sample was determined using conductivity meter (LF91, German). High heating value (HHV) was determined by modified Dulong's equation presented in the supplementary information (Eq. S(1)). The Y_{car} and average oxidation state of biochar-carbon (AOS_C) can be calculated using following equation Eq (1) and Eq (2).